Ninth International Conference on Porphyrins and Phthalocyanines (ICPP-9)

July 3-8, 2016
Nanjing, China

Preface

In this book are gathered together all the abstracts of presentations given at the Ninth International conference on Porphyrins and Phthalocyanines (ICPP-9) in Nanjing China, July 3-8, 2016. A pdf version of this Book of Abstracts is also available online on the congress webpage.

The thickness of this Book of Abstracts reflects the success of ICPP-9: 510 participants from 37 different countries have contributed for a total of 540 abstracts, a record participation in ICPP history. This book is a summary of the most recent progresses accomplished by the scientific community involved in all research topics associated with porphyrins, phthalocyanines and related macrocycles.

The abstracts are divided into five categories as described below:

Plenary Lectures (3)	designated as PLENARY	pages 1-3
Award Lectures (10)	designated as AWARDS	pages 4-13
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In the Table of Contents (page vii) are listed the presentations in each of the five above categories, arranged following the alphabetical order of the name of their presenting author. The Author Index provided at the end of this book is the exhaustive listing of all authors with the page numbers of their presentations.

The abstracts assembled here are all related to one of the 45 symposia organized by nearly one hundred symposium organizers. The program book distributed to each participant and also available online contains all the information on the schedule (time and place) of each of these abstracts. The contact details of each participant is available as well.

Professor Karl M. Kadish, president of the Society of Porphyrins and Pthalocyanines, at University of Houston and Yuanyuan Fang, congress secretary, are warmly thanked for their support and help during the book preparation.

June 2016

Zhongping Ou
Chairman of ICPP-9

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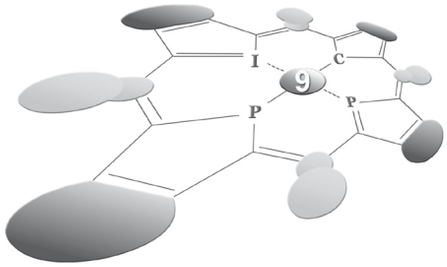

Ninth International Conference on Porphyrins and Phthalocyanines (ICPP-9)

July 3-8, 2016, Nanjing, China

Organized by
Society of Porphyrins and Phthalocyanines (SPP)

Hosted by
Jiangsu University
Jiangsu Chemical Industry Association (JSSCCE)

Co-hosted by
Anhui Normal University
Hunan Normal University
Professional Committee of Material Chemistry , JSSCCE

Scope of the Conference

All aspects of porphyrins, phthalocyanines and related macrocycles will be discussed in the form of Plenary Lectures, Keynote Talks, Symposium Lectures, short oral presentations and posters over the full five-day period of the meeting. Five scientists will be honored by Lifetime Achievement Awards in 2016 and two JPP/SPP Young Investigator Awards will also be presented at the meeting. All awards will be accompanied by highlighted award lectures.

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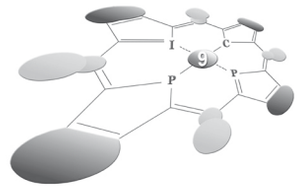

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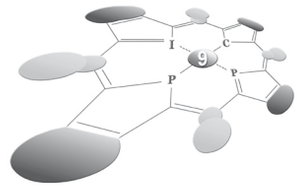

PLENARY

Self-assembling Tetrapyrroles

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Green photosynthetic bacteria can capture light efficiently even at 100 m under water surface[1] thanks to their special organelles, called chlorosomes, which agglomerate homologues of bacteriochlorophylls (BChl's) *c*, *d*, *e*. Chlorosomes are the most efficient natural antenna system whereby scarce photons can be harvested and transformed into biochemical energy. After understanding how the self-assembly of these natural tetrapyrroles operates,[2] our group has mimicked[3] and extended[4] the self-assembly algorithm by employing different recognition motifs as well as various solubilizing groups grafted onto porphyrins,[3,4] chlorins,[5] and more recently phthalocyanines.[6] Artificial light-harvesting constructs were thus designed and implemented into devices.[7] A particular feature is related to the inherent chirality of the BChl's. This lecture will address recent progress towards understanding how the chirality of tetrapyrrolic tectons is translated at the supramolecular level upon self-assembly, and how chiral helical superstructures are formed from an apparently achiral tecton, like *meso*-tetrakis(4-sulfonatophenyl)porphyrin ($TPPS_4$).[8]

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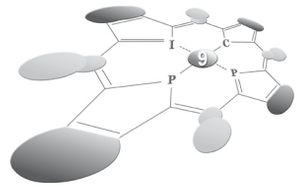

PLENARY

N-Confused Corroles: Novel Ligands for Higher Oxidation States of Metals

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Since the discovery of porphyrin isomer, N-confused porphyrin (**NCP**),[1] we have been involved in the porphyrin analog chemistry, especially, that of confused porphyrinoids. The unexpected rich chemistry of **NCP** inspired us to explore other confused porphyrinoids, which we call "confusion approach",[2] and until now, various confused porphyrinoids (expanded, contracted, isomeric) have been successfully synthesized and revealed their peculiar chemistry.[3] Among them, however, the chemistry of contracted tetrapyrrolic macrocycle, corrole (N-confused corroles, **NCC**s), remains mostly unexplored due to the presence of a set of confused isomers (**NCC1-5**), which possess an NNNC core with different arrangement of the confused pyrrole ring (Figure 1).[4] To examine their properties, we have synthesized various metal complexes of **NCC**s including Cu(III), Zn(II), Rh(III), and Ir(III) metals. As expected, stabilization of higher oxidation states or anodic shifts of the oxidation potentials were observed. Herein, the details of the structures and properties of **NCC** metal complexes are described.

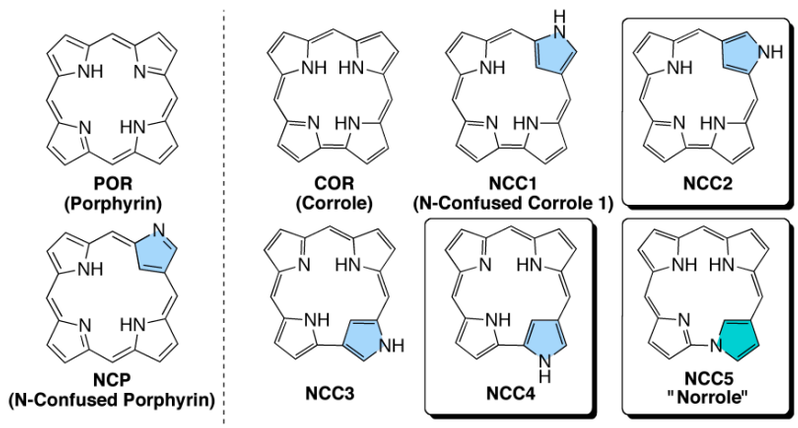

Figure 1. Structures of porphyrin, corrole and their isomers.

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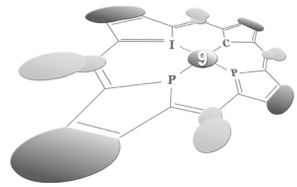

PLENARY

U-Turn Electron Transfers in Chemistry and Biology

Nicholas F. Polizzi, Ting Jiang, David N. Beratan, and Michael J. Therien

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Prevailing views of biological electron transfer (ET) maintain that electrons traverse the shortest effective pathway from a donor to an acceptor. We describe an efficient ET mechanism that requires the electron to travel farther. In U-turn ET, light absorption polarizes donor electron density *away* from the acceptor to maximize the yield of singlet ET products. We elucidate this strange electronic trajectory by employing a porphyrin-based donor chromophore in which wavelength-selective electronic excitation produces oppositely polarized excited states. Ultrafast pump-probe transient absorption experiments show that U-turn ET avoids donor excited-state deactivation that occurs by intersystem crossing. This unrecognized paradigm is in fact very old: Purple bacteria use U-turn ET in the primary event of photosynthesis. We examine the reasons that compel biology to muster U-turn ET.

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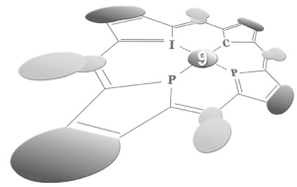

Phthalocyanine-based multifunctional ensembles

Giovanni Bottari

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AWARDS

Phthalocyanines (Pcs) are planar, aromatic macrocycles that possess interesting optoelectronic features such as high molar absorption coefficients and rich redox chemistry, properties which can be fine-tuned by varying the nature of the Pc's peripheral substituents and/or the metal center in the macrocycle's inner cavity. As a consequence of their synthetic versatility and unique physical properties, Pcs have been widely utilized as building blocks for the preparation of molecular and supramolecular donor-acceptor (D-A) ensembles in which photoinduced energy/electron transfer events can be triggered/modulated as a function of the electronic character of the Pc molecular or supramolecular counterpart(s).[1]
In this context, the preparation and study of some Pc-based, D-A systems in which the porphyrinoid has been connected, covalently or through supramolecular interactions, to molecular species with interesting structural and electronic features such as endohedral metallofullerenes (Figure 1a),[2a,b] tetracyanobutadiene,[2c] or polycyclic aromatic hydrocarbons (PAHs) such as corannulenes and cyclopenta[*hi*]aceanthrylenes will be presented. Additionally, some examples of appropriately-functionalized Pcs in which supramolecular interactions have been used to promote i) the regio-, stereo- and atropselective synthesis of a non-tethered *cis*-1 C_{60} fullerene bisadduct racemate using a conceptually novel "supramolecular-directed" functionalization approach (Figure 1b)[3a] and ii) the formation of highly stable Pc *H*-aggregates which present reversible acid/base-controlled, assembly/disassembly features (Figure 1c)[3b] will be shown.

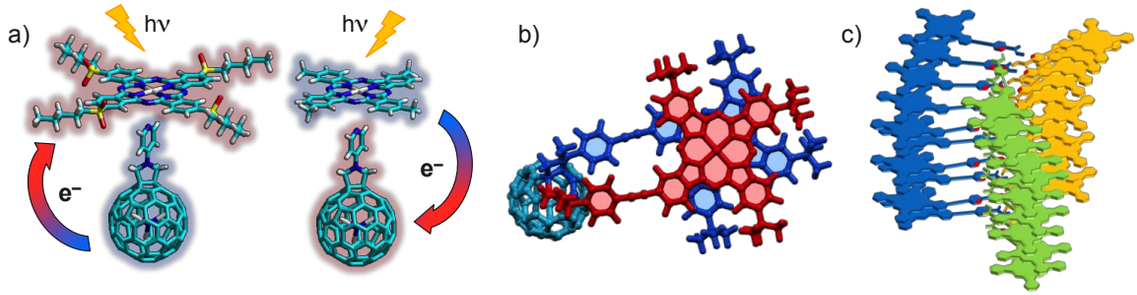

Figure 1: Phthalocyanine-based molecular and supramolecular ensembles.

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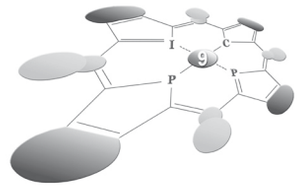

Porphyrins, Phthalocyanines and Pdt – The Last 50 Years

Stanley B Brown

University of Leeds, Leeds, UK and Photopharmica Ltd, Leeds, UK

AWARDS

Porphyrins are key to life and phthalocyanines and other heterocyclics are major components of a host of technological developments. Fifty years ago, the key steps in porphyrin biosynthesis had largely been elucidated, but we were still discovering the huge range of biological activities with which haem and porphyrins are associated, for example in the many manifestations of cytochromes P450. The detailed mechanisms of how haem carries out its catalytic role in catalase, peroxidase, P450 and other enzymes were under intense study.

At the same time, the importance of the breakdown of haem was only being realised, with the discovery of haem oxygenase, though its mechanism of action was largely unknown. This very mechanism, catabolic in the sense of removal and breakdown of haem from haemoglobin through bilverdin and bilirubin (with its implications for jaundice), was shown to be biosynthetic in plants and algae, where the bile pigments are functional units in photosynthesis. In the 1970/80s, we were able to make some contributions to the greater understanding of these processes in experiments which took us through a range of experiences from cannulating the bile duct of a rat and following the subsequent breakdown of its haemoglobin under an ^{18}O enriched atmosphere, to collection of thermophyllic algae from Yellowstone National Park and following their biosynthesis of phycocyanine in the lab, to studies on haemolytic jaundice in Scottish atlantic salmon.

It was inevitable that, with a broad interest in porphyrins, I should be drawn into PDT, especially since we had published several papers on porphyrin aggregation around the time of Tom Doherty's work on haematoporphyrin derivative, a complex mixture of porphrin oligomers, eventually marketed (in slightly cleaned up form) as Photofrin. This interest took us to much work on ALA as a PDT pro-drug and then to phthalocyanines and eventually phenothiaziniums as novel PDT drugs. We established our own Company, Photopharmica Ltd, raised funds to support the development of these photosensitisers, initially for cancer, but latterly as antimicrobial agents, obtained several patents and embarked on Phase I and II clinical studies which have now been completed.

The chemistry, biology and clinical aspects of this work will be discussed, along with an appraisal of what the future might hold.

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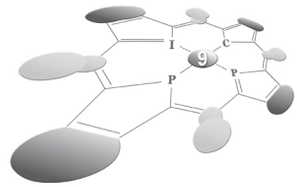

A Molecule for all Seasons: the Heme

Paolo Ascenzi[a] and Maurizio Brunori[b]

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AWARDS

If life without heme-Fe were at all possible, it would definitely be different. Indeed this complex and versatile iron-porphyrin macrocycle upon binding to different "globins" yields hemeproteins crucial to sustain a variety of vital jobs for the cell, generally classified, for convenience, within a limited number of functional families.
Over-and-above the repertoire of functions to be outlined, one should not underestimate the spectacular progress in molecular genetics seen over the last 30 years, which led to the discovery of many hitherto unknown novel hemeproteins in prokaryotes and eukaryotes.
In this talk I shall highlight a few basic aspects of the Chemistry of the hemeprotein universe, in particular those relevant to the control of heme-Fe reactivity and specialization, as sculpted by sets of specific interactions with different protein moieties. And in addition I shall focus on two quite interesting « novel » hemeproteins whose physiopathological role is still a challenge.

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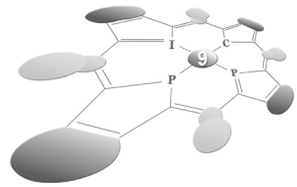

Some thoughts on the study of porphyrin and phthalocyanine

Naisheng Chen

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AWARDS

Porphyrin is a kind of widely existing in animals and plants, is the key material for carrying oxygen molecules in breathe process and photosynthesis respectively. But, the phthalocyanine is the substance that has not be seen in nature. Its source is the only way to artificial synthesis. However, because these two types of substances in the composition of the same nitrogen complexes, having closed circular conjugate system on molecular structure, its highly delocalized π electron, π electron number follow the Huckel 4n+2 rule, show the aromatic chemical properties that is prone to electronphilic substitution reaction than the addition reaction and the oxidation reaction, and similarity in the synthesis method and the application field.So,they was classified as the same research field .Even so, due to the many differences in their composition and structure, we should pay more attention to their special characteristics and to establish composition-structure-property-function relationship.

The development of the field of porphyrin and phthalocyanine, as in this fields of chemistry, is based on the synthesis of new species. Every new composition or the new structure of the compounds appear, will drive the development of related subjects, and even promote the progress of society and people's life style change. Now the synthesis of new species should be based on the study of the composition-structure-property-function relationship of existing species, and realize the design synthesis. Synthesis of these new species may form a scientific virtuous cycle, people effectively prepare useful substances for humans and the environment to reduce the waste of resources and environmental pollution.

By now, the researching team of porphyrin and phthalocyanine in China is growing, and the research results are increasing day by day. We should strengthen the academic communication and cooperation between domestic and foreign counterparts, focus on basic research and at the same time as far as possible change the new discovery to a new invention even new product, and applied them to the current environment, energy, information, life and other fields, for the benefit of mankind.

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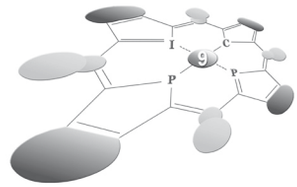

Porphyrin supramolecular systems in aqueous solution: chiroptical probes, multicomponent arrays and molecular switches.

Alessandro D'Urso

Department of Chemical Science, University of Catania, Catania, Italy. adurso@unict.it

AWARDS

Nature has employed porphyrins in a wide range of biological systems and for a broad range of purposes.[1] Chemists have been fascinated by the challenging syntheses of nature-inspired systems and always porphyrins represent the attractive building blocks to design supramolecular complexes. However these molecules hide manifold trouble; even if the peripheral charged groups make these macrocycles water-soluble, however porphyrins remain mainly hydrophobic molecules, preserving the well-know tendency to aggregate. This ''dichotomy'' is worthy of special attention because it plays a central role in the non-covalent syntheses of quite complex porphyrin arrays.

Here we will present how a rationalization of the spontaneous self-assembly paradigm offer tremendous potentialities to obtain a wide variety of complex systems, having specific functionality and properties. In particular we will propose an overview of the our developments in non-covalent syntheses of multi-porphyrin supramolecular species in aqueous solution: *i)* using chiral templates (biopolymers or inorganic complexes) we transfer, detect and/or amplify the matrix handedness, observing for some of such systems the chiral memory phenomenon;[2] *ii)* even we have proposed some metalloporphyrins as chiroptical probe for unusual DNA conformation (Z-DNA), demonstrating the ability of porphyrins to sense the DNA helix handedness, even in competitive environment (embedded between two portions in B-form);[3] *iii)* combining calixarenes and porphyrins is possible to obtain multicomponent arrays, governed by precise hierarchical rules, which together with a rational functionalization of the molecular components leads to supramolecular entities of well-defined and tunable stoichiometry.[4] Finally we are investigate the potency of porphyrins as a proteasome inhibitor, which is the new strategy to cure of tumors.[5]

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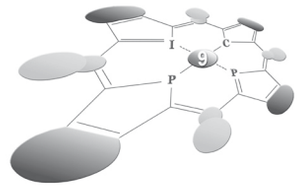

Boron Dipyrromethenes and Related Systems: Synthesis, Reactivity and Property

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AWARDS

Boron dipyrromethenes (BODIPYs) have received intense research interests due to their excellent chemical and physical properties, and has found wide applications in various research fields.[1] In this area, over the last few years, my research group has been devoted to the development of alternative and improved new synthetic platforms and methodologies for the facile synthesis and fine tune of BODIPY dyes and related systems, investigated their reactivity, property and potential applications. In specific, we have (i) developed a set of alternative and improved new methodologies[2-3] for the facile access to functionalized BODIPYs, based either on the *de novo* synthesis of novel BODIPY platforms[2] (3,5-diiodoBODIPY and 3-halogenated benzoBODIPY) or on a set of new regioselective postfunctionalization methodologies for the BODIPY core[3], including β-formylation[3a-b], α-chorination with $CuCl_2$[3c], and the stepwise bromination with liquid bromine[3d]; (ii) synthesized a series of novel functional dyes (like far-red to near-infrared BODIPYs[4] and bisBODIPYs[5]) and photosensitizers[4b,5c] for biomedical applications; (iii) the development of a set of new methodologies for the facile access of the pyrrolyldipyrromethene skeleton[6], the core structure for prodigiosin derivatives, including the first one-pot synthesis of pyrrolyldipyrromethene[6a-b], featuring with easy and readily accessible starting materials and the avoiding use of expensive transition metal catalyst; iv) the synthesis of a series of prodigiosenes and their boron complexes (pyrrolylBODIPYs). Herein, we discuss each of these research areas, giving an overview of these past achievements by my group as well as a sense of our current and future goals.

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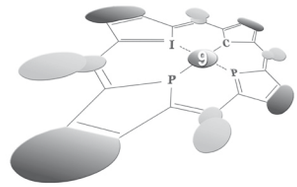

Synthetic Porphyrinoids Chemistry

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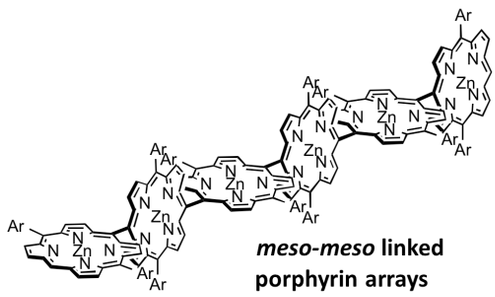
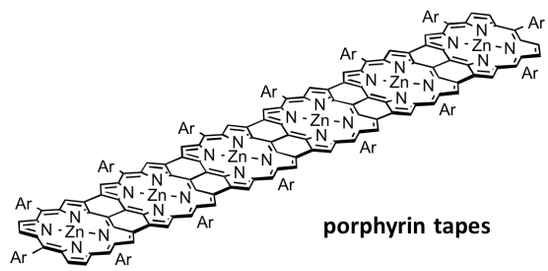
AWARDS

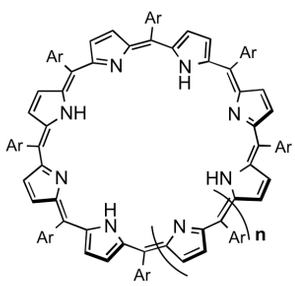
In recent years, porphyrinoids have emerged as promising functional molecules, which possess characteristic properties that are not shared by normal porphyrins. In the last three decades, we have been continuously exploring novel porphyrinoids including 1) extremely long *meso-meso* linked porphyrin arrays, 2) extensively π-conjugated porphyrin tapes, 3) *meso*-aryl substituted expanded porphyrins, 4) Möbius aromatic and antiaromatic expanded porphyrins, 5) porphyrin pincer molecules, and 6) ring-contracted subporphyrinato borons. In this presentation, the chemistry of these representative porphyrinoids will be provided.



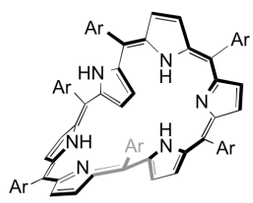
***meso-meso* linked porphyrin arrays**



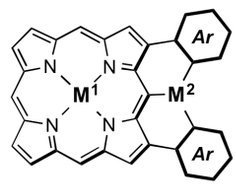
porphyrin tapes



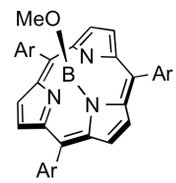
***meso*-aryl substituted expanded porphyrins**



Möbius aromatic molecules



porphyrin pincer complexes



ring-contracted subporphyrinato borons

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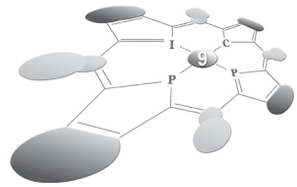

Non-porphyrin pyrrolic macrocycles

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[b]*Shanghai University*

AWARDS

This lecture will summarize efforts in the Sessler group to develop and study non-porphyrinic macrocycles. Early work on expanded porphyrins will be reviewed briefly with an emphasis on texaphyrins at potential therapeutics and beta-pyrrole substituted expanded porphyrins as receptors for anions and cations. Newer work with expanded porphyrins involving studies of their electronic properties, including anti- and semi-aromaticity effects, and as building blocks for self-assembly will also be included. Much of the presentation will focus on so-called calixpyrroles, non-conjugated pyrrolic macrocycles that are formal analogues of porphyrinogens. Their use as anion and ion pair receptors will be discussed in the context of creating extractants and transporters that may be useful in addressing several real-world problems. Studies of modified calixpyrroles as precursors for the creation of non-covalent electron transfer model systems, logic devices, non-covalent oligomers, ion flux regulators, and sensors will be reported. Further insights can be gleaned from the selected references below.

This work has benefited from support from the U.S. National Science Foundation, the U.S. Department of Energy, Office of Basic Energy Sciences, the Robert A. Welch Foundation, the Korean World Class University program, and Shanghai University. Collaborations with a number of groups, including but not limited to those of Profs. Dongho Kim, Shunichi Fukuzumi, Jong Seung Kim, Philip A. Gale, Injae Shin, Christopher Bielawski, Eric Anslyn, Christophe Bucher, Dirk Guldi, Pradeepta Panda, Changhee Lee, Jan Jeppesen, and Tomas Torres, are also gratefully acknowledged. This work could not have been accomplished without the help and dedication of many, many talented undergraduate and graduate students and postdoctoral fellows. I am in their debt.

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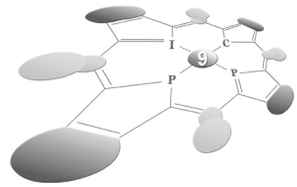

Design and Creation of Novel Porphyrinoids Based on the Structure-Property Relationship

Soji Shimizu

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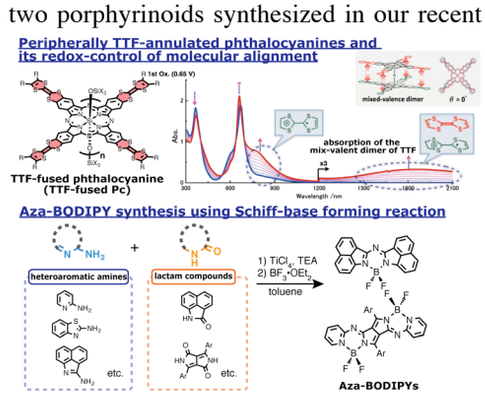
AWARDS

Porphyrins and phthalocyanines are fascinating conjugated molecules due to their unique optical and electrochemical properties arising from the 18π-electron conjugated system. Structural modification of these molecules by contraction and expansion of the conjugated systems, changes in the molecular symmetries, and so forth, which directly provides significant perturbation to their properties, has been an important research direction, and the knowledge of the structure-property relationship has been accumulated during the long history of the porphyrin and phthalocyanine chemistry. In order to further enrich the molecular chemistry of porphyrinoids towards application studies relating to the photo-energy conversion, such as photodynamic therapy, organic photovoltaics, and organic electronics, we have designed and synthesized a various kind of novel contracted, core-modified, expanded, and peripherally-functionalized porphyrinoids,[1–3] based on the structure-property relationship of porphyrinoids, especially from the view point of spectroscopic properties as well as supramolecular interactions. On the occasion of the award lecture, two porphyrinoids synthesized in our recent research, peripherally tetrathiafulvalene (TTF)-annulated phthalocyanine (Pc) and its μ-oxo oligomers[4] and aza-BODIPYs, a half structure of phthalocyanines,[5] will be presented. The TTF-annulated Pc systems were designed as a molecular wire, in which molecular alignment can be controlled in a supramolecular manner, while a new synthetic method of aza-BODIPYs, which was aimed for improving fluorescent properties in the near infrared region, was established using Schiff base forming reaction of lactams and heteroaromatic amines. In the presentation, our recent trial of the application studies on organic photovoltaics and organic rechargeable batteries using these novel porphyrinoids will also be reported.



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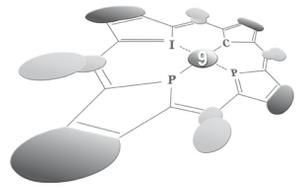

Phthalocyanines: Old dyes, New Molecular Materials

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AWARDS

Phthalocyanines (Pcs)[1] have emerged as excellent light harvesting antennas for incorporation into D-A systems, mainly in connection with carbon nanostructures, like endohedral metallofullerenes, SWCNT and graphene, as acceptor or donor moieties, in which the Pc has been attached, covalently or through supramolecular interactions. They are among the few molecules that reveal an intense red and NIR absorption and therefore, constitute also promising dyes in molecular photovoltaics. On the other hand Subphthalocyanines (SubPcs),[2] are intriguing compounds. Their 14 pi-electron aromatic core associated with their curved structures render them also appealing building blocks for the construction of multicomponent photo- or electroactive assemblies. Recently, the development of an improved synthetic methodology for axially substituted SubPc allowed the efficient synthesis of a variety of SubPc-based hybrids. To enhance the understanding of the nature of these curve pi-extended surfaces, we have undertaken a series of studies, including the synthesis and characterization of SubPc-based capsules. SubPc pi-systems can be also organized at supramolecular level. During this talk an overview of the results obtained by our group in the field of Pcs and SubPcs during the last few years will be shown.

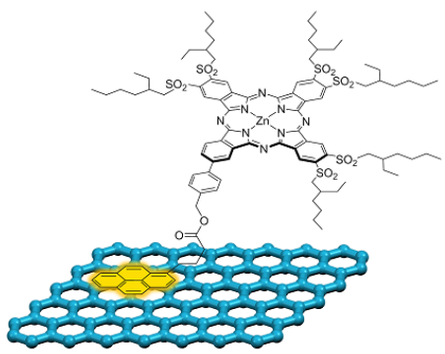

Figure 1: Phthalocyanine-based supramolecular ensemble.

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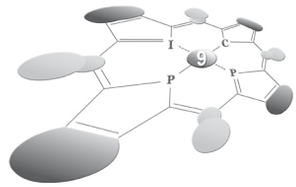

Spectroscopy and Raman imaging studies of phthalocyanines in diagnostics and treatment of cancer in human tissue- submitted to the International Conference on Porphyrins and Phthalocyanines

Halina Abramczyk, Beata Brożek-Płuska

[a] *Technical University of Lodz, Institute of Applied Radiation Chemistry, Laboratory of Laser Molecular Spectroscopy, Wroblewskiego 15, 93-590 Lodz, Poland.*

We will discuss some fundamental properties of phthalocyanines in solutions, films and at biological interfaces of human cancerous and noncancerous tissues using conventional and new emerging methods of molecular spectroscopy. We will introduce also some fundamental principles of Raman imaging as a new, emerging and noninvasive technology of tissues mapping to monitor distribution and localization of photosensitizers in live cells and human tissues. The applications of the femtosecond pump-probe transient absorption spectroscopy of phthalocyanines will also be discussed. The properties of phthalocyanines will be based on results obtained in our laboratory for zinc and aluminum phthalocyanines.
We will demonstrate how the combination of Raman spectroscopy, IR spectroscopy, femtosecond spectroscopy, fluorescence imaging and Raman imaging techniques can be used to obtain unique insight into vibrational features of cell/ tissue and intracellular processes occurring on the time scale from femtoseconds to nanoseconds in normal and cancerous human tissues as well as localization of photosensitizers.

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Acknowledgements
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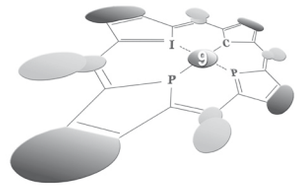

The extraordinary energy transfer capabilities of the phycobilisome

N. Adir[1], S. Bar Zvi[1], R. Ben Harosh[1], L. David[1], S. Ghosh[1], D. Harris[1], O. Tal[1], I. Eisenberg[2], N. Keren[3], Y. Paltiel[2], C. Nganou[4], M. Mkandawire[4], R.E. Blankenship[5], D. Kirilovsky[6]

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The phycobilisome (PBS) pigment-protein complex is the main antenna in cyanobacteria and red algae. PBS function appears to be far more robust than expected when analyzed in vivo and in vitro, performing internal energy transfer over large distances in a wide spectrum of configurations and surroundings. In the past, a major issue in the study of the PBS is its inherent lack of stability. Although containing a class of proteins call linker proteins, assumed to provide functional and assembly directionality, upon isolation in buffers close to or below the ionic strength of the cytoplasm, the PBS disassembles and the linkers are lost. We have developed cross-linking methods for stabilization of the PBS in low salt without losing functionality, allowing the analyses of the entire PBS using: crystallography, single particle reconstruction from Cryo-TEM images [1], ultra-fast [2] and high-resolution surface spectroscopies [3]. We have utilized these structures to suggest the unique properties of the PBS, and to identify the differences between species that live in different environments. The robustness of the PBS components suggests that they could be used in non-biological settings according to quantum principles. There are significant scientific challenges to real world applications of phycobiliproteins in such devices, including de-coherence that erodes operation of a quantum device and control issues. We have used isolated Phycocyanin (PC) that self-assembles into bundles of nanowires [3]. These nanowires exhibit long range energy transfer through hundreds of individual units.

In addition, we have used coupled cross-linking/mass spectrometry to identify more precisely the interaction interfaces between subunits along the energy transfer pathway, as well as control sites that can alter the flow of energy to avoid photodamage. This includes a new model for the interaction between the PBS and the Orange Carotenoid Protein (OCP). The OCP has been found to be activated under strong illumination, and in its activated form can almost totally inhibit energy transfer to the reaction centers in vivo as well as quench PBS fluorescence in vitro [4]. Previous models could not explain how an external small protein could have an effect of the internal chromophores of the PBS. In the model presented here, we will show how protein-protein interactions alter the PBS structure and chromophore environments.

Acknowledgements: this work is supported by the US-Israel Bi-National Science Foundation (2009406 and 2014395) and the Israel Science Foundation (1576/12)

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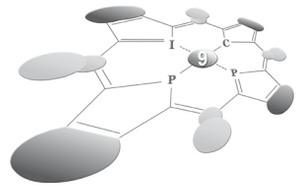

High-valent iron phthalocyanine, porphyrin and porphyrazine μ - dimers: the insights from spectroscopies and DFT calculations

Pavel Afanasiev

Institut de Recherches sur la Catalyse et l'Environnement de Lyon, IRCELYON, UMR 5256, CNRS – Université Lyon 1, 2, av. Albert Einstein, 69626, Villeurbanne, France.

Nitrogen, carbon and oxygen-bridged diiron porphyrin and phthalocyanine complexes have been intensely investigated during the last years. Recently the interest to these macrocyclic binuclear complexes have been renewed after discovery of interesting catalytic properties of in the oxidation of hydrocarbons, formation of C-C bonds and oxidative dehalogenation of poly- and perfluorinated aromatics [1-3]. μ-Nitrido diiron phthalocyanine $[PcFe^{+3.5}NFe^{+3.5}Pc]^0$ is a particularly efficient catalyst, able to catalyse the oxidation of methane under near-ambient conditions.

Our goal was to understand electronic properties of these complexes and to propose a rationale for the exceptional activity of μ-nitrido dimers. We compared the properties of structurally similar μ-carbido, μ-nitrido and μ-oxo dimers of iron phthalocyanine, porphyrin and porphyrazine. Extended X-ray fine structure spectroscopy, high resolution X-ray emission spectroscopy and resonant inelastic X-ray scattering were applied to study geometry and electronic structure of iron species in the series. The data provided by core hole spectroscopies were compared to the results of DFT calculations and provide a coherent description of the structural and electronic properties of complexes as a function of the nature of axial atom and of macrocycle. All complexes have equivalent iron centers with formal iron oxidation degree of 3, 3.5 and 4 for the μ-oxo, μ-nitrido and μ-carbido dimers, respectively. However the bond length to the bringing atom changed in an unexpected sequence Fe-O > Fe-N < Fe-C. According to the X-ray emission spectroscopy, the μ-nitrido dimers are low spin compounds, with the highest covalency in the series. At the same time, red-ox non-innocence of the brigding μ-carbido ligand was supposed.

The DFT calculated geometry and electronic structures, as well as core-hole spectra of hypothetical high-valent oxo-complexes were compared in order to explain catalytic activity trends and to estimate the prospects of spectroscopic observing of such species. The possibilities of EXAFS and XES techniques to detect such species are critically analysed. It appears that the terminal Fe=O bond is the longest in the oxo complex of nitride dimers due to strong trans-effect of nitrido-ligand. The corresponding LUMO of the oxo complexes has the lowest energy within the series explaining their highest oxidative power. Combined experimental and theoretical studies show that catalytic properties can be tuned by the appropriate structural modifications of the macrocycle.

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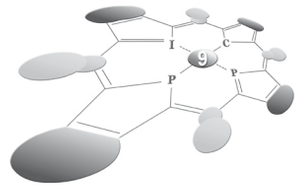
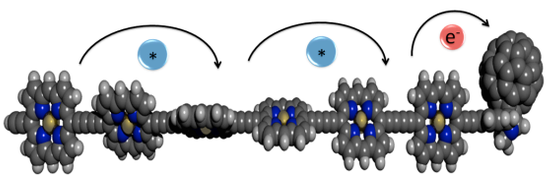


Delocalization and Electron Transfer in Conjugated Systems

Bo Albinsson

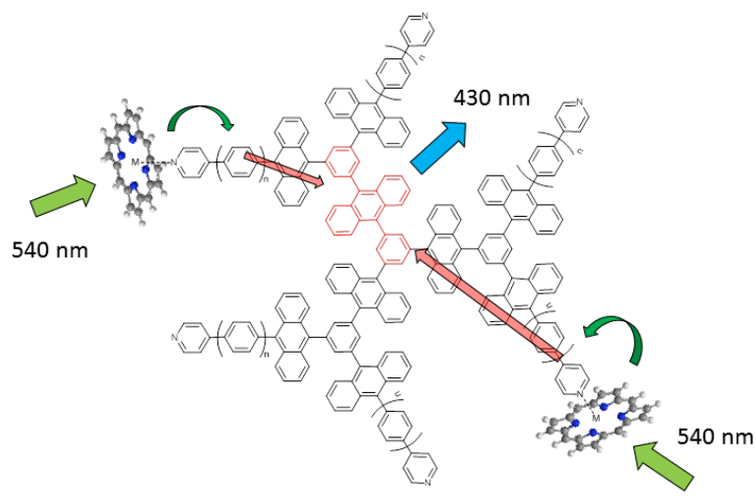
Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden

Delocalization in large conjugated organic systems has a profound influence on the performance of photo voltaic devices such as bulk heterojunction solar cells. In this talk I will discuss two systems where we have studied how the degree of delocalization governs the rate of charge separation and triplet-triplet annihilation up-conversion (TTA-UC), respectively.



In the first example, electron transfer reactions in fullerene appended porphyrin oligomers, $\mathbf{P_n\text{-}C_{60}}$, were found to depend strongly on the conformation of the porphyrin oligomer. It was shown how excitation of different conformations or restriction of oligomer conformation through chemical templating greatly affects the rates and efficiency of the charge separation. Twisted conformers of $\mathbf{P_2\text{-}C_{60}}$ showed a 4 times faster charge separation rate compared to planar conformers.[1] For longer oligomers, excitation of twisted conformers can have the opposite effect since excitation energy could localize too far away from the fullerene electron acceptor for efficient charge separation.[2]

In the second example, I will discuss how rapid triplet excitation energy migration in conjugated 9,10-diphenylanthracene (DPA) oligomers and dendrimers sustain TTA-UC. The dendrimer is sensitized two times through triplet energy transfer from a non-covalently associated porphyrin and rapid triplet energy migration leads to efficient up-conversion without the need for diffusion.[3] It is expected that further development of this system will lead to an efficient platform for diffusion free TTA-UC in solid matrices.



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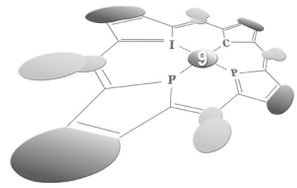

Structural Basis for Heme Acquisition in *Corynebacterium glutamicum*

Shigetoshi Aono

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Heme can be used as an iron source by some pathogenic bacteria, which have the heme acquisition system(s) to uptake heme. The typical heme acquisition system comprises several heme-binding proteins and an ABC transporter. The ABC heme transporter, HmuT-HmuUV is conserved in Gram-positive and Gram-negative bacteria. In this heme transporter system, HmuT, HmuU, and HmuV act as a substrate (heme)-binding protein, a heme permease, and an ATP-binding protein, respectively.

In this study, the crystal structure of the heme-binding protein HmuT (CgHmuT) from Gram-positive bacterium Corynebacterium glutamicum will be reported at 1.4 Å resolution. The overall structure of CgHmuT reveals a bi-lobed topology formed by an N- and C-terminal domain. A heme molecule coordinated by His141 and Tyr242 is bound in a cleft between the N- and C-terminal domains. Though the global fold of CgHmuT is similar to that of HmuT from Yersinia pestis (YpHmuT), the coordination structure of the heme is different from each other. While two heme molecules are bound to YpHmuT, CgHmuT binds a single heme molecule with His141 and Tyr242 as the axial ligands.

Intriguingly, CgHmuT binds a heme with two different orientations. Though the previously reported heme-binding proteins have the interaction between proteins and heme propionate groups in addition to axial ligation to iron, such interactions with heme propionates are absent in CgHmuT. The presence of two different conformations in CgHmuT might be due to a lack of specific interactions between the heme and protein except for the axial ligations.

EPR spectroscopy reveals the heme in CgHmuT is a mixture of high-spin and low-spin states, indicating one of the axial ligand of the heme is in equilibrium between the ligated and unligated states. EPR spectra of wild-type, H141A-, and Y242A-CgHmuT suggest His141 will be reversibly dissociated/associated from/to the heme. The equilibrium between the six- and five-coordinate states in CgHmuT would be responsible for the regulation of heme-binding affinity to control the heme transport reaction between CgHmuT and HmuUV.

The crystal structures of H141A and Y242A variants have also been determined in this study. I will discuss the molecular mechanism of heme recognition and heme transport by CgHmuT based on these structures.

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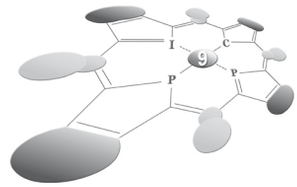
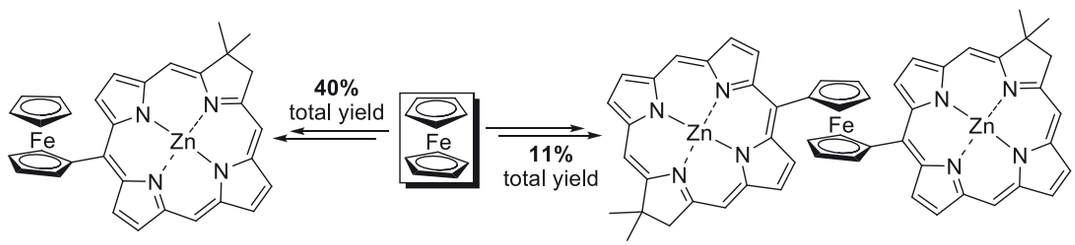


Ferrocene substituted chlorins – synthesis and properties

Anna I. Arkhypchuk, Eszter Borbas

Department of Chemistry – Ångström, Uppsala University, Ångströmlaboratoriet, Lägerhyddsvägen 1, 75120 Uppsala, Sweden

Chlorins are tetrapyrroles with one reduced double bond compared to porphyrins. They widely used in biological imaging and sensing applications, as well as in photodynamic therapy (PDT).[1] Recently, we started project were chlorins are utilized as light harvesting antennae for different responsive units, for example near infrared-emissive lanthanide complexes.[2] The obtained dyads are not only linear combinations of the subunits, but have properties which are distinct from those of the separate building blocks. Thus, the introduction of the electrochemically responsive ferrocene unit is particularly attractive. Combining ferrocene with chlorin cores would give rise to a new series of the compounds. We developed two synthetic protocols which allow the preparation of ferrocenes bearing one or two chlorin units in just 4 steps, with an overall yield reaching 11% and 40%, respectively. Details of the synthesis, as well as a detailed study of the electrochemical and optical properties of the compounds will be presented.



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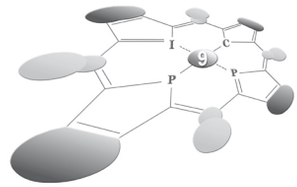

Synthesis and characterization of out-of-plane corrole complexes with large electropositive metals

John Arnold

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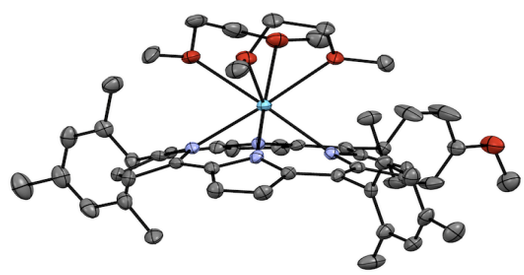
This presentation will focus on our recent studies aimed at preparing unusual corrole complexes with alkali- early transition-, lanthanide-, and actinide metals. Through a combination of two main synthetic routes, we have been able to isolate and fully characterize the first examples of corrole complexes from a number of different groups across the periodic table.



Molecular structure of lanthanum corrole 1·4.5DME, determined by single-crystal X-ray diffraction.

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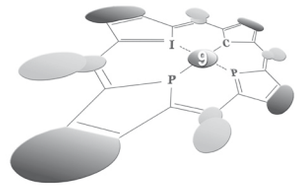

Light Induced Electron Transfer in Fused Porphyrin-Imidazole-Phenol and Porphyrin-Catalyst Dyads as Biomimetic Models of PSII.

Ally Aukauloo,[a] Athanassios Coutsolelos,[b] Georgios Charalampidis,[b] Shyamal Das,[c] Annamaria Quaranta,[c] Maylis Orio,[d] Winfried Leibl[c] and Marie Sircoglou[a]

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Photosystem II is the enzyme in the photosynthetic machinery that captures sunlight to oxidise water through a four-electron and four-proton process. As such this enzyme holds all the chemical facets to perform one of the most desirable photochemical transformation for the development of a solar-based fuel. In effect, chemists are developing chemical assemblies that can reproduce the photochemical and catalytic events to use sunlight to split water. Beyond the foreseeable technological deployment, this research has also helped to gain more insights in the understanding of these natural processes. We are currently developing supramolecular assemblies consisting a porphyrin chromophore an electron relay and a catalyst as minimalist models of Photosystem II. We will discuss on our latest findings in this field.

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2. "Intramolecular photoinduced electron transfer in cobalt(II) chlathrochelate-zinc porphyrin assemblies leading to long-lived Co(I) species. " Sanae El Ghachtouli, Guillot Régis, Winfried Leibl, Aukauloo Ally Porphyrins Phthalocyanines **2014**, 18, 1125–1130
3. Successive light-induced two electron transfers in a Ru-Fe supramolecular assembly: from Ru-Fe(II)-OH2 to Ru-Fe(IV)-oxo. C. Herrero, A. Quaranta, M. Sircoglou, K. Senechal-David, A. Baron, I. M. Marin, C. Buron, J.-P. Baltaze, W. Leibl, A. Aukauloo, F. Banse, Chem. Sci., **2015**, 6, 2323-2327
4. Fused Porphyrin-Imidazole-Phenol Dyad as Biomimetic Models of Light Regulated Electron Transfer Initiator of PSII. (Manuscript)

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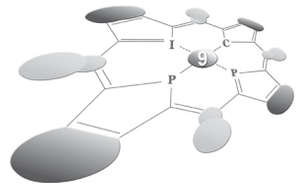

Organic Electronics of Phthalocyanines Assisted by Electric Double Layers in Ionic Liquids

Kunio Awaga

Department of Chemistry & Research Center for Materials Science, Nagoya University

Charge carrier control is a key issue in the development of electronic functions of semiconductive materials. Beyond the simple enhancement of conductivity, high charge carrier accumulation can realize various phenomena, such as optoelectronic conversion and chemical reaction, magnetic ordering, and superconductivity. Electric double layers (EDLs), formed at solid-electrolyte interfaces, induce extremely large electric fields. This results in a high charge carrier accumulation in the solid, much more effectively than solid dielectric materials. In the application of the EDLs to organic electronics, phthalocyanines (Pcs) are promising materials, because they can form highly-oriented robust thin-films, which are insoluble in the electrolytes even under the carrier injection porcesses.

In this presentation, we firstly describe recent developments in the field-effect transistors (FETs) of Pcs with gate dielectrics of ionic liquids (ILs),[1] which have attracted much attention due to their wide electrochemical windows, low vapor pressures, and high chemical and physical stability. After discussing the factors controlling the mobility and threshold voltage in these types of IL-FETs, and showing the ionic liquid dependence of the transistor performance, we describe the control of ambipolar performance of the IL-Pc-FETs.[2]

Secondly, we report a novel architecture of photodetectors utilizing the transient photocurrent response, having a [Metal/Ionic Liquid/Phthalocyanine/Metal] structure. The high capacitance of the formed electric double layers at the ionic liquid interfaces is concluded to yield high charge separation efficiency within the phthalocyanine layer.[3] We demonstrate the intrinsic benefits of these photodetectors, namely their effective operation under high steady-state lighting, responding only to changes in light intensity, and their ability to react to several light sources simultaneously.

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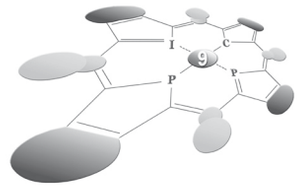

Controlled Self-assembly of Porphyrin and Applications

Yong Zhong[a], Jiefei Wang[a], Yanqiu Liu[a], Na Zhang[a], Feng Bai[a*]

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Porphyrin self-assembly nanomaterials, as visible-light harvesting materials in the artificial photosynthetic systems that mimic natural photosynthesis, have been well designed and developed via molecular self-assembly with non-covalent interactions including electrostatic force, metal-ligand coordination, π-π stacking, hydrogen bonding as well as host-guest interactions[1-5]. And porphyrin self-assembly with well-defined structures have drawn much attention in a wide range of fields including light-energy conversion, photonics as well as photodynamic therapy due to their attractive photophysical, photochemical and electronic properties in the visible-light region. We report a surfactant self-assembly induced micelle encapsulation method to fabricate porphyrin nanocrystals using the optically active precursor zinc porphyrin (ZnTPP). Through confined non-covalent interactions of ZnTPP within surfactant micelles, nanocrystals with a series of morphologies including nanodisk, tetragonal rod, and hexagonal rod, as well as amorphous spherical particle are synthesized with controlled size and dimension[2,3,5]. A phase diagram that describes morphology control is achieved via kinetically controlled nucleation and growth as shown in Figure 1. Due to the spatial ordering of ZnTPP, the hierarchical nanocrystals exhibit both collective optical properties resulted from coupling of molecular ZnTPP and shape dependent photocatalytic activities in photo degradation of methyl orange (MO) pollutants.

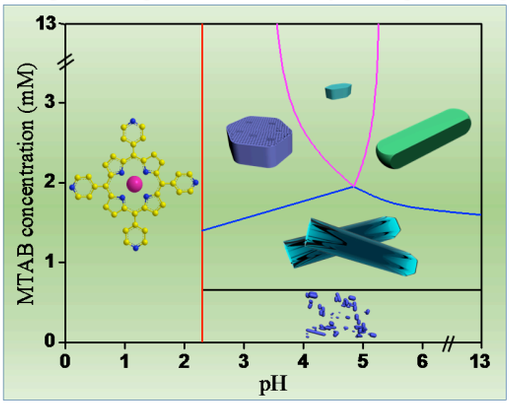

Figure 1. Nanocrystal morphology evolution with the surfactant concentration and pH

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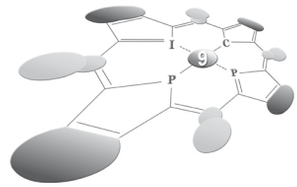

Conjugated supramolecular materials for electro-optical applications

Dario M. Bassani[a]

[a]*Institute of Molecular Sciences, CNRS UMR5255, Univ. of Bordeaux, France*

The assembly of small molecules into active materials is a major aspect of bottom-up engineering for organic electronic devices. With this in mind, we investigate the use of molecular recognition motifs to direct the formation of selected architectures possessing unique ground- and excited-state electronic properties. In this approach, designed non-covalent interactions are used to direct the spatial arrangement of electro- and photo-active compounds in view of imparting specific functionalities such as energy transfer in photo- and electro-luminescent devices, or controlling the emission polarization in fullerene self-assembled ribbons. Various examples will be presented, coveting the reversible morphological transitions between different architectures and the use of H-bonding to either promote complete mixing of different chromophores or their phase separation in response to a self-sorting behavior.

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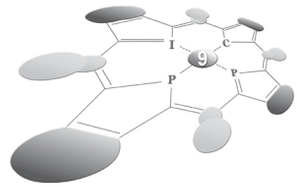

Boron Subphthalocyanines and Boron Subnaphthalocyanines; Very Versatile Materials with Robust Chemistry for Application in Organic Photovoltaics

Timothy P Bender[a,b,c]

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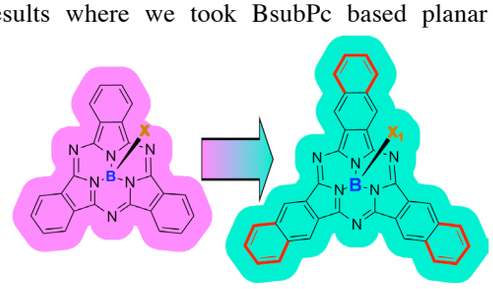
For some time, our group has been focused on the design and synthesis of derivatives of boron subphthalocyanine (BsubPc)[1] for application in organic electronics[2] with a specific focus on organic photovoltaics and light emitting diodes; during this presentation however I will focus specifically on their application in organic photovoltaics. I will begin by focusing on our efforts with regards to synthetic variants of BsubPcs and their application in planar heterojunction organic photovoltaic cells (OPVs, organic solar cells, OSCs). After summarizing this work, I will then outline our very recent results where we took BsubPc based planar heterojunction OSCs and put them in the ambient environment on the roof of our building in downtown Toronto during the summer of 2015. What we found was that during that time, the BsubPc based cells were remarkably stable. We were able to form a structure property relationship to their stability in the ambient environment. Recently, we have also shown that BsubPcs are deficient triplet harvesters from pentacene.[3,4] They are amongst only a few materials known to facilitate this process.



In parallel we have also been exploring the concept of complementary absorption engineering by either the chemical modification of BsubPcs or by pairing BsubPcs with alternative materials having complementary absorption profiles. For example, I would outline or unpublished or recently published activities where we have shown that a highly substituted BsubPc can yield a red shifted absorption profile of approximately 100 nm. This shift is equivalent to that of boron subnaphthalocyanines (BsubNcs). We have also recently been exploring the chemistry of BsubNcs themselves. I will outline our results and the application of our BsubNcs in OPVs.[5] Time permitting, I will also outline the pairing of a BsubPc with phosphorus tetrabenzotriazacorrole (a phthalocyanine analogue) which yielded a unique gray organic photovoltaic cell and our group's recent exploration of the bulk-heterojunction OPV space whereby BsubPcs are fullerene alternatives, although we are not the first to do so.[6]

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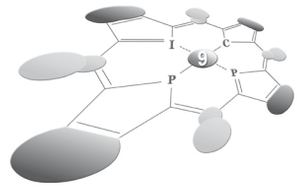

Photosensitizers for Antibacterial PDT: Synthesis, Singlet Oxygen Generation, Hydrophilicity Control and Toxicity Assays

Dmitry B. Berezin[a], Andrey V. Kustov[b,c], Evgeniy A. Venediktov[b], Vladimir V. Makarov[a], Sergey O. Kruchin[b], Dmitry V. Belykh[d]

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The significant increase of resistance of many pathogenic microorganisms to widely used antibiotics and antiseptics is the major reason for searching new low toxic drugs with a sufficient therapeutic width. Bacteria reveal many mechanisms for adaptation to antibiotics promoting the increase of strains resistance. The alternative way of treatment which allows to suppress pathogenic flora is the antibacterial photodynamic therapy (PDT)[1-3]. As for the case of treating tumors drugs (photosensitizers, PS) here, being located into an inflammation seat, produce under light action reactive oxygen species that destroy bacterial cells and stimulate regenerative processes. In comparison with antibiotics an antibacterial action of PDT is not weakened during the treatment as bacteria are not able to cultivate mechanisms to become resistant towards oxygen reactive species.
Our work is aimed not only on the synthesis and spectral identification of new porphyrin, chlorin, phthalocyanine and corrole PS containing biologically active fragments such as pipirazine, quinoxaline-N-oxide, etc., but suggest broad photo-physical, thermodynamic and microbiological study. PS behavior in a solid state and solutions is studied with different techniques including calorimetry, spectroscopy and solubility. Biologically active sites of macrocyclic platform of PS are designed to increase solubility of the molecule in polar media, provide better penetration through cell membranes and an additional antibacterial effect.
The hydrophilicity of PS is studied by UV-Vis and fluorescent spectroscopy in relation to their association in a water-rich media. The solubility in presence of different surfactants as well as distribution coefficients in the system water – 1-octanol for PS is measured. Efficiency of potential PS is proved by their low aggregation degree in model solutions causing acceptable photo-physical parameters as red-shifted Q-band in the absorption spectra, high yield and lifetime of singlet oxygen. The photo-physical, microbiological and histological studies performed provide the important information about sensitizers ability to generate singlet oxygen under various conditions, their antibacterial action towards standard and antibiotic-resistant strains, toxicity for laboratory animals.
This work was supported by the Russian Scientific Foundation (Grant 15-13-00096).

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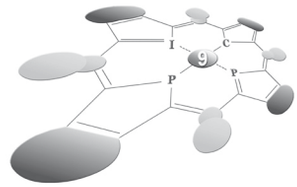

Insights into Sensitivity and Distinctive Chiroptical Response of Arylporphyrins in Molecular and Supramolecular systems

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The usefulness of Electronic Circular Dichroism (ECD) in the structural studies of chiral molecular and supramolecular arrays that contain porphyrins or metalloporphyrins is already widely recognized. Due to unique combination of favorable geometric and electronic features the spectroscopic response by porphyrins can provide rich and sensitive informations not only regarding the substrate structure itself but also for the effect of environmental conditions. A single CD Cotton effect in the Soret region, a bisignate CD curve when a through-space porphyrin–porphyrin exciton coupling takes place or a distinctive set of multiple CD bands in case two or more porphyrins adopt a chiral mutual orientation at a very close distance at ca. 3-4 Å demonstrate the porphyrin multifaceted CD response. Importantly, the latter can be observed either when the porphyrins or metalloporphyrins are covalently attached to a chiral scaffold or when they interact non-covalently with chiral hosts forming supramolecular host-guest complexes or aggregates[1]. Yet, in more complicated cases the relationship between the experimental ECD response within porphyrin Soret band and the most probable molecular or supramolecuar structure cannot be rationalized without a thorough computational analysis with also attention to environmental factors.

In this presentation we will discus some recent results that illustrate the application of porphyrins as a versatile chiroptical sensors and will address some still existing limitations in the analysis. The first examples include covalently linked porphyrins to achiral scafolds forming the so called, tweezers[2], then linked to chiral biopolymers, such as DNA[-3], peptide nucleic acids (PNA)[4], and to locked nucleic acids (LNA)[5]. Finally, we will also discuss non-covalent DNA-porphyrin inter-molecular interactions where a conformational transition from right-handed B-DNA to left-handed Z-DNA can sensitively be monitored by a dual CD response: an extrinsic ICD within porphyrins Soret region and an intrinsic CD bellow 300nm related to nucleotides double helix.[6]

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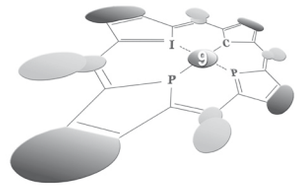

FRET-based Ratiometric Detection of Heavy Metal ions

Mengliang Zhu, Dongli Zhang, Wenxin Lu, Jinghui Zhang and Yongzhong Bian

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Fluorescent sensors for detecting transition- and heavy-metal ions in environmental and biological systems have received considerable attention. In comparison with single emission intensity-based "turn-off" or "turn-on" sensors, ratiometric sensors can afford self-calibration by dual-channel detection and thus perform precise analyses against various environmental and instrumental factors. One of the most frequently applied mechanisms for ratiometric sensing is the binding-induced modulating of intramolecular fluorescence resonance energy transfer (FRET), which is highly dependent on the distance between the donor and acceptor, the overlap integral between the donor emission and acceptor absorption, and the relative orientation of the transition dipoles. Hence the binding-induced changes of the spatial and electronic structure can effectively modulate the FRET efficiency within a donor-acceptor system, consequently leading to change in the fluorescence intensity.

In order to develop heavy-metal ion sensors, we have proposed a new strategy for ratiometric fluorescent detection that is based on the rational integration of two sensing mechanisms of a binding-induced modulating of FRET efficiency coupled with a metal-chelating quenching of fluorescence. Synergistic coupling of these two functions leads to exceptionally large change in the emission ratio, thus allowing for ratiometric detecting of metal ions with improved sensitivity. As proof-of-concepts, a BODIPY-porphyrin dyad (**1**) and a series of phthalocyanine-porphyrin(Zn) hetero-oligomers (**2**-**4**) have been designed for ratiometric fluorescent detection, which show excellent selectivity and sensitivity toward Ag^+ and Pb^{2+} respectively.

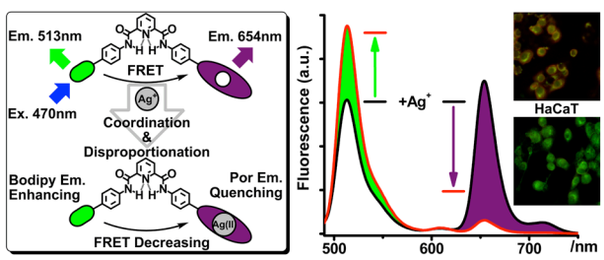

Figure 1. Ratiometric fluorescent detection of Ag^+ by the BODIPY-porphyrin dyad (**1**).

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Synergic multiporpyrin systems for combined imaging and photodynamic therapy by two-photon excitation

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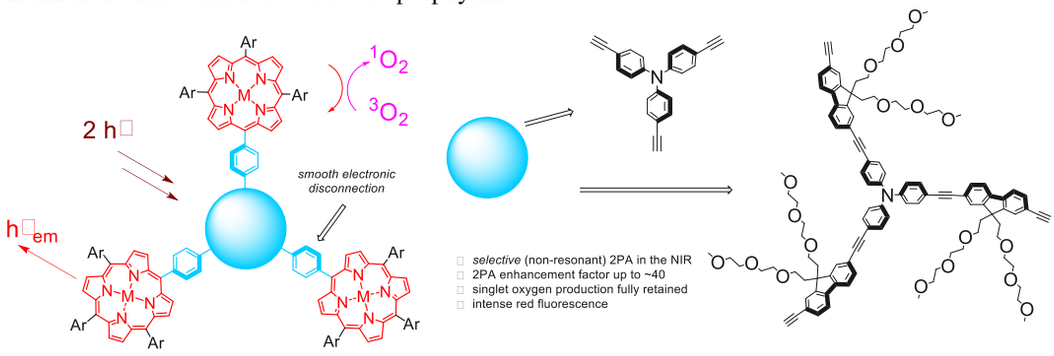
Photodynamic therapy (PDT) is a medical technique used in oncology for resection of tumors as well as in ophthalmology in the treatment of age-related macular degeneration. The use of a two-photon (2P) excitation instead of standard excitation offers new perspectives for PDT, especially for small solid tumors as two-photon absorption (2PA) offers several advantages including highly localized excitation and increased penetration depth in tissues.[1] This however calls for the use of optimized 2P photosensitizers that should combine very large 2PA cross-sections in the biological spectral window (700-1100 nm) and high singlet oxygen quantum yields.
Most of the photosensitizers currently used clinically or in clinical trials are porphyrin derivatives (porfimer sodium and verteporfin). These compounds exhibit high singlet oxygen quantum yields but low 2PA cross sections (10 GM and 50 GM, respectively) in the NIR.[2] Dramatic enhancement of the 2PA cross-sections can be achieved in porphyrinoids, conjugated porphyrin oligomers, planarised fused or bridged porphyrins or supramolecular assemblies. The extension of the π-conjugated system involves the porphyrin or porphyrinoid macrocycles thus leading to major modification of their photophysical properties such as marked broadening and red-shift of the Q-bands. Yet possible consequences are weakening of fluorescence and photosensitizing properties. In that context, we have implemented a route towards porphyrin-based 2P photosensitizers exhibiting very large 2PA in the NIR while maintaining the fluorescence and the excellent photosensitization properties of the porphyrin moiety. Our molecular engineering approach, based on a smooth electronic disconnection between 2PA octupolar or quadrupolar cores and the peripheral porphyrins, leads to a major increase in (non-resonant) 2PA responses in the NIR, while fully retaining fluorescence and photosensitization characteristics of isolated porphyrins:



This strategy relies on efficient 2P excitation to a higher excited-state located on the 2PA module followed by total and ultrafast through-bond energy transfer to the lowest lying excited state located on peripheral porphyrin and can be generalized to different platforms authorizing the grafting of targeting units.

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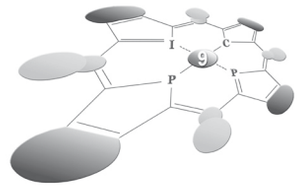

Coordination of ^{213}Bi into porphyrins: the filiation elements are important as well

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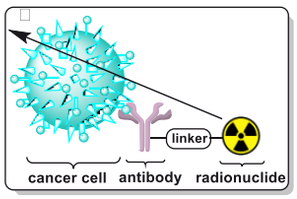
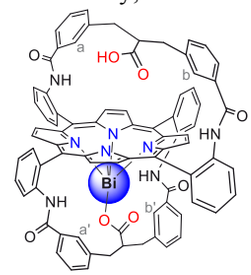


α-radio-immunotherapy principle

α-radio-immunotherapy (α-RIT) is a promising cancer therapy based on the delivering of cytotoxic α-radiation (left). Indeed, the high linear energy transfer and short path lengths of α-particles make them highly destructive to the genetic material.[1] For instance, therapeutic activities of antibodies labelled with the ^{213}Bi α-emitter have been proved on bone marrow cancer cells.[2] Bifunctional chelates for ^{213}Bi, mostly developed in the 90's (CHX-A"-DTPA, C-DOTA and derivatives), still suffer from slow complexation rates or low *in vivo* stability,[3] hence the importance of designing innovative ligands.



bis-strap porphyrin complex 1_{Bi}

Conversely to non functionalized porphyrins, strap porphyrins bearing overhanging carboxylic acid group(s)[4] incorporate bismuth almost instantaneously at room temperature, leading to stable metalloporphyrins as $\mathbf{1_{Bi}}$ (right).[5,6] They have been subjected to ^{213}Bi radiolabelling experiments with success: for the first time, an α-emitter has been incorporated in a porphyrin. Insertion of ^{213}Bi in porphyrin **1** at pH 7 is up to 80 % at 75 °C (35 % at 40 °C) after only 5 min!

Interestingly, we will show that the coordination properties of the daughter elements of bismuth 213, namely lead and thallium have to be controlled as they also form dinuclear species that undergo new dynamic processes.[7] For instance we have observed with the cold isotopes that pre-complexation of **1** with Pb^{II} influences Bi^{III} insertion rate with 300 fold increase.[8] While developing water-soluble counterparts of ligand **1**, we further realised a competitive study with CHX-A"-DTPA, the "gold standard" for ^{213}Bi.

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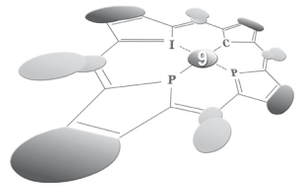

Charge Transport through Single Porphyrins and Related Molecules

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Charge transport through and between molecules is central to many important processes in nature. In particular, studying the conductivity of single molecules can contribute to a better understanding of charge transport through molecules, and also help develop better molecular wires and other building blocks of molecular electronics, light harvesting devices, etc. We will discuss the results of different experiments designed to understand these processes at the single molecule level with a specific focus on porphyrins. We measure the conductivity of molecules using the Scanning Tunneling Microscope break-junction (STM-BJ) method that utilizes repeatedly formed circuits where one or a few molecules are trapped between two electrodes, at least one of which has nanoscale dimensions. The statistical analysis of thousands of measurements yields the conductance of single molecules.

One particular interest has been the role of the molecule-electrode contact in charge transport. In the simplest analysis this contact can present a substantial barrier to charge injection, which can have important consequences in devices such as dye sensitized semiconductor nanoparticle solar cells. We have investigated this phenomenon using porphyrins with a variety of anchoring groups, including aniline, pyridyl and benzoic acids.[1] Interestingly, and contrary to previous reports, the principal effect is to change the effective length of the molecule through which charge is transported. Furthermore, the conductivity appears to scale quasi-linearly with molecular length. Futher experiments reveal hapticity dependent charge transport through carbodithioate terminated porphrins.[2]

In porphyrin species with more than two anchoring groups there is ambiguity as to the charge transport pathway as the molecule can bridge the nanoscale gap of the STM-BJ using anchoring groups at different locations in the molecule. Using porphyrins only two anchoring groups it is possible to distinguish between two possible charge transport pathways in a porphyrin species with four anchoring groups.[3] In addition, these results show that single molecule conductivity experiments can distinguish between porphyrin isomers of same mass.

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New NIR phosphorescent benzoporphyrin complexes for photonic applications

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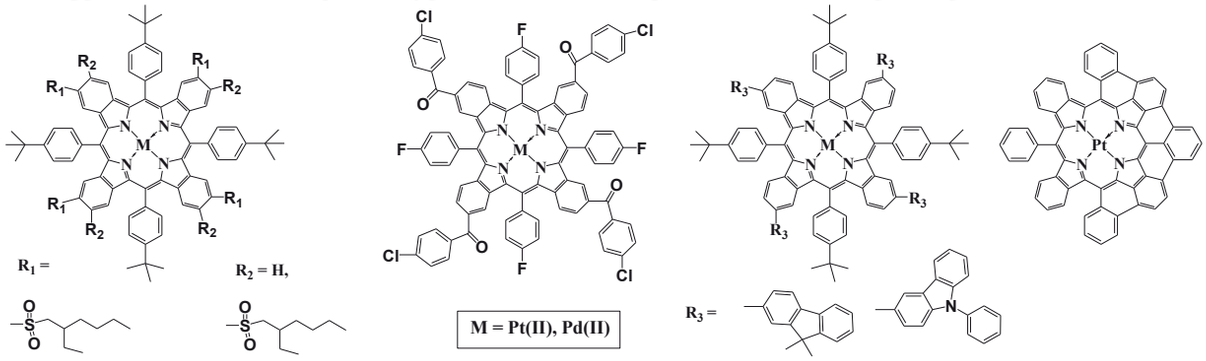
Dyes showing strong room temperature phosphorescence are of high interest for numerous applications. NIR phosphorescent dyes[1] are of particular promising for application in NIR OLEDs and solar concentrators, in vivo sensing and imaging of oxygen,[2] triplet-triplet annihilation (TTA) based upconversion. Therefore, synthesis of new pi-extended porphyrins which possess high chemical and photochemical stability, strong absorption and emission, preferably at longer wavelengths, remains of high interest.

Here we report new Pt(II) and Pd(II) complexes with benzoporphyrins which explore various synthetic modifications (Figure). The first group represents extremely electron-deficient sulfon derivatives which possess unmatched solubility, high resistance to photooxidation and efficient thermally-activated delayed fluorescence. Readily available benzophenon-porphyrins and pi-extended benzoporphyrins feature bathochromically shifted absorption and emission spectra. Finally, we explored rigidization of the porphyrin macrocycle via intramolecular bridging via Scholl reaction, resulting in compounds with remarkable photophysical properties. The new dyes were applied as indicators in optical oxygen sensors and as triplet sensitizers for organic upconversion.



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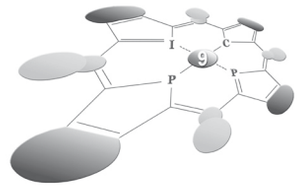

Application of Octaethylporphyrin Structural Motif for Supramolecular Chirogenesis

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Supramolecular chirogenesis is a smart combination of supramolecular chemistry and chirality taking place in non-covalently linked multicomponent assemblies.[1] Porphyrin stuctures are of particular interest to study this phenomen owing to their unique spectral, physico-chemical, and synthetic properties. Among a wide variety of porphyrin derivatives, octaethylporphyrin (OEP) is one of the simplest porphyrins, yet being easily accessible via the standard synthetic procedure or commercially available from many reagent suppliers.

For example, ethane-linked $(ZnOEP)_2$ exhibited considerable optical activity upon interaction with chiral guests.[2,3] Thus, monodentate ligands resulted in formation of the stable 1:2 supramolecular chiral complexes and induction of the noticeable exciton couplet CD signals in the absorption region of porphyrin. The mechanism of asymmetry transfer from chiral guests to achiral $(ZnOEP)_2$ consists of two major steps. At the first step there is formation of the host-guest complex resulting in the initial *syn*-to-*anti* conformational switching. The second step is another structural deformation in $(ZnOEP)_2$ induced by the size difference of ligand's substituents at the chirogenic center resulting in asymmetric screw formation in the supramolecular complexes. For example, when the bulkiness order of the guest substituents around the chiral center coincides with the substituents' priority rule, the (*R*)-enantiomer yields a negative first Cotton effect and a positive second Cotton effect, while the guest with the (*S*) absolute configuration produces CD signal of the opposite signs. In the solid state the situation is different; (*R*)-ligands upon interaction with $(ZnOEP)_2$ induce a positive first Cotton effect, whilst the corresponding (*S*)-ligands produce a mirror image CD spectra.[3] The inverted sign is due to formation of chiral aggregates of opposite screw sense.

For investigation of the weak host-guest interaction mode a special tetrameric $(NiOEP)_4$ host has been designed.[4] This host satisfies the major requirements: (1) total inertness towards most of the conventional host-guest binding modes, (2) possession of an open cavity between the two bis-porphyrin subunits owing to the *syn*-orientation in $(NiOEP)_4$, which allows chiral guest molecules to be incorporated into it and thus to interact with the host in a stereospecific manner, and (3) presence of a spectrally separated B electronic transitions aligned along the diacetylene bridges and located at the low energy region due to the enhanced interporphyrin interactions through the unsaturated linkage. The chirogenic process in $(NiOEP)_4$ induced optical activity in the region of B electronic transitions due to the corresponding host-guest interactions with various chiral solvents. In particular, (*R*)-solvents yield a positive first and negative second Cotton effects, while the (*S*)-enantiomers give the opposite signs.

Further prospects of the application of OEP structural motif and consideration of the 12 Principles of Green Chemistry for supramolecular and chiroptical devices will be presented.[5]

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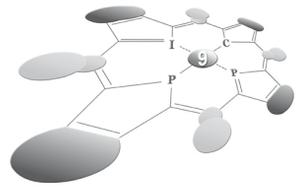

Rare Earth Phthalocyanines: How their Radical Nature Allows for a Versatile Behavior Towards Polluting Gases

Marcel BOUVET, Jean-Moïse Suisse

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Among tetrapyrrole derivatives, due to their radical nature, lanthanide(III) double-decker complexes are easily oxidized and reduced, which make them good candidates to operate as sensing materials for the detection of redox active species. Their particularly high conductivity allows for building various conductometric transducers, among them resistors, field-effect transistors and Molecular Semiconductors – Doped Insulators (MSDI) Heterojunctions. Oxidizing species induce an increase of majority charge carriers, leading to a current increase in p-type resistors, whereas their effect is inverted in MSDI where the electronic transport is governed by minority charge carriers. We will also see how volatile organic compounds like toluene can induce a current modification, by a decrease of the mobility of charge carriers, with a high sensitivity and a very short response time.

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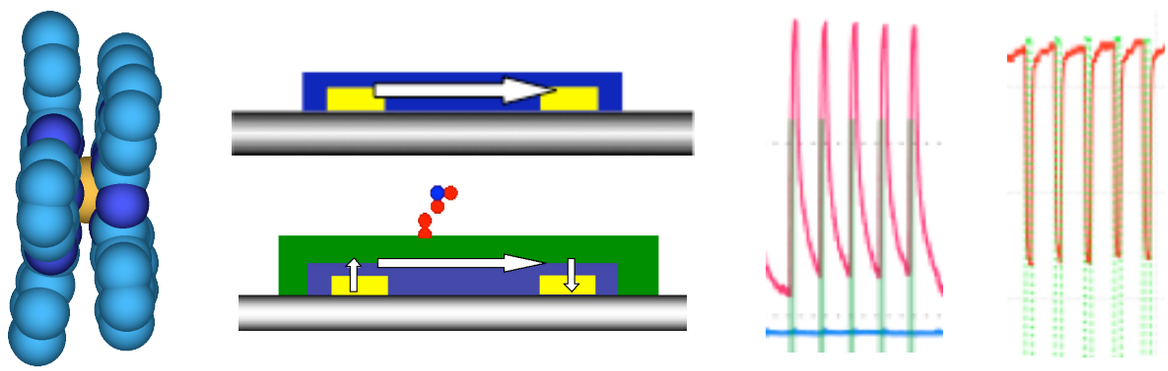

From left to right: Lanthanide bisphthalocyanine, resistor and MSDI devices, positive response of a MSDI to ammonia and negative response of a resistor to toluene

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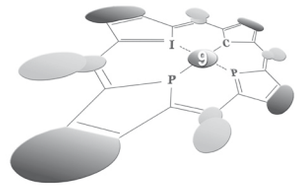

Exploring the Chemistry of Vitamin B_{12} derivatives with Reactive Oxygen Species

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Cobalamins (Cbls, vitamin B_{12} derivatives) are essential macrocyclic cobalt complexes which are closely structurally related to porphyrins. Cobalamins serve as cofactors for two important enzyme reactions in mammals. It is now recognized that up to 20% of individuals over the age of 65 are Cbl-deficient. Since isolated from liver seventy years ago, Cbl research has focused on its essential cofactor role in the B_{12}-dependent enzyme reactions. However Cbl also exhibit other 'non-enzymatic' effects which have led to a recent reappraisal of its biological functions. For example, the close relationship between Cbl status and several diverse chronic inflammatory diseases is difficult to solely ascribe to its co-enzyme activities. Indeed, Cbl has been used for decades to treat several inflammatory diseases including sepsis, arthritis, Alzheimer's disease, multiple sclerosis, and chronic fatigue syndrome, with little understanding as to why Cbl is beneficial. These diseases share a common factor - elevated levels of Reactive Oxygen and Reactive Nitrogen Species (ROS/RNS). Furthermore, larger amounts of inactive B_{12} analogs have been found in the blood of older individuals and patients with neurological disorders. Others have proposed that Cbl analogs result from endogenous modifications of the Cbl corrin ring by strong oxidants.

In order to evaluate the potential importance of direct reactions between cobalamins and ROS/RNS in biological systems, information on the rates, products and mechanisms of these reactions are required. This presentation will focus on recent studies on the reactions of a series of ROS/RNS with vitamin B_{12} complexes. Whilst many ROS/RNS simply oxidise the metal center of cobalamins, the most powerful oxidants abstract hydrogen atoms from the corrin macrocycle. Ultra High Performance Liquid Chromatography combined with High Resolution Mass Spectrometry (UHLPC/HRMS) is a powerful method to separate and identify corrinoid complexes with minor structural modifications compared with the parent corrin macrocycle. Complementary mammalian cell studies also show that physiologically relevant concentrations of B_{12} prevent ROS-initiated cell death.

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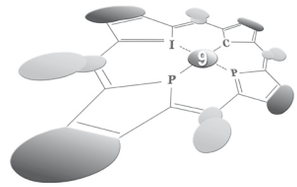

An examination of Fluorescence Resonance Energy Transfer between phthalocyanines and nanomaterials

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Photodynamic therapy (PDT) is a minimally invasive treatment modality of tumour cells, which requires laser beam light of appropriate excitation wavelength, a viable photosensitizer (such as a phthalocyanine) and molecular oxygen [1]. Phthalocyanines are known photosensitizers for PDT, but often have issues getting to the cancer site and can be difficult to excite due to interference from biological compounds. Nanoparticles bound to phthalocyanines can offer solutions to both issues because they can help passively target the cancer cells and can provide another target for excitation that can then transfer its energy to the phthalocyanine through a process known as fluorescence resonance energy transfer (FRET). The nanoparticles chosen for this work were graphene quantum dots (GQDs) and upconversion nanoparticles (UCNPs). Both of these nanoparticles are considered to be relatively non-toxic to the body and should assist with the passive targeting of the cancer cells. The UCNPs do have a fluorescence advantage over the GQDs however, in that they can be excited in the near infrared, which gets very little biological interference, and can emit at lower wavelengths that can coincide with a phthalocyanine's absorbance [2]. This should allow for a greater amount of energy to be received by the phthalocyanine. Fig. 1 highlights the general idea of FRET in UCNPs. However, the GQDs do display the quantum confinement effect like regular quantum dots, and can have their emission tuned to the required wavelength for FRET [3]. In this work, various aluminium and zinc tetra-substituted phthalocyanines were either covalently bonded or mixed with these nanomaterials, and then their photophysical properties were assessed to determine their PDT and FRET viability.

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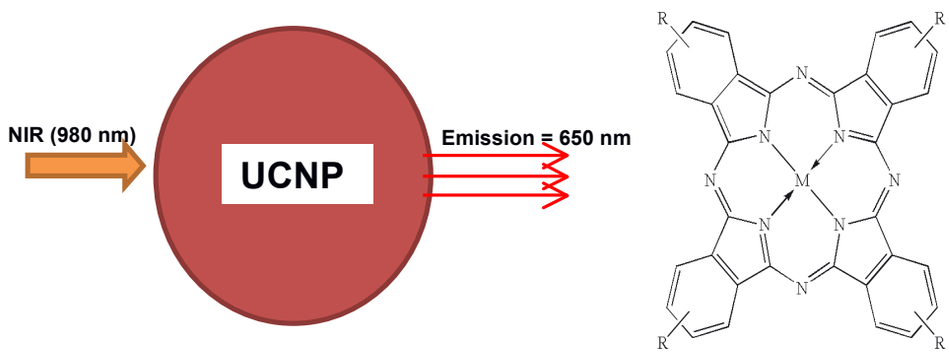

Fig. 1: General representation of FRET between a UCNP and a phthalocyanine.

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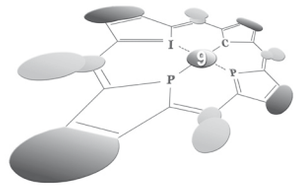

New Chemistry of O-BODIPY: Boron-oxygen-saccharide Conjugates

Bowen Liu,[a] Nina Novikova,[a,b] David C. Ware,[a] Bridget L. Stocker,[c] Mattie S. M. Timmer,[c] Cather M. Simpson,[a,b] Penelope J. Brothers[a,b]

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[b] *The MacDiarmid Institute for Advanced Materials and Nanotechnology, New Zealand*
[c] *School of Chemical and Physical Sciences, Victoria University of Wellington, New Zealand*

F-BODIPY dyes (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) are a well-known group of fluorescent molecules which comprise a dipyrrin framework with a BF core and exhibit sharp fluorescence emissions with high quantum yields. F-BODIPYs are used as probes for a wide variety of biomolecules, typically linked to the target analyte via a tether appended to the to dipyrrin backbone. Although BODIPYs are widely used as fluorescent labels and chemosensors, chemical modifications, including the link to the tether, have been almost exclusively confined to the dipyrrin carbon framework, leaving the BF core intact. Various reports in the literature have described strategies for the synthesis of boron-functionalised BODIPYs by substitution of the F-BODIPY fluoride atoms, including methods for producing BODIPYs bearing 4,4-alkoxide or 4,4-aryloxide substituents (O-BODIPY). Many important biomolecules bear oxygen-containing functional groups, which suggested to us the possibility of directly linking an O-BODIPY fluorophore to a target biomolecule through the O-BODIPY oxygen atoms. The new chemistry we have recently developed towards this aim will be described. In particular, we have explored the direct connection of O-BODIPY to carbohydrates through B-O-C links and have produced examples of 1:1 and 2:1 BODIPY saccharide complexes, characterised through a range of spectroscopic techniques, X-ray crystallography and absorption and emission spectroscopy.

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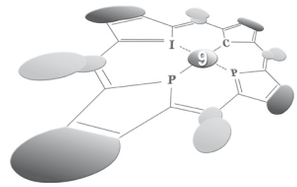

Isocorroles and Isoporphyrins – NIR responsive dyes with broken conjugation

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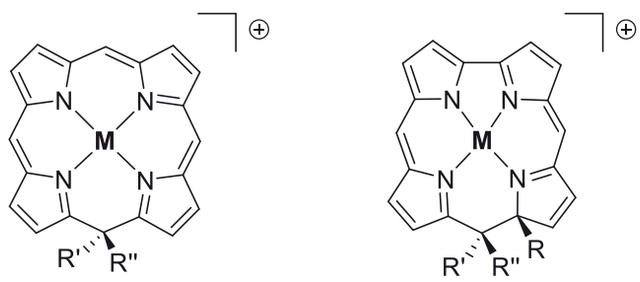
NIR absorption is a useful feature for optical applications in sensoric, medical and energy related research areas. Several strategies are known to optimize NIR behavior for molecular dyes. Typical porphyrinoid examples for such dyes are characterized by enlarged π-systems or by peripheral hydrogenation like in the natural chlorin and bacteriochlorin-like macrocycle families. Another possibility to tune porphyrinoids towards NIR absorption lies in the possible breaking of the macrocyclic conjugation. This approach, however, often leads to sensitive dyes and requires significant synthetic effort. Two prominent structures of this latter class are the little studied isoporphyrin and the isocorrole moieties shown below.



Isoporphyrin *Isocorrole*

We have recently gained access to novel derivatives of both macrocycles by metal template syntheses.[1,2] In this paper we will discuss preparative aspects and unexpected properties of our new compounds.

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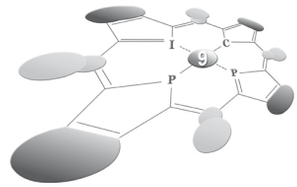
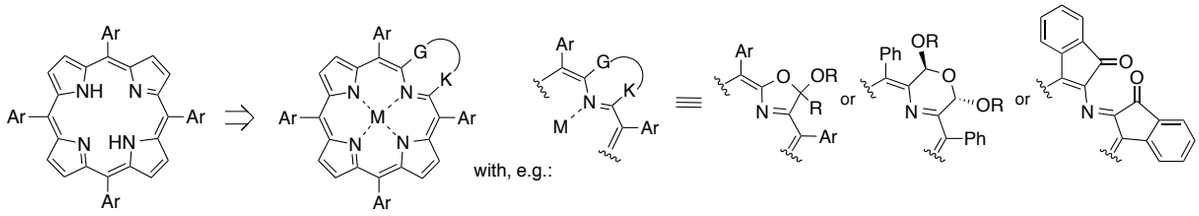


Synthesis of NIR Absorbing Porphyrinoids Containing Non-pyrrolic Building Blocks by Conversion of Porphyrins

Christian Brückner

Department of Chemistry, University of Connecticut, Storrs, Connecticut, 06269-3060, U.S.A.

The modulation of the electronic properties of the 'pigments of life' (primarily porphyrins and hydroporphyrins) primarily with respect to their longest wavelengths of absorption and emission is desirable for their utilization in numerous technical and medical applications. Our group developed synthetic strategies toward the conversion of one or two pyrrolic building blocks in porphyrins into different heterocycles, forming so-called 'pyrrole-modified porphyrins'.[1] Drawing largely on our most recent or unpublished work,[2] we report on the scopes and limits of this synthetic approach to achive NIR-absorbing chromophores, to which extend these modifications affect the chemical reactivity, conformation, and photochemical properties of the resulting porphyrin-, chlorin-, and bacteriochlorin-analogues. The utilization of the chromophores in photochemotherapeutic, chemosensing, and imaging applications is highlighted.



meso-Tetraarylporphyrin Pyrrole-modified Porphyrin

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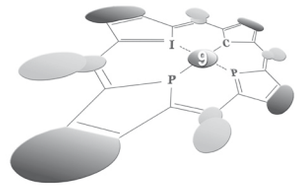

DNA Constructs with Multifunctional Porphyrin Units Covalently Attached

Karl Börjesson[a], Jerker Mårtensson[b], Bent Nordén[b], Marcus Wilhelmsson[b], Tom Brown[c] and Bo Albinsson[b]

[a]*University of Gothenburg, Sweden*
[b]*Chalmers University of Technology, Sweden*
[c]*University of Oxford, UK*

DNA is attractive as a building block in bottom-up approaches of nanotechnology. The small size of the double helix, 2 nm width, together with its stiffness offers a material with high spatial resolution potential. The strongly selective hydrogen-bonding pattern of the Watson & Crick base pairs enables assembly of multidimensional structures from 1D DNA molecules in a rational manner. However, to increase the potential usefulness of dynamic DNA nanoconstructs, the transition from freely diffusing to surface-attached networks, and the site specific incorporation of functionalities are important. We have shown that covalently bound porphyrins can fulfil both these demands.[1] In aqueous solution, the hydrophobic porphyrin anchors a DNA duplex with high affinity to lipid membranes.[2, 3] This soft method of anchoring the DNA allows for lateral diffusion on the surface.[4] It also introduces a compartmentalization of the DNA-porphyrin supramolecular system, with the DNA part in aqueous solution and the porphyrin part in the lipid membrane, enabling external chemical stimuli to selectively target the DNA or porphyrin part of the system. The porphyrin is not only an anchor but can also be used as a functional unit and we have used it to transfer energy from the water phase into the membrane, perform redox chemistry,[5] and as a coordination site.[6]

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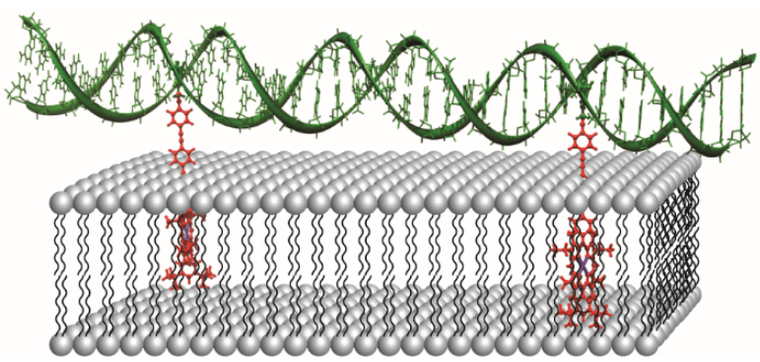

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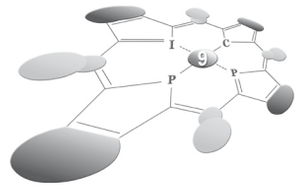
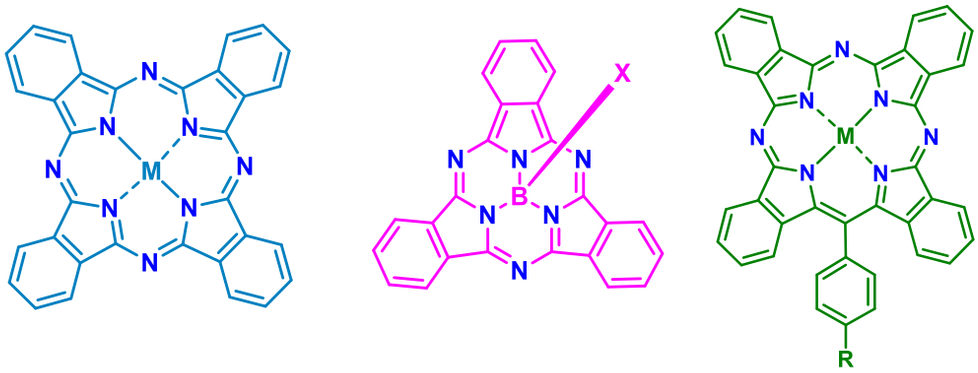


TribenzodiazaSubporphyrins (Sub-TBDAPs)

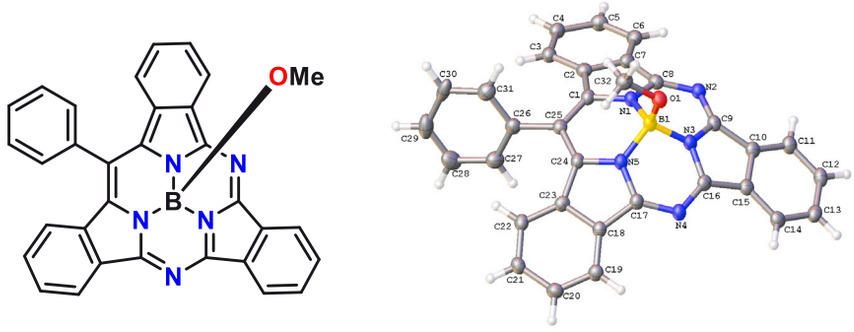
Andrew N Cammidge, **Sonia Remiro-Buenamañana**

School of Chemistry, University of East Anglia, Norwich NR47TJ UK

Phthalocyanines (Pc) and subphthalocyanines (SubPc) are well known macrocycles, than can be synthesised in good yields following established conditions. Much rarer are the hybrid structures that are intermediate between Pc and porphyrin parents. The recent development of a straightforward and high yielding synthesis of *meso*-aryltetrabenzotriazaporphyrins (TBTAPs 1)[1] in our group has made these compounds readily accessible for the first time.



Research on Subporphyrin structures has gained recent momentum with several intriguing derivatives and properties reported. Before our work, however, hybrid structures were unknown. In this presentation the extension and development of our synthetic method developed for phthalocyanine hybrids is described for application to synthesis of contracted hybrid structures – the SubTBDAPs.[2]



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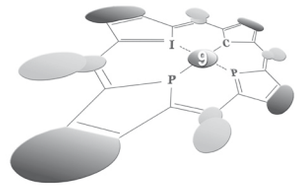

Carbon Nanotube-Templated Synthesis of Covalent Porphyrin Network for Oxygen Reduction Reaction

I. Hijazi,[a] T. Bourgeteau,[a] R. Cornut,[a] A. Morozan,[a] B. Jousselme[a] and S. Campidelli[a]

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The fabrication of functional hybrid materials that preserves and combines the properties of their building blocks is a central issue of nanosciences. Among the different classes of nanomaterials, carbon nanotubes are promising for electronics, catalysis and composite applications. Within the context of sustainable development and renewable energy, we and others envisioned the use of functionalized or doped carbon nanotubes in electrocatalytic systems.[1,2] In such systems, the catalytic sites need to be supported on conducting materials. Carbon nanotubes, thanks to their electrical conductivity and their high surface area appear as the ideal material for that purpose.

In actual proton exchange membrane fuel cell devices (PEMFC), the reactions at the electrodes and in particular the reduction of oxygen is performed by platinum nanoparticles. The cost of platinum encourages the development of new catalysts based on non-noble metals. In nature, the reduction of oxygen is performed by iron porphyrins in the active center of enzymes. Thus bio-inspired catalysts based on cobalt or iron macrocycles have been extensively studied for oxygen reduction reaction (ORR).[3,4]

Here, we describe the formation of a covalent network of porphyrins around MWNTs. Our approach is based on adsorption of ethynylporphyrins followed by the dimerization of the triple bonds. The nanotube acts as a template for the formation of the polymeric layer. The nanotube hybrids were characterized and tested for the ORR in a series of electrochemical measurements in acidic conditions. Compared to similar systems in which monomeric porphyrins are simply physisorbed, the nanotube hybrib showed a higher activity, a higher current density, a lower overpotential and a four electrons reaction pathway.[5]

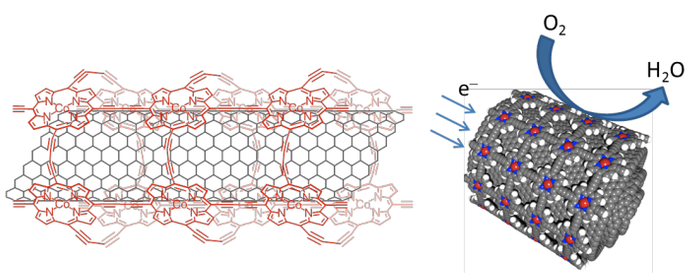

Figure. Representation of a MWNT with cobalt porphyrins polymerized at its surface for oxygen reduction reaction.

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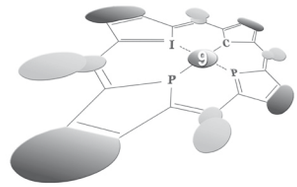

Unravelling the Relationship between Peripheral Substituents and their Steric and Electronic Effects in Corroles Derivatives

Gabriel Canard[a,b], Di Gao[a], Anthony D'Aléo[b], Christine Videlot-Ackermann[b], Emmanuel Terazzi[d], Michel Giorgi[c], Teodor Silviu Balaban[a]

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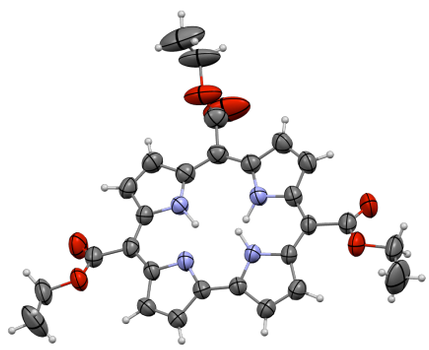
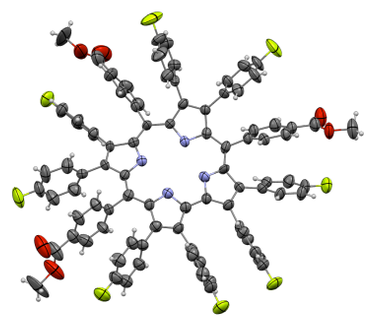
[c]*University of Geneva, Fédération des Sciences Chimiques de Marseille – Spectropole FR 1739, 13397, Marseille, France.*





The out-of-plane distortion of the porphyrin skeleton has a strong impact on the electrochemical and/or the photophysical properties of porphyrin derivatives featuring a macrocycle that can be saddled, ruffled, waved or domed. Considering the resemblance between corrole and porphyrin derivatives, one would expect an analogous relationship between the corrole's substitution and the macrocycle conformation. The first part of this presentation will illustrate how the corrole's *per*-aryl substitution impacts the macrocycle conformation and tunes the electrochemical and hole transport properties of the corresponding copper complexes.[1,2,3] The introduction of *meso*-ester groups on corroles will be the subject of the second part which will show how these simple groups are affecting the photophysical and electrochemical characteristics of the parent macrocycle despite their low steric hindrance.[4]

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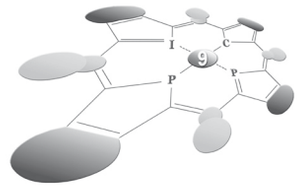

Hydrogen and Oxygen Evolution Reactions Catalyzed by Single Site Metal Porphyrins and Corroles

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E-mail: ruicao@snnu.edu.cn

Catalytic hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are key steps involved in artificial photosynthesis for solar-energy conversion for the production of clean, carbon-free, and renewable energy sources, and thus they are considered to be appealing ways to eliminate the energy and environmental problems caused by burning fossil fuels. Extensive efforts have been made to develop efficient and robust catalysts for these two processes. Research on mononuclear metal complexes has attracted increasing attention recently because not only they are capable of catalyzing HER and OER as efficiently as multinuclear metal complexes, but also there are several advantages in synthesis and mechanism studies by using single site catalysts. In this talk, we will introduce hydrogen and oxygen evolution reactions catalyzed by single site metal porphyrins and corroles.

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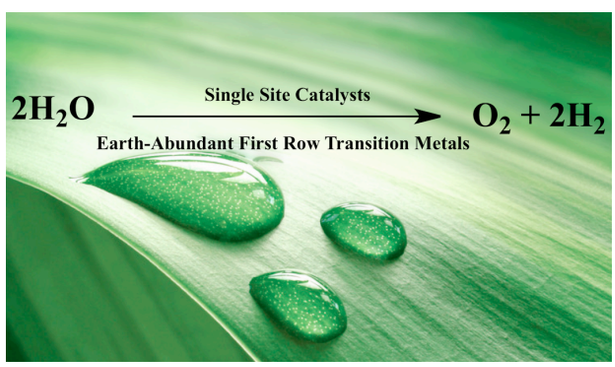

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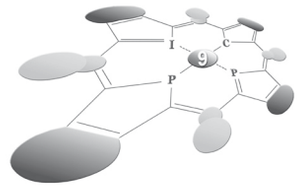

Vibrational Coherence and Kinetic Studies of Heme Proteins

Paul M. Champion[a]

[a]*Northeastern University, Boston, MA*

Transient absorption kinetics, resonance Raman, and vibrational coherence spectroscopies are used to investigate the mechanisms of small molecule, protein-protein, and protein-DNA binding in carbonmonoxide oxidation activator protein (CooA) and *Tt*-HNOX, among others. Thermally accessible low frequency (< 200 cm^{-1}) modes of heme proteins are compared and the properties of the distal pocket packing and conformational disorder are revealed by ultrafast kinetic studies. The coupling of low-frequency modes when heme proteins bind to target biomolecules, such as DNA or their electron transfer partners, is also discussed.

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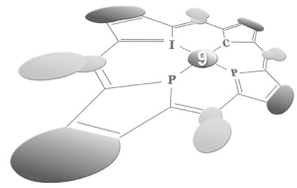

Group 9 Metalloporphyrin-Catalyzed Hydrogenation of Carbon-Carbon Aliphatic Bond with Water

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Hydrocracking of fossil fuels increases the energy content of hydrocarbons via carbon-carbon activation and hydrogenation process. It can be benefited from mild reaction conditions, reduced cost and increased safety if hydrogen gas can be replaced with water or other solvents as the hydrogen source(s). Recently we have reported the rhodium and iridium porphyrin catalyzed carbon-carbon sigma-bond hydrogenation of [2.2]paracyclophane with water under neutral conditions.[1,2] Now we report the comparative studies of group 9, including cobalt, metalloporphyrin-catalyzed hydrogenation of [2.2]paracyclophane.

Acknowledgements
We thank the Research Grants Council of Hong Kong (400212) for financial support.

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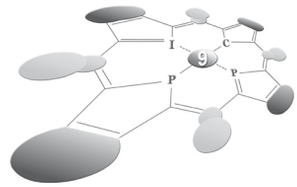

Synthesis of the Landmark Octafluoroporphyrin

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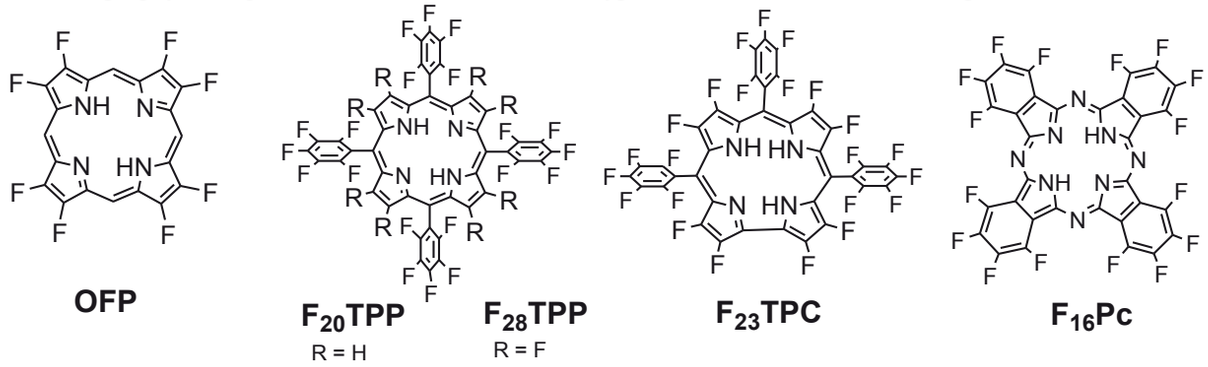
Fluorinated porphyrinoids are interesting as their e-deficient nature renders them ideal systems to model biomimetic monooxygenations. In fact, one of us employed Fe and Mn-F_{20}TPP to demonstrate for the first time in 1981[1] a robust and high-yielding catalytic model of cytochrome P450, which has spurred widespread interest in polyhalogenated metalloporphyrins as oxidation catalysts. Today, a variety of polyfluorinated porphyrinoids such as F_{20}TPP, F_{28}TPP, F_{23}TPC, and F_{16}Pc are known (figure), among which we made seminal contributions.[2,3]
The fact that the iconic octafluoroporphyrin (**OFP**) is still missing from the list of known compounds is not due to a lack of efforts. Numerous attempts in the past to make this compound have failed[4] including our own decade-long pursuit of it, beginning at Michigan State U, then at the Hong Kong U of Sci & Tech,[5] and recently in Taiwan. We are happy to announce that it is finally synthesized. The synthesis was achieved by condensing two molecules of tetrafluoro-dipyrrylmethane-2-carboxaldehyde in the presence of Mg(II) salts to give Mg**OFP**, whose X-ray structure revealed an essentially flat structure. The fluoro-groups impart as much as 0.5 V anodic shifts for porphyrin ring oxidation/reduction, as well as hypsochromic shifts in the Uv-vis spectra.



In this talk, I will review the past efforts, detail the synthetic approaches, and present the X-ray structure, spectroscopic and redox properties, as well as discussion of the prospects of such perfluorinted porphyrins.[6]

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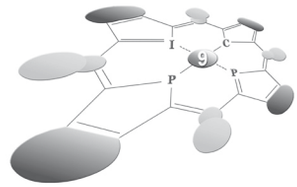

Photosensitizer Reactions with Iron Porphyrin

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Ruthenium trisbipyridine ($Ru(bpy)_3^{2+}$) and rhenium bipyridine tricarbonyl $Re(bpy)(CO)_3Cl$ complexes are strong oxidants and reductants at their electronically excited-states. The photoexcited complexes react with iron porphyrin to give oxidized heme products.
Rhenium complexes with imidazole (im) and diimidazole derivatives, im-C-C-C-im (im3Cim) and im4Cim have been prepared ($Re(bpy)(CO)_3im$, $Re(bpy)(CO)_3im3Cim$, and $Re(bpy)(CO)_3im4Cim$). Binding and electron transfer reaction of these complexes and the hydrolysis products of cytochrome *c* by proteolytic enzymes, microperoxidase-8 (AcMP8) have been studied. Binding constants are in the order of 2×10^4. Electron transfer from excited and bounded $*Re(bpy)(CO)_3im3Cim$ to Fe(III)AcMP-8 is about 5×10^9 s^{-1}. This fast rate indicates that the electron transfer with porphyrin through axial ligand is very efficient.
Similar reaction were performed with $Ru(bpy)_2(im)_2^{2+}$ complex. At alkali pH, $Ru(bpy)_2(im)_2^{2+}$ were bound to iron through imidazolate coordination. The luminescence of $Ru(bpy)_2(im)_2^{2+}$ is completely quenched in AcMP8Ru. Transient kinetics measurements showed the decay rate to be greater than 1×10^{12} s^{-1}. Ruthenium bipyridine complex with a carboxyl group substituted bipyridine has been prepared and reacted with MP8 to yield N-terminus bound RuMP8 complex. The luminescence decay rate has been measured as 1×10^9 s^{-1}. By using semiclassical electron transfer theory, we found the electron transfer efficiency through axial position of iron porphyrin is as good as through porphyrin edge.
Though Fe-porphyrin has very short lifetime, the extremely efficient electron accepting ability of TiO_2 nanoparticles may compete with the Fe-porphyrin decay. Photooxidation of Fe-porphyrin on TiO_2 nanoparticles to produce compound 2 were demonstrated.

Keywords: iron-porphyrin, compound 2, microperoxidase-8, Ruthenium trisbipyridine complex, rhenium bipyridine tricarbonyl complex

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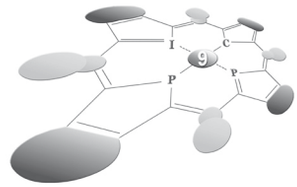

Metal Porphyrin-Catalyzed Alkylcarbene C-H Insertion and Cyclopropanation

Annapureddy Rajasekar Reddy, Fei Hao, Kai Wu, Zhen Guo, Jinhu Wei, Cong-Ying Zhou and Chi-Ming Che*

HKU Shenzhen Institute of Research & Innovation, Shenzhen, China; State Key Laboratory of Synthetic Chemistry and Department of Chemistry, The University of Hong Kong, Hong Kong, China

Transition metal-catalyzed carbene C-H insertion and cyclopropanation of α-diazocarbonyl compounds have been widely studied and used in organic synthesis, but related reactions involving alkylcarbenes generated from alkyldiazomethanes are underdeveloped. As alkyl group is electronically and structurally different from carbonyl groups, new reactivity and selectivity of alkylcarbene C-H insertion/cyclopropanation and hence new applications can be envisioned. We recently found that alkyldiazomethanes generated in situ from stable *N*-tosylhydrazons are effective carbene source for intramolecular sp^3 C-H bond insertion. Ruthenium porphyrins have been proved to effectively catalyze intramolecular alkylcarbene insertion to C-H bonds leading to a variety of substituted tetrahydrofurans and pyrrolidines in up to 99% yield and with up to 99:1 *cis*-selectivity. The reaction displays good tolerance of many functionalities and the operation is simple without the need of slow addition via syringe pump. A one pot reaction from alkyl ketones as substrates has also been realized. From the synthetic point of view, the C-H insertion of *N*-tosylhydrazones can be viewed as reductive coupling between C=O bond and C-H bond to form a new C-C bond. The synthetic utility of the reaction has also been illustrated by a short synthesis of a pyrrolizidine alkaloid, (±)-pseudoheliotridane. DFT calculation showed that the *trans* CO ligand plays a crucial role on the stability and reactivity of ruthenium-alkylcarbene reaction intermediate.

The construction of nitrogen-containing polycycles is of siganificant importance in organic synthesis since they are present in a number of bioactive natural alkaloids and pharmaceuticals. Following above work, we have developed an efficient and chemoselective cobalt(II) porphyrin-catalyzed intramolecular cyclopropanation of *N*-alkyl indoles/pyrroles with alkyldiazomethanes in situ generated from hydrazones. The reaction enables rapid construction a series of polycyclic cyclopropane-fused indoles and pyrrolines in moderate to high yields and with high chemo-selectivity from simple starting materials. These N-containing polycyclic compounds can be readily converted to a variety of N-heterocycles with potential synthetic and biological interest. We also found that the use of bulky 2,4,6-triisopropylbenzenesulfonyl hydrazones as carbene precursor enables the cyclopropanation to occur under milder condition and with shorter time than its N-tosylhydrazones counterparts, which is of advantage for the synthesis of instable polycycles

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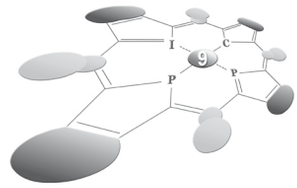

A PEG-free Biomimetic Porphyrin Nanoplatform for Personalized Cancer Theranostics

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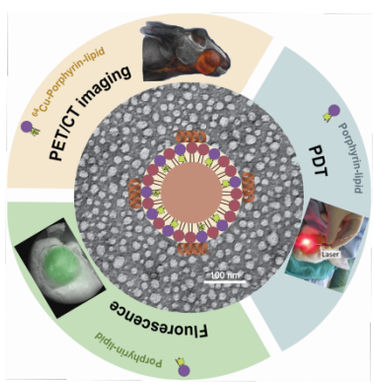
PEGylation is the most commonly adopted strategy to improve nanoparticles' vascular circulation by mitigating the uptake by reticuloendothelial system. However, there are many concerns (immunogenicity, etc.) in regards to its wide clinical applicability, thus inspiring the hot pursuit of PEG-free systems. We introduce here a novel PEG-free, porphyrin-based ultra-small nanostructure mimicking nature lipoproteins (PLP) that is intrinsically theranostic for positron emission tomography (PET), fluorescence, and photodynamic therapy (PDT). The biomimetic nature of PLP enables its favorable pharmacokinetic behaviors without the need of PEGylation. The inherent metal chelation of PLP enabled PET imaging for non-invasive disease diagnosis and quantitative assessment of drug delivery. The fast tumor intracellular trafficking of PLP allows for rapid nanostructure dissociation upon tumor accumulation to release monomeric porphyrins, thus unleashing the power of low-background near-infrared fluorescence imaging and activatable PDT. We demonstrated the general applicability of the PLP nanoparticles for sensitive and accurate detection of various primary and metastatic tumor types in clinically relevant animal models [1]. Using a large head and neck cancer (HNC) animal model, we present compelling evidence that PLPs facilitate accurate detection of primary tumor and metastatic nodes, and particularly enable visualizing the lymphatic drainage from tumor to regional lymph nodes by both pre-operative PET and intra-operative fluorescence imaging to guide surgical intervention [2]. The insight of metastatic lymphatic pathways might permit the identification of unknown primaries and recurrent tumors with greater sensitivity to significantly improve cancer patients' surgical outcome. Additionally, we demonstrated for the first time that PLP-PDT affords complete eradication of primary tumors and blockage of tumor metastasis without damage of adjacent critical structures, thus providing an alternative approach to radiation treatment and chemotherapy to treat HNC subtypes that are surgically inaccessible or adjacent to critical anatomical structures to increase therapeutic efficacy and decrease long-term toxicity [2]. Therefore, PLP offers a biomimetic theranostic nanoplatform for pre-treatment stratification using PET and NIR fluorescence imaging and for further customized cancer management via imaging-guided surgery, PDT, or/and potential chemotherapy.



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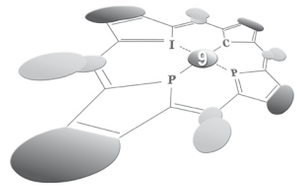

The Cooperative Anticancer Manner of Zn (II) Phthalocyanine and Small Molecula targeted-based Drug Gefitinib Conjugates

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The occurrence and development of malignant tumour is extremely complex. It involves different pathological processes, multiple genes and signal transduction pathways. The attempts to treat malignant tumour with monotherapeutic approach are not always efficient. The use of combination therapies with different therapeutic mechanisms, which shows advantages over monotherapeutic approach, is the important development direction in future. The combinations of PDT and chemotherapy can achieve "win-win cooperation" showing synergistic therapeutic effect: enhanced therapeutic efficacy, retarded tumour metastasis and recurrence, reduced side effects and drug resistance.

Herein we designed and synthesized conjugates of photosensitizer zinc phthalocyanine and small molecule targeted-based drug gefitinib. The combination of these two components exhibit synergistic anticancer effects. Having gefitinib as the targeting moiety, the conjugate 3 exhibites higher specific affinity to BxPc-3 (EGFR+) cell than HT-29 (EGFR-) cell; the conjugate 3 shows a higher cytotoxic effect (IC_{50} = 5.337 μM) in dark due to gefitinib and maintains high phototoxicity (IC_{50} = 0.011 μM). Therefore, in vivo targeted tumour imaging and anticancer activity are also observed.

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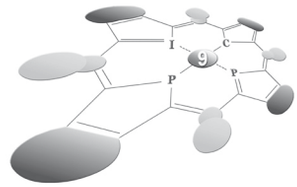

Nitrogen and sulfur co-doped anatase-phase TiO_2 hollow boxes with enhancing visible photocatalytic performance

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Owing to its chemical stability, nontoxicity, and low cost, TiO_2 has been recognized as an attractive photocatalyst for air and water purification, and solar energy conversion. TiO_2 as perfect semiconductor, it has a high photocatalytic activity under UV light, the electrons are arouses from the valence band to the conduction band form electron-hole pair under the UV light. However, due to the electron of TiO_2 are difficult arouse under visible light, and the electron-hole pair have high recombination rate lead to low utilization. So its limited photo catalytic activity in the visible light region, which is still one of its main drawbacks. In order to enhancing the TiO_2 utilization ratio in the visible light, we using $TiOF_2$ as precursor and DL-Methionine as nitrogen and sulfur source, through one-step calcinate synthesis of the nitrogen and sulfur co-doped anatase-phase TiO_2 hollow boxes(N, S-co-doped TiO_2) with different proportion of DL-Methionine of photocatalytic materials. The synthesized photocatalysts are characterization by TEM, SEM, XRD, UV-Vis DRS, XPS; and theirs activity were evaluated though photodegradation Rhodamine B(RhB) under the visible light irradiation. The photodegradation results indicate the N, S-TiO_2 photocatalyst exhibited the highest activity in the photodegradation reaction tests of RhB under visible light irradiation and the degradation rate is 60.82%. What's more, the 5-recycles test showed that N, S-TiO_2 photocatalyst could be reused and its activity kept stable.

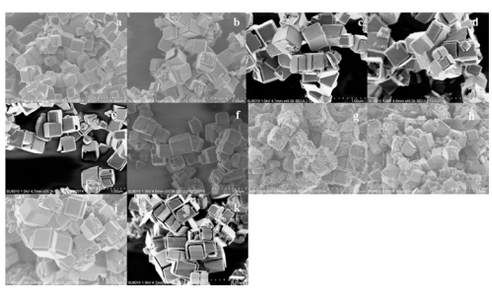

Fig. 1 The SEM of samples

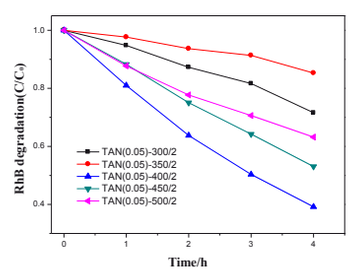

Fig. 2 RhB photodegradation

Acknowledgements: this work was supported by National Natural Science Foundation of China (No. 20702064, 21177161and 31402137), Hubei Province Science Fund for Distinguished Yong Scholars (2013CFA034).

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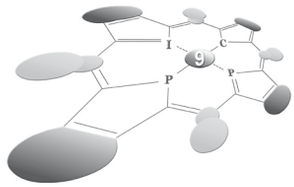

The red-shifted phycobiliprotein complexes isolated from the chlorophyll *f*-containing cyanobacterium *Halomicronema hongdechloris*

Min Chen

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Phycobilisomes, the main light-harvesting complexes in cyanobacteria, absorb light ranging from green to red, where chlorophylls have poor absorbance. It is commonly accepted that these complexes only absorb green and orange light, complementing chlorophyll absorbance. Here, we present a new phycobilisome that absorbs red and far-red light, having red-shifted absorption peaks of 653 and 712 nm. These red-shifted phycobiliprotein complexes were isolated from the chlorophyll *f*-containing cyanobacterium, *Halomicronema hongdechloris*, grown under monochromatic 730 nm (far-red) light conditions. They are significantly smaller than typical phycobilisomes, comprising mainly allophycocyanin cores, formed from allophycocyanin subunits and core-membrane linker proteins. Ultrastructural imaging demonstrates that cells grown under far-red light possess more layers of appressed thylakoid membranes, with a reduced distance between the membranes, compared with cells grown under white light. Spectral analysis of dissociated and denatured phycobiliprotein complexes show that the same bilin chromophore, phycocyanobilin, is exclusively used in both phycobilisomes, suggesting that the red-shifted absorption features are due to altered states of this chromophore within the protein complexes. Our biochemical and structural analyses suggest that these red-shifted absorption features reflect a reduced phycobilisome and altered binding states of pigments within the protein complexes. These new red-shifted phycobilisomes have implications for flexible strategies in chromatic acclimation, which would improve light-harvesting efficiency.

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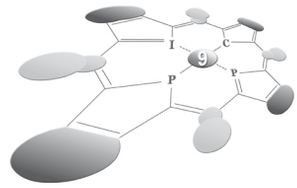

Advanced Materials based on Porphyrins and Graphene Oxide *via* Colloid and Interface Protocols

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Advanced optoelectronic materials with regard to pi-conjugated species have attracted great expectations both from scientific and technological communities[1-3]. In this lecture, we will present our recent advancements concerning the controllable assembly of pi-conjugated molecules such as porphyrins, graphene oxide (GO), phthalocyanines, and anthracenes, *etc*. In these works, the controllable assembly and tunable functions has been achieved *via* colloid and interface methods, wherein surfactant-assisted self-assembly occurred at the oil/water interface, layer-by-layer assembly occurred at the liquid/solid interface, and interfacial assembly occurred at the air/water interface, are employed as the assembly protocols. As shown in Figure 1, the following three issues will be mainly discussed[3-10]: (i) high-performance photocatalytic/catalytic systems and/or nanoelectronic gas sensors; (ii) qualified organic optoelectronics/electronics of high stability and excellent electrical performances; (iii) supramolecular assemblies of controllable chiroptical properties wholly composed of achiral porphyrins.
The paradigms addressed herein suggest that colloid and interface protocols are one of the most useful scaffolds for the construction of pi-conjugated molecules-based advanced functional materials of tunable structures and functions.

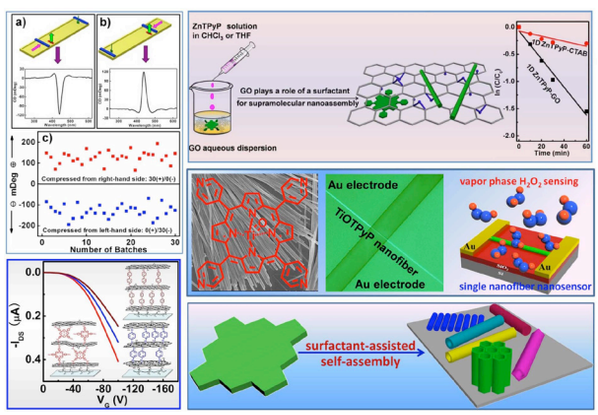

Figure 1. Pi-conjugated molecules-based advanced functional materials tuned by colloid and interface protocols.

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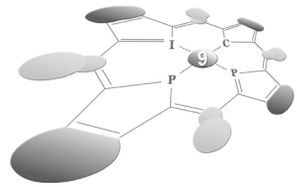

Controlled Aggregation Structure and Improved Performance for Stable Ambipolar Organic Field-Effect Transistor Based on An Asymmetrically Substituted Tris(phthalocyaninato) Europium Semiconductor

Yanli Chen* [a,b], **Xia Kong** [a] **and Jianzhuang Jiang** [c]

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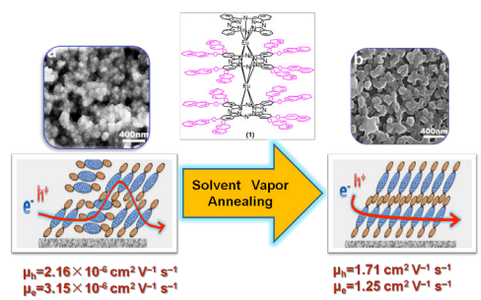
A new phthalocyanine-based semiconducting molecule with an asymmetrically octanaphthoxy-substituted triple-decker molecular structure, (Pc)Eu[Pc(ONh)$_8$]Eu[Pc(ONh)$_8$] (**1**) was designed and synthesized. Organic field effect transistor (OFET) devices fabricated by the solution-based QLS technique from the heteroleptic tris(phthalocyaninato) europium complex **1**, with a low-lying LUMO energy level (–4.0 eV) and suitable HOMO–LUMO separation of 1.07 eV, were revealed to exhibit air-stable balanced ambipolar performance with the low mobilities of 2.16×10^{-6} for holes and 3.15×10^{-6} cm^2 V^{-1}s^{-1} for electrons, respectively, and current on/off ratio of ~10^2. However, a simple solvent annealing over the QLS films not only induces significantly improvement over the molecular packing and ordering as well as the film-crystallinity but also achieves the successful fine controlling over the aggregation mode from *J*-type in the QLS films to *H*-type in the solvent-vapor-annealed (SVA) films according to AFM and SEM observationsand the XRD, UV-vis and polarized UV-vis results.This in turn results in the significant improvement in the device performance with good on/off ratio of 10^6 and in particular the record high and balanced carrier mobilitiesof 1.71 for holes and 1.25 cm^2 V^{-1}s^{-1} for electrons. The combination of molecular design and interface engineering ensures the π-conjugated marcocyclic compound to possess appropriate HOMO/LUMO energy levels and in particular excellent charge mobilities that lead to high-performance air-stable ambipolar OFETs.[1-2] The present result will be helpful for the design and preparation of air-stable and high performance OFET devices with potential application in the ultra-low-cost, large-area complementary integrated circuits through the integrated molecular design and engineering process.



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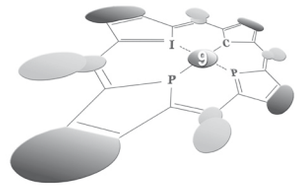

Zinc phthalocyanines in photodynamic antimicrobial chemotherapy

Zhuo Chen, linsen Li, Yaxin Zhang, Jincan Chen, Ping Hu, Mingdong Huang

State Key Laboratory of Structural Chemistry and Danish-Chinese Centre for Proteases and Cancer, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

Photodynamic antimicrobial chemotherapy (PACT) is one of the promising technique to address the prevalent challenge of antibiotic resistance. It is based on an initial photosensitization of the infected area, followed by irradiation with visible light, producing singlet oxygen which is cytotoxic to bacteria. Here, we conjugated mono-substituted ZnPc-COOH with a series of oligolysine moiety with different number of lysine residues (ZnPc-$(Lys)_n$ (n=1, 3, 5, 7, 9)) to improve the water solubility of the ZnPc conjugates. We measured the photosensitizing efficacies and the cellular uptakes of this series of conjugates on several different types of bacteria. Our results showed that ZnPc-$(Lys)_5$ has the highest photodynamic efficacy compared to the other conjugates investigated.

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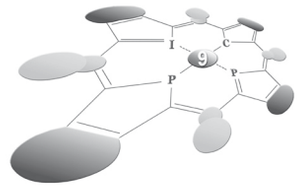

2-Aza-21-carbaporphyrin Derivatives as Versatile Chirality Sensors with Memory

Piotr J. Chmielewski[a]

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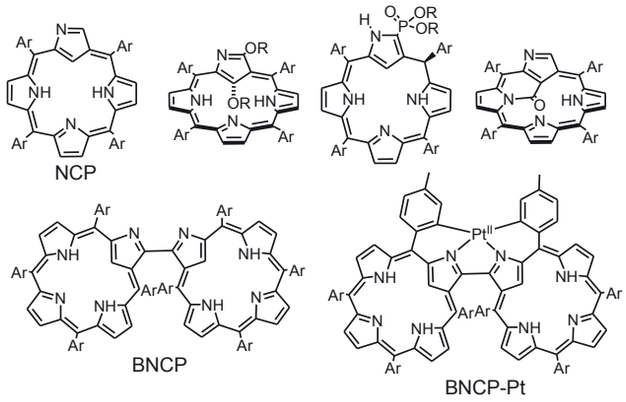
2-Aza-21-carbaporphyrin, also known as N-confused porphyrin (NCP) is an aromatic prochiral tetrapyrrole. The prochiral character of that system is a direct consequence of the macrocyclic ring structure with the effective C_s point symmetry. Relatively small structural modifications that remove the symmetry of the ring can transform NCP or its complexes into configurationally stable chiral species of point chirality.[1] The separation of stereoisomers is possible for the others indicating planar chirality, but these systems slowly racemize due to a ring-configuration inversion released upon certain chemical processes.[2] The directly linked 3,3'-bis(N-confused porphyrin) (BNCP) is axially chiral, although BNCP is configurationally unstable in solution in the free base state preventing separation of the enantiomers. The configurational lability of the BNCP ligand implies racemization, but it simultaneously provides a mechanism for a unidirectional change of configuration, which can be induced by a chiral factor, thus resulting in the enantiomerization of the bis(porphyrin) system.[3] The induced enantiomeric excess can be memorized by a proper metallation of macrocyclic crevices of both subunits of the dimer.



External platination of the dimer yields a semi-rigid system BNCP-Pt allowing separation of stereoisomers with opposite helicity as well as induction of the diastereomeric excess and stereoselective formation of bigger assemblies upon oxidative addition to the metal center or partial protonation of the ligand.

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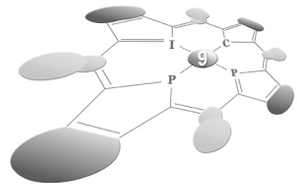

Activatable Theranostic Agents for Near-infrared Fluorescence Imaging and Photodynamic Therapy

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Photodynamic therapy (PDT) using combinations of chemical photosensitizers, light, and molecular oxygen has long been used successfully to treat cancers and other nonmalignant conditions. Compared with conventional chemotherapy, photosensitizers become cytotoxic only in regions that receive the appropriate wavelength of light. However, problems with water-insolubility, limited tumor selectivity, and poor pharmacokinetics of PDT agents have been the main drawbacks to their clinical application. In particular, nonspecific activation of singlet oxygen generation in normal tissues causes prolonged skin photosensitivity, thereby limiting their utility as theranostic agents.

My laboratory has been developing various types of activatable and dual-targeted photosensitizing agents as smart theranostics for selective near-infrared fluorescence imaging and photodynamic therapy of cancers as well as inflammatory diseases. These activatable photosensitizing agents were prepared in the form of self-assembled nanoparticles or in combination with plasmonic nanomaterials such as gold nanorods and graphene oxides. Recently we succeeded to develop small-sized theranostic agent by using low molecular weight conjugate with simplest chemical structure. In their native state, photosensitizers are nonfluorescent and nonphototoxic, but it became highly fluorescent and phototoxic at the target sites. I am going to show the results obtained from *in vitro* and *in vivo* studies by using these theranostic agents.

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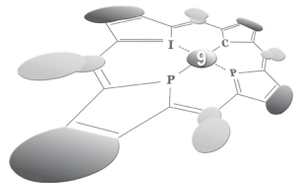

Human tryptophan 2,3-dioxygenase (TDO) protein degradation: Structural determinants-submitted to the International Conference on Porphyrins and Phthalocyanines.

Maria Almira Correia[a], Sung-Mi Kim[a], YongQiang Wang[a], Shay Karkashon[b], and Syun-Ru-Yeh[b]

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The hepatic hemoprotein tryptophan 2,3-dioxygenase (TDO) catalyzes the irreversible oxidation of L-tryptophan (Trp) to N-formyl-L-kynurenine. TDO critically regulates the flux of Trp through the kynurenine and serotonin pathways, thereby controlling systemic Trp levels and physiologic function. It has been implicated in various diseases, including neurodegenerative diseases and cancers, and thus is an important target for drug discovery. Despite its importance, very little is known about the regulation of human TDO (hTDO) protein turnover required for its cellular homeostasis. Herein we report that hTDO turnover occurs largely via ubiquitin (Ub)-linked proteasomal degradation (UPD) pathway, and we define the structural features critical therein. Characterization of hTDO ubiquitination reveals that at the least 3 cellular E3 Ub-ligases participate in this process, in the rank-order gp78>CHIP>HRD1. Using Ub-remnant and proteomic LC-MS/MS analyses, we have identified 15 Lys-residues as hTDO-ubiquitination sites. Of these, 10 were previously identified in mouse liver extracts, and 5 were identified herein for the first time to our knowledge. Furthermore, although these 15 target sites are distributed throughout the hTDO-monomer and tetramer surface, 5 of these lie in the negatively charged Glu-rich helix-loop-helix domain, which may be important for interaction with the positively charged residues of the E2-E3 Ub-ligase complexes**.**

Trp, the preferred substrate is known to "induce" TDO enzyme via stabilization. Structural analyses reveal that Trp binds hTDO at both the active site and an exo-site that also binds aMethylTrp (aMeTrp). Glove-box (anaerobic) *in vitro* hTDO-ubiquitination analyses reveal that inclusion of Trp indeed stabilized hTDO and appreciably protected it from ubiquitination more than aMeTrp and 1N-MeTrp. ^{35}S-pulse-chase analyses in HepG2 cells revealed that exo-site aMeTrp-binding prolonged the intracellular half-life of parent wild-type (WT) hTDO, 2-fold. Site-directed mutagenesis of exo-site residues considerably accelerated hTDO degradation, despite aMeTrp presence. By contrast, deletion of hTDO N- and/or C-terminus (ΔN, ΔC, ΔN/ΔC) greatly stabilized the protein in the order ΔN/ΔC>ΔC>ΔN, consistent with a processive proteolytic process. The extreme hTDO C-terminus is rich in acidic (Asp/Glu) and phosphorylatable (Ser) residues. Relative to the WT, mutation of these Asp/Glu-residues to Gly stabilized hTDO, whereas that of Ser to Gly had no effect. When the exo-site mutation was incorporated into the hTDOΔN/ΔC mutant, its stability was lost, being degraded just as rapidly as the full-length hTDO exo-site-mutant. Collectively, these findings reveal that although the exo-site along with the N- and C-termini are important structural features in hTDO turnover, the structural integrity of the exo-site Trp-binding is a critical determinant of its UPD. Supported by NIH grants GM44037, DK26506, GM086482 (SRY) and DK26743 (Liver Center).

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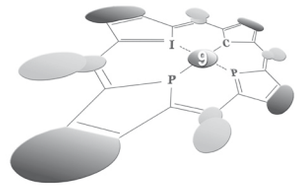
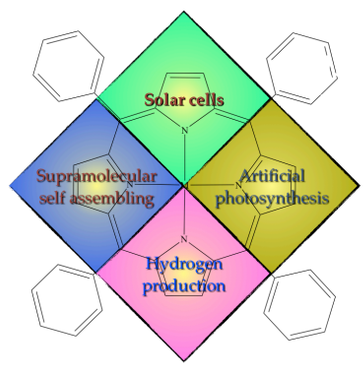


Bioinspired Solar energy conversion strategies based on hybrid porphyrin derivatives

A. G. Coutsolelos

Bioinorganic Chemistry Lab, University of Crete, Department of Chemistry, 70013 Heraklion, Crete, Greece

Natural processes of photosynthesis have increasingly inspired the fabrication of nanostructured molecular materials with advanced light-harvesting and electron-transfer features. [1-6] In this context, supramolecular chemistry allows diverse and disparate molecular building blocks to be amalgamated into highly ordered architectures. These mimic the key functions of the photosynthetic reaction center; light harvesting, charge separation, charge transport, and catalysis. [7,8] Porphyrinoids, the basic building block of chlorophylls, have emerged as an exceptional class of light harvesters and electron donors in such supramolecular electron donor-acceptor hybrids [9-12].



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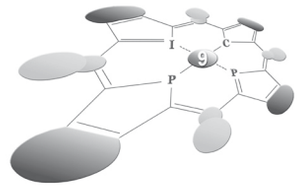

Silicon Porphyrins - New Aspects of Chemistry and Photophysics

Maxwell J. Crossley [a], **Sutharsiny Indusegaram** [a], **and Victor Akpe** [a]

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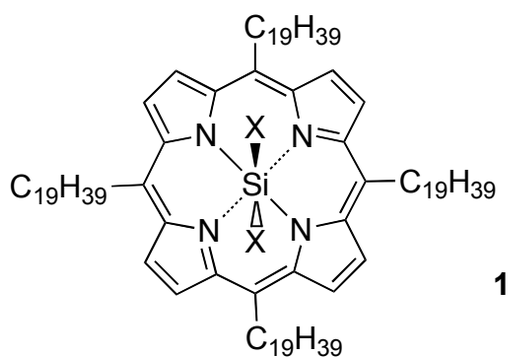
While silicon(IV) phthalocyanines have been well studied over many years, the same is not the case for silicon(IV) porphyrins. There are a number of significant properties of the silicon(IV) phthalocyanines such as their ability to stack through μ–ligation that brings about enhanced conductivity and interesting structures from a materials viewpoint [1].

An impediment to the study of silicon porphyrins has been the need for a reliable, efficient methodology for insertion of silicon into a pre-formed porphyrin. We present a solution to this problem that allows the generation, from a range of porphyrin types, of multi-gram amounts of silicon porphyrin, *e.g.,* **1**, in high yields.

Chemistry at both the bound silicon ion and the porphyrin periphery is reported. In this way functionalised silica surfaces and self-assembled optical fibres [2] are produced and new compounds for photosensitisation of energy up-conversion and for electron-transfer reactions were synthesised and evaluated.



1 X = Cl, OH, O-Si(Por)-OH

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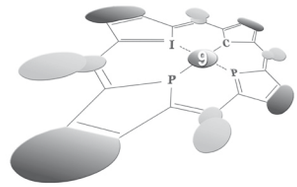

Graphene Decorated Biomimetic Donor-Acceptor Conjugates for Modulating Electron Transfer Dynamics

Gary N. Lim, Chandra B. KC, and Francis D'Souza*

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Graphene,[1] an all carbon atom hexagonally arranged in a planar condensed ring system of quasi infinite size, has become a rising star within the family of carbon nanomaterials in recent years. This one atom thick material known for its extraordinary strength, high flexibility, optical transparency, elasticity, and unique electrical and optical properties has made researchers seeks immediate applications in the areas of flexible sensor arrays and optoelectronic devices.[2]

Sequential electron transfer or electron transfer/hole transfer between energetically well-positioned entities of photosynthetic reaction centre donor-acceptor models is one of the commonly employed mechanisms to generate long-lived charge separated states.[3] Wealth of information, applicable towards light energy harvesting and building optoelectronic devices, has been acquired from such studies. The focus of this talk is to highlight our recent progress in the design, construction and electron transfer properties of tetrapyrrole-nanocarbon graphene hybrids.[4] The self-assembly methods developed to build the tetrapyrrole-nanocarbon graphene hybrids involving pi-pi stacking with the help of suitably functionalized tetrapyrrole and graphene materials will be discussed. Photoinduced electron transfer leading charge separation in these conjugates, and modulation of rates of charge separation and charge recombination upon pi-stacking the donor-acceptor conjugates on graphene will be discussed.

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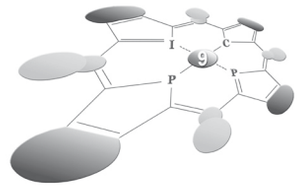

Protein- and Sugar-Based Phthalocyanine Biohybrids

Andrés de la Escosura,[a] Eduardo Anaya-Plaza,[a] Francesca Setaro,[a] Eveline van de Winckel,[a] Joona Mikkila,[b] Mauri A. Kostiainen[b] and Tomás Torres[a]

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Phthalocyanines (Pc) constitute one of the most promising families among photosensitizers (PS). Key properties of Pc include high stability and absorption coefficient at the near-infrared (NIR) spectral window, long-lived fluorescence and high $^1O_2$ quantum yields. Formulation of the hydrophobic and highly aromatic Pc macrocycle in biologically related media is however an important prerequisite for biomedical applications. Inclusion of cationic, anionic or hydrophilic substituents at peripheral positions of the macrocycle, or axially bound to the central metal, leads to water-soluble Pc compounds. Yet, Pc tend to stack into *H*-type aggregates in aqueous conditions, self-quenching the excited state and thus limiting their applicability. A much more promising strategy to tune the PS solubility, aggregation and photochemical properties is their incorporation into nano-structured architectures. Among them, the use of nanostructures derived from biology is highly desirable, considering their biocompatibility and highly defined organizational features.

In this presentation we will discuss about phthalocyanine-based biohybrid materials in combination with two different kinds of biological nanoscale assemblies: cellulose nanocrystals (CNC) and protein cages. Regarding the former, the supramolecular immobilization of Pc derivatives onto the surface of sulfated CNC has led to the development of photoactive cellulose nanocrystals.[1] Concerning protein cages, 10 nm Pc nanospheres were previously self-assembled in a cooperative manner inside virus capsids as delivery vehicles.[2-3] Water-soluble Pc dendrimers can also be incorporated into these biological nanocontainers.[4] Finally, we have recently demonstrated the hierarchical organization of Pc dyes and protein cages into higher-order photoactive crystals.[5] The obtained ternary face-centered cubic (fcc) packed cocrystals, with diameters up to 100 μm, retain the optical properties of the pristine dye molecules, such as fluorescence at 695 nm and efficient light-induced $^1O_2$ production. Considering that $^1O_2$ is utilized in important technologies such as photodynamic therapy (PDT), water treatments, diagnostic arrays and as an oxidant in organic synthesis, our results demonstrate a powerful methodology to create functional biohybrid systems with unprecedented long-range crystalline order.

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New multicomponent, phthalocyanine-based ensembles for energy conversion schemes

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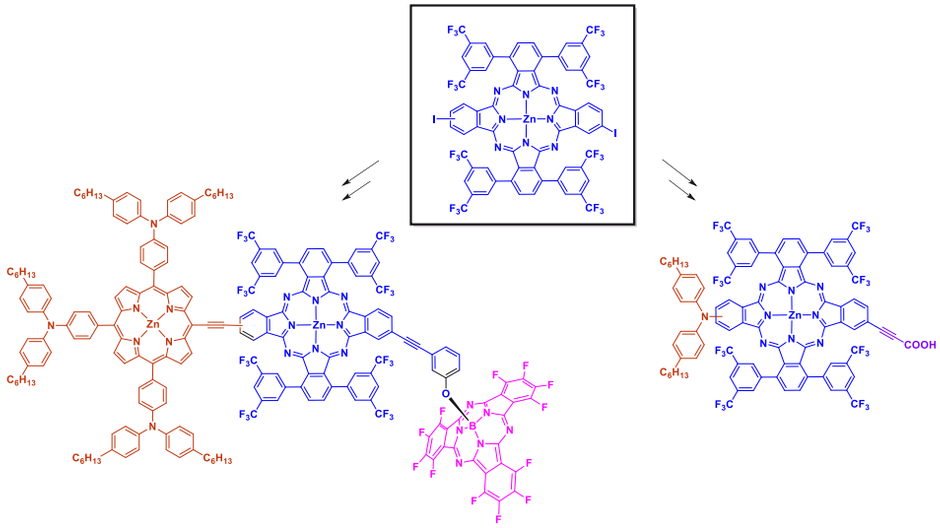
Appropriate face-to-face functionalized phthalocyanines (Pcs)[1] are very attractive building blocks for the preparation of multicomponent systems. For instance, unsymmetric functionalization of crosswise-substituted Pcs derivatives with donor and acceptor moieties may afford promising "push-pull" chromophores for dye-sensitized solar cells (DSSCs).[2] Also, unsymmetrical functionalization with other electroactive macrocycles lead to multicomponent ensembles with photoinduced charge separation abilities. Last, linking appropriate coordinative units in a linear fashion to the Pc core may afford to construct Pc-based supramolecular cages by metal-mediated self-assembly, able to encapsulate other different electroactive species.
We report here on the preparation of push–pull ABAC Pcs, functionalized with both electron-donating, phenylamino groups and anchoring/electron-withdrawing carboxy groups in a face-to-face manner. We have determined their ability to perform as efficient sensitizers in DSSCs. Also, multicomponent porphyrin-Pc-subphthalocyanine conjugates, showing an appropriate redox gradient to facilitate ultimate charge separation from the donor porphyrin to the acceptor subphthalocyanine after photoexcitation, have been prepared and studied. Chemical approaches towards the preparation of supramolecular Pc-cages will be also delineated in this talk.



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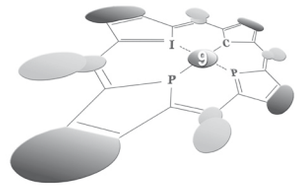

Phthalocyanine based optical fiber sensors

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Among the different gas detection technologies, optical systems based on optical fibers can be very useful in specific applications like the monitoring of road tunnels or wide spaces. Various techniques exist which are almost all based on the deposition of a sensitive layer reacting with the gases, changing its optical properties (complex refractive index). Two kinds of sensors can be distinguished: extrinsic sensors where the sensing element is not part of the optical fiber (remote spectroscopy of a chemochromic membrane) [1] and intrinsic sensors based on a coating directly deposited on the fiber. In that case, refractive index changes of the sensitive layer induce changes of the transmission of light. A lot of different interrogation technologies were used [2].
Phthalocyanines are good materials for gas sensing [3]. These organic molecules are known to be sensitive to oxidizing or reducing gases at ppm concentrations and have been proposed as the chemically active component of both conductive and optical gas sensors. Another major advantage is their remarkable chemical and thermal stability. Among the different phthalocyanines, Lanthanide bisphthalocyanine ($LnPc_2$) complexes with a "double-decker" structure attracted a lot of attention because of their electrochromic properties leading to strong optical changes in the visible and NIR range [4-6]. Another advantage is that the gasochromic effect can be observed in the telecom wavelength range [1300-1600 nm], which allows then to use standard and low cost equipment. It is also well known that the coating method has a big impact on the response time and that the gas desorption can be rather slow at room temperature. Heating the substrate is not practical with optical fibers and therefore optical alternatives need to be found. This paper will describe the use of lanthanide bisphthalocyanines for optical gas sensing, in particular for NO_2 and the various interrogation and coating methods.

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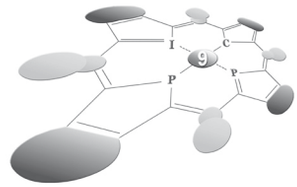
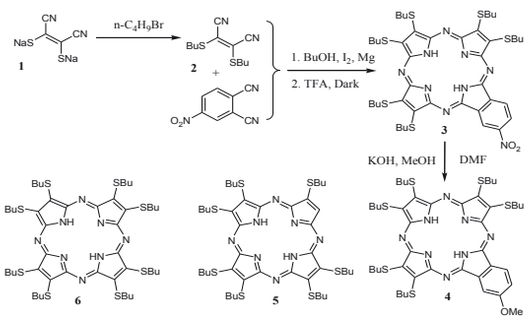


Synthesis of Novel Asymmetrical Cobalt Monobenzo-Thioporphyrazines and their Bio-inspired Catalytic Property

Kejian Deng*, Peng Zhou, BingguangZhang, ChangjunYang, ZehuiZhang

Key Laboratory of Catalysis and Material Sciences of the State Ethnic Affairs Commission & Ministry of Education, College of Chemistry and Material Sciences, South-Central University for Nationalities, Wuhan, 430074, China. Tel: +8627-67843930; Fax:+8627-67842752; E-mail: dengkj@scuec.edu.cn;

Recent developed approaches involved the application of green oxidants such as O_2 or H_2O_2 and highly effective catalysts[1], among which the bio-inspired catalysis may be one of the best approaches[2]. Two novel monobenzoporhyrazines bearing nitro and methoxyl respectively on fused benzene ring were successfully synthesized. Also, an asymmetrical porphyrazine 5 with one butylthio branch at the pyrrolic β-positions substituted by hydrogen atom was successfully isolated in the course of synthesis of symmetric octakis(butylthio) porphyrazine 6. Their corresponding cobalt complexes **7**, **8**, **9** and **10** were subsequently obtained and characterized. Their catalytic ability was assessed by aerobic oxidation of benzoin, showing and the highest benzil yield of 95.6% at room temperature through 2mol% CoPz **8** in THF in presence of 10mol% DBU.



Scheme 1 Synthesis of metal-free poly(butylthio) porphyrazine and substitutented monobenzoporhyrazines

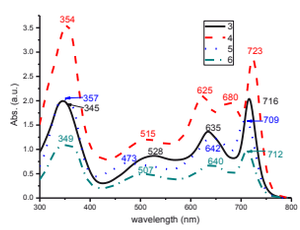


Figure 2. UV-Vis for freebase Pz 3, 4 ,5, 6.

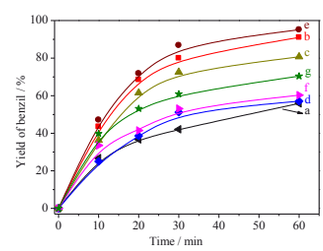


Figure 3 Aerobic oxidation of benzoin catalyzed by CoPzs* in presence of 10 mol% DBU in THF.

* a: in the absence of CoPz; b: 10mol% complex **7**; c: 2mol% complex **7**; d: 1mol% complex **7**; e: 2mol% complex **8**; f: 2mol% complex **9** ; g: 2mol% complex **10**.

Both catalytic experiments and DFT calculations demonstrated that the catalytic activity of the cobalt thioporphyrazine was affected mainly from extended π-system of peripheral fused benzo ring and secondarily from electron-donating substitutents. A possible mechanism was also presented from the in situ UV-Vis spectra, in which a novel and characteristic absorption peak of metal-oxo was observed. And the detailed characterization of reactive kinetics and expansion of oxidation of alcohols needs to be further studied.

Acknowledgement: This work was financially supported by National Natural Science Foundation of China (Nos. 20977115 and 21272281), Natural Science Foundation of Hubei Province, PR China (2014CFB919) and the S&T Plan Innovation team for of Wuhan city (2015070504020220).

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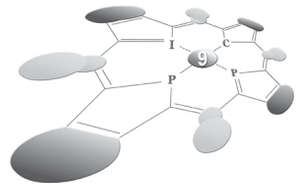


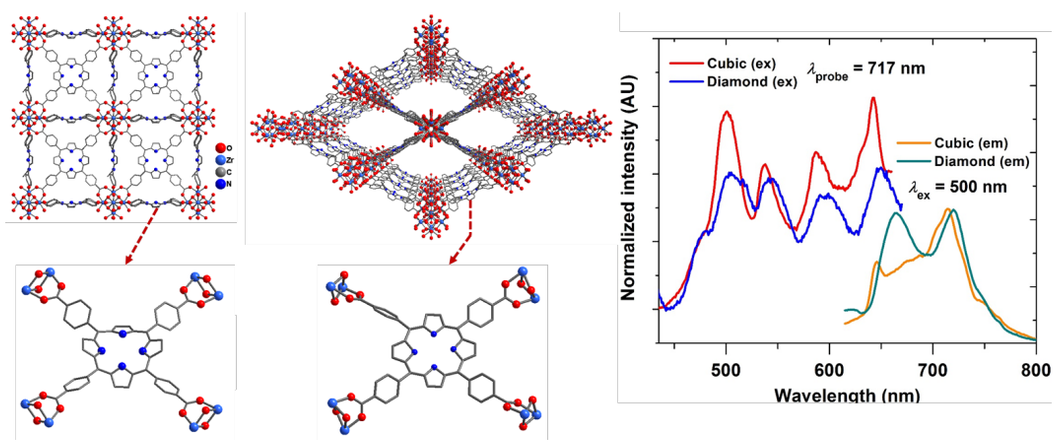
Porphyrin based Metal-Organic Frameworks (MOFs): New Materials for Electro-optics and Energy Conversion

Pravas Deria, **Mashni Jamil, Jack J. Pertile**

Southern Illinois University, Chemistry & Biochemistry, Carbondale, USA

Tuning the underlying electronic and optical properties of porphyrins are of tremendous importance for various optoelectronic and energy conversion applications. However, modulation of their optoelectronic properties involves typically extensive synthesis, aimed for example, at conjugation length expansion and incorporation of substituents that alter porprhyrin frontier molecular energy levels. Such multi-step syntheses often suffer from poor macromolecular solubility; introducing sidechains provides a tool to mitigate this issue and direct their self-assembly.

Metal organic frameworks (MOFs) are solid state, crystalline, hybrid materials that offer easy solution to these problems. Their scalable hydrothermal syntheses involve self-correcting assembly to ensure new platforms with perfectly aligned porphyrinic chromophores in various topological morphologies.[1, 2] Such assembly, similar to the LH-antenna complexes, provides a unique means to tune their electronic as well as excitonic properties as a function of relative orientation of porphyrin linkers in MOF crystals. In this presentation we will discuss two key phenomena: (a) light harvesting and large exciton displacement and (b) effect of distortion in the porphyrin planarity as a function of MOF-topology and related flexibility. These phenomena are hard to achieve in homogeneous system but can be achieved easily within MOFs enforced by topological demand: for example, non-planarity in the porphyrin rings can be introduced without the extensive ring functionalization. Likewise, with various spatial orientations achievable for a given porphyrinic moiety, their exciton coupling and displacement can be modulated as a function of MOF topology, enabling the development of new light-harvesting materials.



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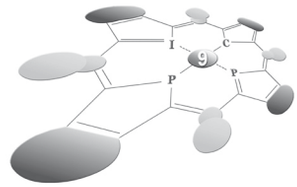
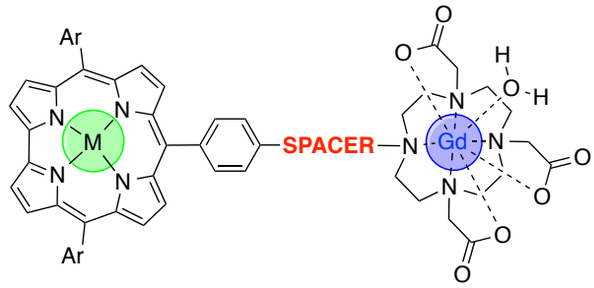


Synthesis of corroles for medical imaging applications

Nicolas Desbois, Clément Michelin, Yi Chang, Claude P. Gros

Université de Bourgogne Franche-Comté, ICMUB-P2DA (UMR CNRS 6302), 9 Avenue Alain Savary, BP 47870, 21078 Dijon Cedex, FRANCE

Imaging techniques are perfect tools for the diagnosis of many diseases, like cancers. The most routinely used analyses at the clinical stage are MRI (Magnetic Resonance Imaging), SPECT (Single Photon Emission Computed Tomography) and PET (Positron Emission Tomography). In the last decade, the concept of coupling different imaging modalities to exploit the complementarities between each technique has emerged.
Our group has described several new potential bimodal imaging contrast agents based on DOTA-like and porphyrin macrocycles.[1,2] Our researches recently focused on the synthesis of corroles for multimodal medical imaging applications.[3,4] We will discuss the design of new potential bimodal MRI/PET contrast agents. These compounds can be also grafted onto folic acid derivative for biovectorization.



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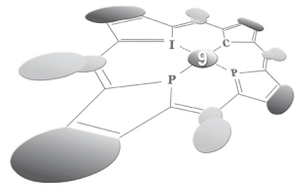

Magnesium Porphine Electropolymerization and Electrografting of *meso*-Diazonium Porphyrins: Towards Sensing Materials

Charles H. Devillers[a], **Abdou K. D. Dimé,**[a] **Seydou Hebié,**[a] **Sébastien Rolle,**[a] **Sophie Fournier,**[a] **Dominique Lucas,**[a] **Hélène Cattey,**[a] **Dmitry V. Konev,**[b,c] **Mikhail A. Vorotyntsev**[b,c,d]

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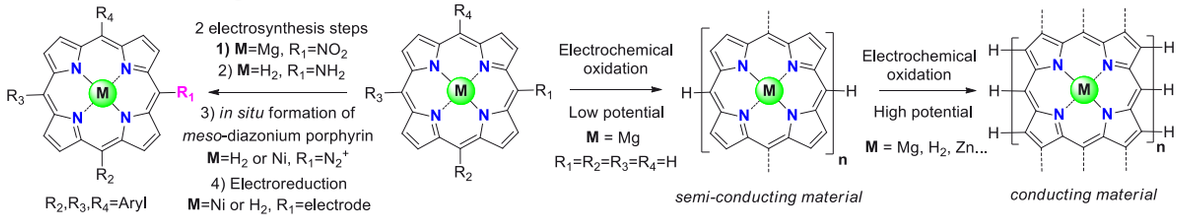
Porphyrin-based thin films are currently used in various fields and for many applications because of their interesting physico-chemical properties.[1] Indeed, these materials are part of different devices for nonlinear optical and optical limiting devices, photoluminescent biosensors, electrochemical or spectrometric sensors, molecular electronic junctions and electrocatalytic systems.

One part of our research is focused on the electrosynthesis of new porphyrin-based materials. Oxidation of magnesium(II) porphine (MgP), the fully unsubstituted porphyrin,[2] leads to new electrodeposited oligomers/polymers *via* C_{meso}-C_{meso} couplings (see scheme below). These new semi-conducting or conducting materials have been then chemically and electrochemically transformed.[3,4] Also, *meso*-triarylporphyrins have been functionalized by electrosynthesis (nitration, nitro function reduction into the amine) and then grafted onto an electrode surface via reduction of an *in situ* generated diazonium-porphyrin.[5-6] Synthesis and characterization of these thin films will be presented in this communication.



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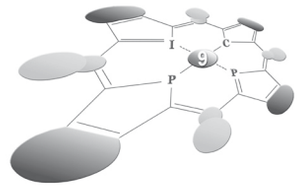

The Enantioselective Sensors Based on Porphyrins Aggregates

Corrado Di Natale[1], Donato Monti[2], Roberto Paolesse[2]

[1] Department of Electronic Engineering, University of Rome Tor Vergata, Via del Politecnico, Rome; Italy
[2] Department of Chemical Science and Technologies, University of Rome Tor Vergata, Via della Ricerca Scientifica 1, Rome; Italy

Chemical sensors for a rapid and reliable chiral discrimination are highly required in many fields, for example the drug industry. However, enatioselective recognition is one of the most challenging tasks for chemical sensors, since the enantiomers share the same physical and chemical properties they behave differently only in a unsymmetrical environment. For this reason the preparation of chiral films is a necessary step to develop enantioselective sensors. In this scenario, the non-covalent approach may represent a simple way to confer chiral properties to an adsorbing surface. We have demonstrated in the past that QCM functionalized with a self-assembled film of chiral porphyrin dyads can distinguish between the two chiral forms of lemonene [1]. However, in these sensors a single layer strongly limits the dynamic range of the sensor.
More recently, we have observed that the supramolecular organization of solid porphyrin layers can offer additional interaction pathways with the target analytes, able to increase the sensing performances [2]. These additional interaction properties can offer promising opportunities for chiral recognition. We explored this approach by using the spontaneous deposition of aggregates from solutions containing appropriately functionalized porphyrin monomer bearing a chiral substituent [3, 4, 5]. The spontaneous aggregation of a tetraphenylporphyrin derivative, bearing a cationic proline- appended functionalities, resulted in a stable sensing films with a peculiar ordered morphology.
The film was used to functionalized the surface of quartz crystal microbalances, in order to measure the adsorbed molecular mass. The results are not completely satisfactory because although enantioselective, the sensors are not reproducible due to the scarce rigidity of the supramolecular interaction. In this talk the properties of this aggregate have been studied with different transducers and in a particular with a liquid gate graphene based transistor. A comparison between the two transducers will offer the opportunity to discuss the transducer role in the design of chemical sensors.

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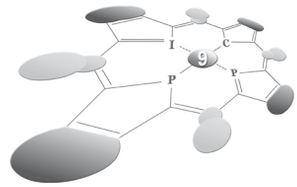

Metallacycles built-in the porphyrin skeleton - submitted to the International Conference on Porphyrins and Phthalocyanines

Ewa Dudziak (Pacholska)[a], **Aleksandra Książek, Michał Szczepaniak, Lechosław Latos-Grażyński**[a]

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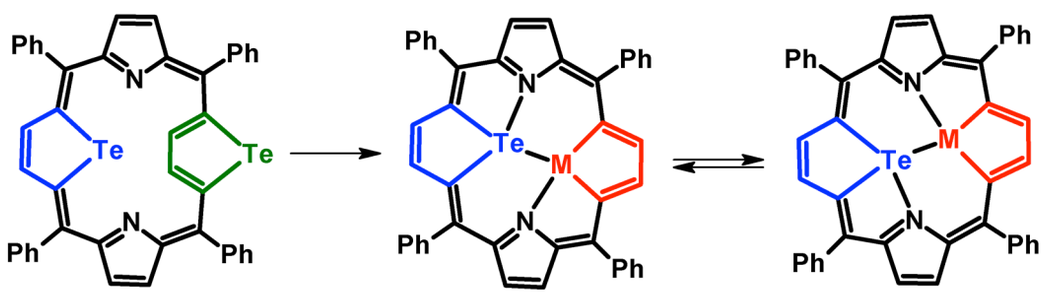
Heteroporphyrins are constructed by the replacement of one or more pyrrole nitrogen atoms of a porphyrin with other atoms. Up to now only a limited range of alternative heteroatoms, mostly group 16 elements (O, S, Se, Te), as well as phosphorus and carbon have been incorporated. Heteroporphyrins typical synthesis based on [3+1] or [2+2] approaches or alternatively, stochastic condensations of mixtures of smaller units, require construction of a suitable synthon containing a heterocyclic ring. Another approach is core-heteroatom substitution within predefined macrocycles, on the porphyrin or porphyrinogen oxidation level. Such a "post-synthetic" modification is represented by the straightforward transformation of 21-telluraporphyrin into 21-oxaporphyrin or by a heteroatom exchange in tetraoxaporphyrinogen leading to tetrathia- and tetraselenaporphyrinogens.
Following the telluraporphyrin theme we proved that 21,23-ditelluraporphyrin[1] (**1**) is a precursor of a new class of heteroporphyrins, namely 21-metalla-23-telluraporphyrins (**2**), with a transition metal built-in the pentacyclic ring. Here I will present examples of this exotic class of metallaporphyrins, containing Pd(II) Pt(II) and Pt(IV).[2]



The main features of **2** are the deformation of the porphyrin skeleton, detected in the solid state and the dynamic behaviour observed in solution by means of ^{1}H NMR. The conformational equilibrium between **2** and the enantiomeric **2'** (provided molecule nonplanarity) involves concerted palladium and tellurium hopping between two pyrrolic nitrogen atoms. The atypical tellurophene unit coordination mode with the bound metal ion located in the tellurophene plane is stabilized by the macrocyclic environment. These metallaporphyrins features reflect the interplay of the palladium or platinum strong coordination preferences and the porphyrin skeleton stabilization.

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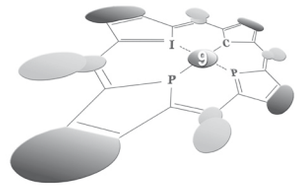

Tumor-site activation in photodynamic therapy: an alternative to targeting strategies

Serkan Alpugan and Fabienne Dumoulin

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To avoid undesired photosensitization issues, it is important to confine the photodynamic generation of singlet oxygen in the tumoral tissues. This is mostly addressed by targeting strategies.[1]
An alternative is to activate the photosensitizer only at the tumor site by benefiting from the particular features of the tumor, which is more acidic, warmer, and more reductive than healthy tissues are. A tumor can also have particularly high concentrations of specific enzymes. The photosensitizer can be covalently bound to a quencher[2] and released only in these particular conditions. Photosensitizers needing a double activation have been reported.[3-4] Another possibility is based on the aggregation of photosensitizer and its disrupting only at the tumor site.[5]
After having explored several aspects of the optimization of the photodynamic efficiency of porphyrinoids,[6-7-8] we get interested in the tumor-site activation strategy. The last developments of our researches in this field, essentially based on the preparation of dimeric and pentameric edifices of porphyrinoids linked by disulfide functions will be detailed.

ACKNOWLEDGEMENTS
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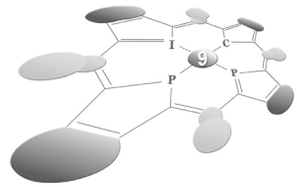

Building up colors: supramolecular arrays of peryleneimides and phthalocyanines on solid substrates

Alexander Efimov[a], **Essi Sariola-Leikas, Hanna Hakola, Lijo George, Arto Hiltunen, Zafar Ahmed, Nuno Candeias, Paola Vivo, Elena Efimova**[a]

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Presentation will cover recently developed a set of perylene and phthalocyanine derivatives from which one can build highly organized multilayered structures on metal oxide surfaces. [1-3] The essential feature of the work is the use of terpyridyl-crowned perylenemonoimides monoanhydrides as the anchoring substances. PMI anchors form a dense and well-organized layer on oxides surfaces (TiO_2, alumina, zinc oxide), are able to interact with the substrate (e.g. inject and electron upon photoexcitation), and are capable to further complexate terpyridyl-crowned substances. Another key point of arrays assembling is a proper choice of bis(terpyridyl)perylenediimide or terpyridyl-phthalocyanine linkers. Combination of these with the PMI anchors allows to assemble highly colored and stable, up to 33-layers thick molecular films by a simple and reproducible procedure. As a proof of concept it has been demonstrated that molecular arrays can be successfully used in solid state DSSC. High absorbance of the multilayered films might eliminate the need of using porous structures, while the possibility to cover easily large surfaces is a great advantage in practical applications. Arrays can be built on flat surfaces, as well as inside the cavities of porous materials or between nano-scaled inorganic patterns (e.g. zinc nanorods), thus allowing to create organic-inorganic hybride structures.

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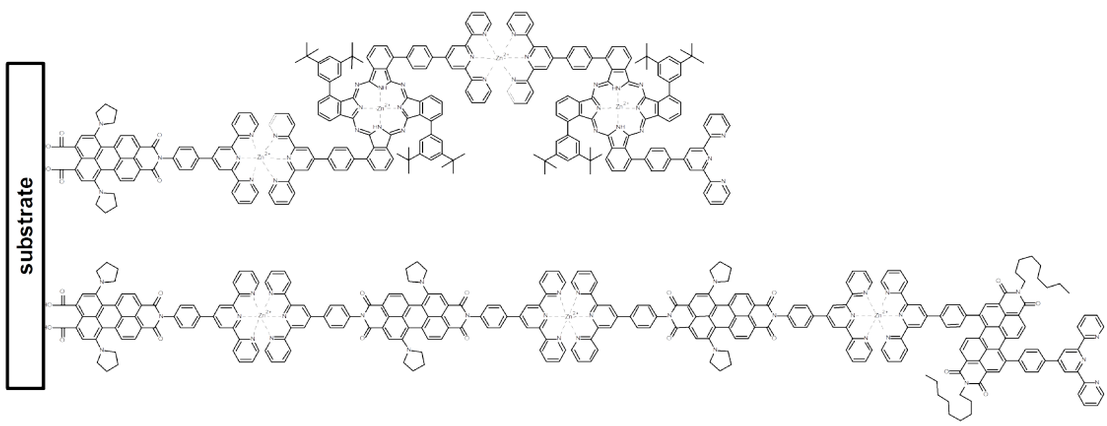

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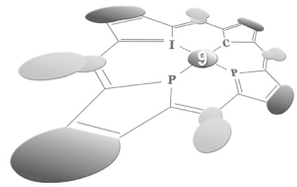

Electropolymerized Metallocorroles as Electrocatlysts for Oxygen Reduction

Lior Elbaz[1], Naomi Levy[1], Atif Mahammed[2], Zeev Gross[2]

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The most active non-precious metal catalysts (NPMCs) for oxygen reduction (ORR) to date are the pyrolyzed catalysts, inspired from Heme-like complexes. These are usually composed of iron and/or cobalt coordinated by nitrogens, claimed to resemble the structure of porphyrins and phthalocynines, on the surface of a carbon support. Unfortunately, the exact structure of the catalytic sites remains a mystery and the solution for this conundrum seems be almost impossible. The advantages of using such catalysts are: (1) their high activity and (2) low price, which is derived from the cost of their precursors. The disadvantages are: (1) low durability compared to precious metal catalysts, and (2) their unknown structure, which limits their further improvement in order to obtain both the activity and durability benchmarks needed to become good alternatives for precious metals.

One of the most promising options to resolve these issues is to find non-pyrolyzed molecular non-precious metal catalysts for ORR that could be tuned to match the necessary requirements. Recently, Metallo-corroles, a relatively new family of molecular catalysts was reported to have very good potential as non-precious metal catalysts for ORR. Inspired from the extensive work on the electropolymerization of metalloporphyrins, and its merits, we electropolymerized of metallocorroles on carbon electrodes to (1) increase their site density in order to overcome their relatively low electrocatalytic turnover frequency (when compared to platinum) and (2) use the proximity of active sites to move from 2- to 4-electroreduction of oxygen. Metallocorroles substituted with anilines were studied and electropolymerized. They show a significant enhancement in the overpotential required for the execution of ORR and tendency for 4-electormn reduction to water.

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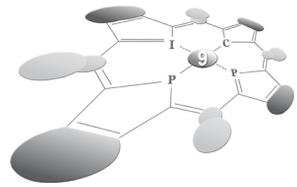
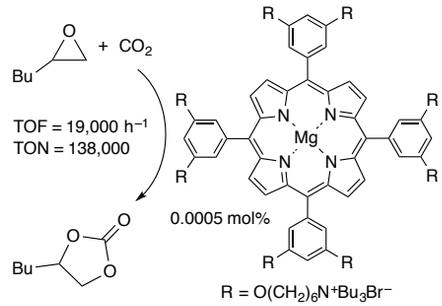


Metalloporphyrins as Catalysts for CO_2 Fixation

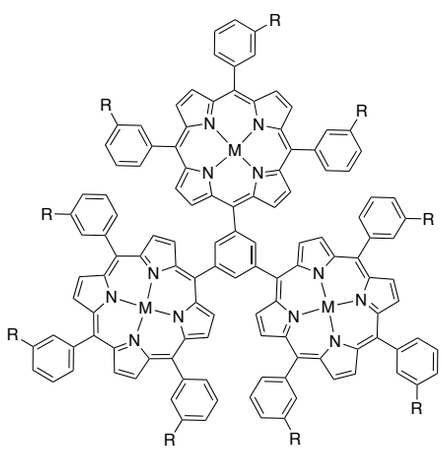
Tadashi Ema and Chihiro Maeda

Division of Applied Chemistry, Graduate School of Natural Science and Technology, Okayama University, Japan

We have developed various metalloporphyrins as bifunctional catalysts for the synthesis of cyclic carbonates from epoxides and CO_2 under solvent-free conditions. CO_2 is an inexpensive, nontoxic, and abundant carbon source for organic synthesis, while cyclic carbonates are valuable chemicals that are used as raw materials for polycarbonates, as electrolytes in lithium-ion secondary batteries, and as polar aprotic solvents. The structures of the bifunctional catalysts were optimized step by step. The metal center, quaternary ammonium cation, halide anion, linker length, the position and number of the quaternary ammonium salt were changed in the screening. As a result, we found that a Mg(II) porphyrin bearing eight nucleophiles at the meta positions showed high catalytic activity (turnover number (TON) = 138,000, turnover frequency (TOF) = 19,000 h^{-1}).



The yields were nearly constant at initial CO_2 pressures in the 1–6 MPa range, suggesting that CO_2 was not involved in the rate-determining step in this pressure range. Interestingly, no reaction proceeded in supercritical CO_2, probably because the epoxide (into which the catalyst dissolved) dissolved in and was diluted by the supercritical CO_2.



The catalytic cycle involved the initial nucleophilic attack of Br^- on the less hindered side of the epoxide to generate an oxyanion, which underwent CO_2 insertion to afford a CO_2 adduct, and the subsequent intramolecular ring closure formed the cyclic carbonate to regenerate the catalyst. Density functional theory (DFT) calculations revealed that the quaternary ammonium cation underwent conformational changes to stabilize various anionic species that are generated during the catalytic cycle. The high activity of the bifunctional catalysts was due to the cooperative action of the Mg^{II} and Br^- and a conformational change (induced-fit) of the quaternary ammonium cation.

Triporphyrin catalysts were also synthesized through Stille coupling reactions. We selected the *m*-phenylene-bridged platform because Br^- ions on the adjacent porphyrin moieties might function as better nucleophiles. As a result of experiments, they showed very high catalytic activity: TON = 220,000 and TOF = 46,000 h^{-1} for the Mg triporphyrin, and TON = 310,000 and TOF = 40,000 h^{-1} for the Zn triporphyrin.

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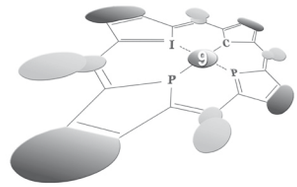

Multiple Cycles of Heme-mediated Radical Transfer in Cytochrome c Peroxidase: Insights from LC-MS/MS and EPR Analysis

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We have recently reported that cytochrome c peroxidase (Ccp1) functions as a H_2O_2 sensor protein when levels of the peroxide rise in respiring yeast.[1] Since H_2O_2 is "sensed" by the oxidation of its protein receptors, we employed high-performance LC-MS/MS to investigate in detail the products of Ccp1 oxidation by 1, 5 and 10 M eq of H_2O_2 in the absence of ferrocytochrome c to eliminate peroxidase activity and allow endogenous oxidation of the peroxidase. We observe strictly heme-mediated oxidation, thereby confirming our unprecedented report of heme-mediated H_2O_2 sensing.[1] Cycles of sequential binding and reduction of H_2O_2 at Ccp1's heme using endogenous donors in the polypeptide result in the incorporation of ~20 oxygen atoms predominantly at methionine and tryptophan residues. Additionally, extensive *intra*molecular dityrosine formation involving neighboring Y36/Y39, Y36/Y42 and Y67/Y71 was uncovered on sequencing of the crosslinked peptides. A total of 24 residues are oxidized by repeated radical transfer from the heme in Ccp1 treated with 10 M eq of H_2O_2. The proximal heme ligand (H175) is among the residues oxidized, revealing that reaction with H_2O_2 labilizes Ccp1's heme but, remarkably, irreversible heme modification is avoided until oxidation of the catalytic distal H52 shuts down heterolytic H_2O_2 cleavage. EPR spectra of Ccp1's high-valent intermediates expose transient tyrosyl radicals[2] on radical-transfer pathways from the heme mapped by the MS analysis and this complementarity of the MS and EPR investigations will be highlighted.

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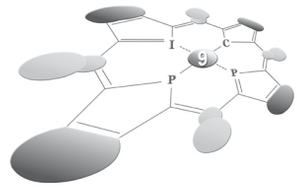

The secret life of phytochromes: mechanisms of photoconversion and interactions

Silke von Horsten, Katrin Anders, Lars-Oliver Essen

Philipps-University, Department of Chemistry, Hans-Meerwein-Str., 35032 Marburg

Phytochromes are red/far-red (r/fr) photochromic photoreceptors, which are able to convert different light conditions into a biological signal. The N-terminal photosensory module of canonical phytochromes consists of a PAS-GAF-PHY tripartite module [1], preceded by an additional N-terminal extension in plant phytochromes. The tetrapyrrole chromophore is buried within the GAF domain but covered by a tongue-like protrusion from the PHY domain. In contrast, cyanobacterial Cph2 lacks the PAS and PHY domains whereby a second GAF domain mimics the structure of the PHY domain [2]. Upon red light irradiation, phytochromes undergo a reversible isomerisation of the chromophore leading to structural changes in the protein and therefore to the formation of the far-red absorbing signaling state (Pfr).

We proposed a tryptophan swap of the W/FxE and WG/AG motifs within the tongue GAF interface as well as a local refolding of the tongue including the PRxSF motif upon Pr→Pfr photoconversion [3,4]. To prove our hypothesis we investigated both states of *Arabidopsis thaliana* phytochrome B by hydrogen-deuterium-exchange mass spectrometry and were able to detect different deuterium exchange rates for the tongue region supporting the idea of tongue refolding. Also different accessibilities for the central hole in the structure could be observed that is framed by the GAF and PHY domains as well as the tongue region and the domain-connecting α-helix. EPR spectroscopic analysis (DEER) of Cph2 from *Synechocystis* sp. likewise hints towards structural changes in the tongue region.

Furthermore, we investigated the phytochrome-associated phosphatase 5 (PAPP5) from *Arabidopsis thaliana*, presenting a significant part of the phytochrome signaling pathway. Addition of arachidonic acid was shown to provoke the activity of the phosphatase, presumably caused by the unfolding of the active site-blocking TPR domain of PAPP5. Moreover, also the interaction with phyA(973-1122) was sufficient to trigger the phosphatase activity. On-going experiments will be presented to map the interaction regions of phyB with down-stream effectors in high detail.

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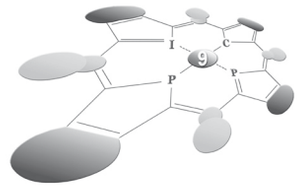

Sinoporphyrin sodium-a novel antineoplastic sensitizing agent for photodynamic therapy

Qicheng Fang

Institute of Materia Medica Chinese Academy of Medical Sciences

Photofrin® was the first anti-cancer photosensitizer developed by the Roswell Park Cancer Institute. In 1996, the US FDA approved the use of Photofrin® in photodynamic therapy (PDT) for treatment of esophageal cancer and other malignancies. Approvals were also given by the government of Canada, France, Netherland, Germany, Japan, and other countries. To date, Photofrin® has been used around the world for nearly 20 years and to treat more than a dozen types of cancers including esophageal cancer, lung cancer, brain tumors, head and neck cancer, eye cancer, throat cancer, chest wall tumors, breast cancer, pleural mesothelioma, peritoneal sarcoma, bladder cancer, gynecological cancer, colorectal cancer, skin cancer. Its efficacy and safety have been fully confirmed.

However, the active ingredient of Photofrin® has not been identified; therefore there are no clear specification and control standards. In addition, a major shortcoming of Photofrin® is the long residence time. The residue of the drug incites skin phototoxicity and causes rashes, blisters, pigmentation, and even skin ulcers. Patients need to avoid direct sunlight exposure for four to six weeks after PDT treatments.

A shortcut of developing new anti-cancer photosensitizers is undoubtedly a comprehensive investigation of Photofrin® to identify the active ingredient. An accurate and reliable HPLC method capable of analyzing porphyrin compounds was established. Using this method, more than 20 porphyrin derivatives were found to exist in Photofrin®. Systematic chemical separation and structure elucidation were carried out. Anti-cancer efficacies of the ingredients were screened. Cold spray mass spectrometry was conducted on components that exhibited strong efficacy. Detailed analyses and comparisons revealed that 95% of the content of Photofrin® was ineffective. The active agent accounts only 1% to 5% of the total content.

Multiple tumor-bearing animal tests show that three isomers have strong anti-cancer photosensitive activities, and the effects of the three isomers are comparable. The efficacy of one part of the isomer is equivalent to that of 10 parts of Photofrin®. Skin phototoxic is low. Preliminary animal trials indicate that, 96 hours after administration of the isomers, skin phototoxic reactions do not occur. Of the three dimer isomers, Bis [1- [6,7-bis [2- (sodium carbonate)] ethyl]1,3,5,8, - tetramethyl- 2-vinylporphin-4- yl] ethyl] ether (DVDMS-2) is chosen as the desired compound since its yield is high, purification is easier, and water-solubility is greater than the other two isomers.

The raw material is abundant. The synthesizing process has been optimized. The operation is simple and safe. The purity of the DVDMS-2 is greater than 98%. The medicine can be mass-produced and the quality can be well controlled. The new medicine is named Sinoporphyrin sodium and is codenamed DVDMS. It possesses Chinese intellectual property right and represents the advent of a new generation of anticancer photosensitizer.

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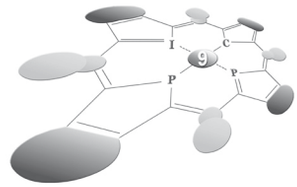

Electrochemistry of Mono- and Bis-Cobalt and Manganese Triarylcorroles and Catalytic Activities for Electroreduction of Molecular Oxygen in Acid Media

Yuanyuan Fang,* Yue Wang, Wenda Wang, Minyuan Chen, Weijie Xu and Zhongping Ou*

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Cobalt and manganese corroles have attracted a great deal of interest over the last two decades of their many potential applications in the fields of catalysis and materials.[1,2] In the present work, four mono-cobalt and manganese triarylcorroles and their dimers linked by a xanthene acyl group were synthesized and characterized as to their electrochemical and spectroelectrochemical properties. The examined mono- and bis-metallocorroles are represented as $(NH_2Ph)(YPh)_2CorM$ and $[(YPh)_2CorM]_2Xac$, respectively, where M = $Co(PPh_3)$ or Mn, Cor = a trianion of the corrole and Y = CH_3 or Cl substituent on the *para*-position of the 5,15-*meso*-phenyl rings of the compound. The structures of the compounds are shown in Chart 1. Each neutral, reduced and oxidized form of the mono- and bis-metallocorroles was characterized by electrochemistry and thin-layer spectroelectrochemistry in nonaqueous media. Rotating-disk and rotating-ring-disk electrode measurements utilized to examine the electrocatalytic activity of the compounds for reduction of O_2 in 1.0 M $HClO_4$. The number of electrons transferred in the catalytic electroreduction of oxygen was calculated from currents at the disk electrode using Koutecky-Levich plots. The characterized UV-visible spectra and redox potentials as well as on the electrocatalytic activity for the reduction of oxygen will be discussed. S*upport from the Natural Science Foundation of China (21501070) and the Foundation of Jiangsu University (15JDG131, 05JDG051*) is greatly acknowledged.

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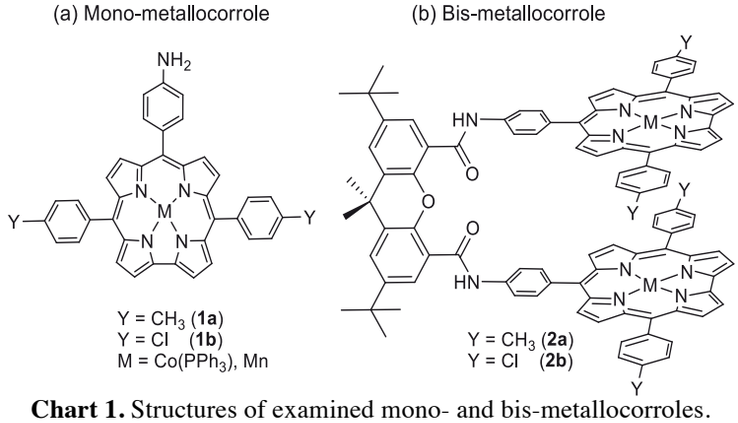

Chart 1. Structures of examined mono- and bis-metallocorroles.

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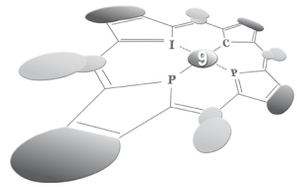
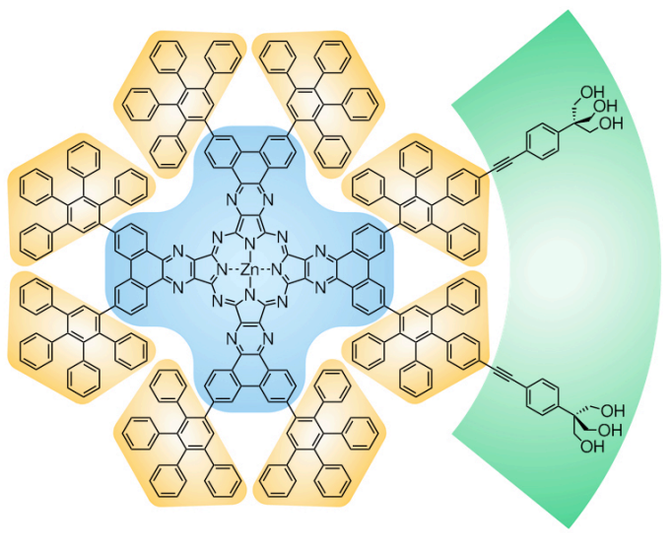


Tackling "desymmetrized" [3+1]Porphyrazines

Rüdiger Faust, Verena Engelhardt, Patricia Löser, and Roman Münnich

University of Kassel, Institute for Chemistry and CINSaT – Center for Interdisciplinary Nanostructure Science and Technology, Heinrich-Plett-Str. 40, 34132 Kassel, Germany, r.faust@uni-kassel.de

Much of our research in recent year has focussed on peripherally functionalized dibenzoquinoxalino-porphyrazines.[1-3] For applications curently under investigation in our labs, we were in need of "desymmetrized" [3+1]porphyrazines in which one quadrant of the tetrapyrrole dye differs from the other three. Access to these systems is provided by either statistical based-induced cyclizations of two differently substituted dinitriles or, more elegantly, by ring-opening reactions using the appropriated sub-porphyrazine.



We have explored both of these synthetic avenues and are presenting in this lecture our results on the preparation of [3+1]porphyrazines along with a discussion of their properties and their usefulness in the targeted applications, among them directional energy transfer systems and photocatalytically active hybrid materials.

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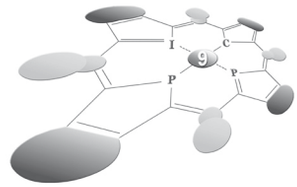

The route via siroheme for making the d_1 heme of the periplasmic cytochrome-type nitrite reductase

Shilpa Bali[a], Stuart J Ferguson[a] , Martin J Warren[b]

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[b]*Department of Bioscience, University of Kent, Canterbury, UK.*

Each polypeptide of cytochrome cd_1 nitrite reductase contains one *c* -type heme centre which functions to provide electrons to the active site modified tetrapyrrole usually called d_1 heme, although strictly speaking it is not a heme. The biosynthetic pathway unexpectedly is routed via siroheme, in common with a route to heme in archaea and bacteria such as the sulfate reducers [1]. Following the cytoplasmic double decarboxylation, which will be discussed [2], of siroheme several steps are needed to complete the formation of d_1 heme. There are three periplasmic proteins involved, NirC NirF and NirN, as well as a cytoplasmic protein of the radical SAM family, NirJ. This talk will discuss what is known about the roles of these proteins in making d_1 heme. The steps involved in the attachment of heme to give the c-type heme centre will also be discussed.

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Parallel- *versus* Perpendicular-Arranged Phthalocyanine-Perylenediimide Conjugated Systems

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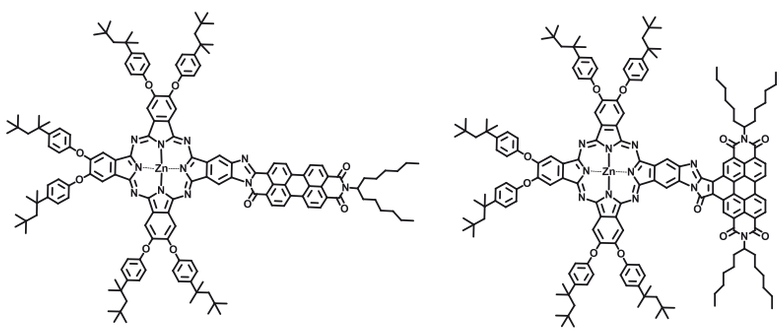
Molecular and supramolecular architectures composed of arrays of photoactive moieties ordered in a suitable disposition are of interest because upon selective light excitation of a given chromophore they can undergo directional multi-step electron and/or energy transfer processes. In this direction, phthalocyanines (Pcs) have attracted much attention because their singular electronic properties[1], and have been combined with a large number of electron-poor systems. On the other hand, perylenediimides (PDIs) have demonstrated exceptional photochemical stability, strong absorption of visible light, and high fluorescence quantum yields. Due to these features, PDI derivatives have been used as active components in organic field-effect transistors and photovoltaic cells[2]. In the recent times, an increasing number of PDIs covalently linked to additional electro-active moieties have been reported, thus broadening the scope of their potential applications.

During the last few years we have been involved in the synthesis and characterization of interesting molecular and supramolecular eletroactive systems based mainly on Pcs and PDIs as building blocks [3]. Herein, we will report the more recent results obtained in our group related with the synthesis and the photoinduced electron transfer properties of the fully conjugated phthalocyanine-perylenedimides arrays in which the Pc unit is connected either through the imide position of the PDI (parallel arrangement or through the PDI bay positions (perpendicular arrangement)[4].



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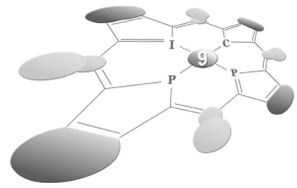

Dominant role of tunneling in tautomerization of porphycenes

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Porphycene [1] and its derivatives are convenient molecular systems for studying hydrogen transfer reactions and dynamics of protons in symmetrical double potential wells. Earlier spectroscopic studies of porphycenes in supersonic jets [2] and in helium nanodroplets [3] revealed vibrational mode-dependent splitting of energy levels, which indicated the influence of quantum effects and suggested that tunneling could be involved in the transfer of protons between the two potential minima. In order to elucidate the role of tunneling in the hydrogen transfer in porphycenes we have thoroughly studied this process in the condensed phase (solutions) by carrying out time-resolved measurements with femtosecond temporal resolution in a broad range of temperatures (20-400K). The technique applied allows recording of hydrogen transfer kinetics for both, ground and the first excited singlet electronic states [4].

Arrhenius curves obtained in the presented experiments can be reproduced only if thermally activated and temperature-independent reaction channels are taken into account. We have identified two of these channels as tunneling from the vibrational ground state (temperature independent) and from the first excited state of the 180 cm^{-1} A_g vibration which modulates the distance between the hydrogen donor and acceptor [5]. Excitation of this vibration accelerates hydrogen tunneling by a factor of up to 100. As a result, tunneling significantly contributes to the mechanism of hydrogen transfer in porphycenes even at room temperature: in 2,7,12,17-tetra-*tert*-butyl porphycene both channels contribute more than 80% at 300 K.

Substitution of the proton by a deuteron significantly reduces the vibrational enhancement effect: deuterium tunneling rates in the ground and excited state of the 180 cm^{-1} vibration are very similar to each other. This unexpected observation should stimulate further theoretical studies of the vibrationally enhanced hydrogen tunneling in porphycenes.

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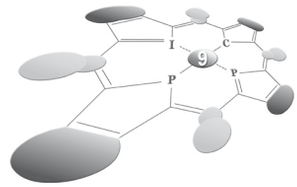

Predicting the degree of aromaticity of novel porphyrinoids

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Electronic and spectroscopic properties of porphyrinoid macrocycles are, to a large extent, determined by the number of π-electrons participating in the conjugation network. Full control of the number of π-electrons implies full control of the aromatic or antiaromatic character of the molecule. To achieve this, knowledge about the electron delocalization pathways within a molecule is essential. Experimentally, these pathways are not easily accessible. Therefore theoretical studies are necessary to complement experiments that aim at systematically synthesizing porphyrinoids with distinct properties.
A computational approach to achieve this is the gauge including magnetically induced current density method (GIMIC). GIMIC is a independent program that is used for the calculation of magnetically induced current densities using London orbitals.[1, 2] Numerical integration of the current flow around molecular rings and along selected chemical bonds can be used for determining current pathways and the degree of aromaticity of various molecules according to the magnetic criterion.[3,4] In my talk I am going to present the GIMIC method and briefly discuss the idea behind it. I will illustrate what type of information is accessible through current density studies and highlight some very recent results showing the potential and the challenges of the method.[5,6]

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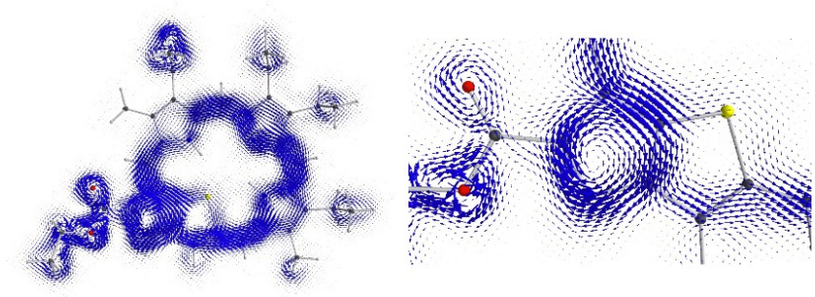

Figure: The calculated magnetically induced current density of an antiaromatic thienopyrrole modified porphyrin obtained in a plane placed 1 bohr above the molecular plane (blue arrows). Diatropic currents are assumed to circle clockwise.

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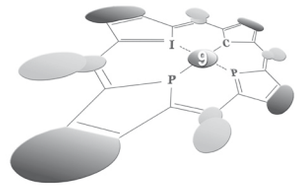

Factors that Govern Function Switching in Multifunctional Heme Enzymes

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Dehaloperoxidase-hemoglobin (DHP) from the marine annelid Amphitrite ornata is an example of a multifunctional heme protein. The multiple functions rely on subtle modulation of the heme iron coordination sphere and the positioning of the highly flexible distal histidine. While the protein is structurally classified as a globin the flexibility of the amino acids in the distal pocket and, in particular, the distal histidine provide a new paradigm for how proteins can modulate reactivity using the protein scaffold. Specifically, subtle changes in structure in response to the binding of the various substrates appear to trigger appropriate changes to permit enzymatic catalysis by peroxidase, peroxygenase and oxidase mechanisms. The globin function is a default, which is maintained by the high redox potential of the iron such that the ferrous oxidation state is favored in the absence of any substrate binding. To relate the observed phenomena to previous observations we could say that substrates in DHP act as allosteric effectors. The difference with respect to allostery in hemglobins is that the main effect of allostery is to alter the oxygen binding equilibrium. Of course, hemoglobins may also evolve to regulate other gases in blood and allostery can play a role there too. But, DHP is a unique example where allostery can give rise to a change in oxidation state and catalytic potential of the heme. Given the relative structural simplicity of the globin fold the changes in structure that give rise to different functions are also relatively simple. For example, evidence will be presented by NMR and resonance Raman spectroscopy that exterior binding of a substrate causes a small reorientation of the distal histidine so that it can hydrogen bond more strongly with a bound ligand. This is an essential feature of the peroxidase mechanism, which requires an acid-base catalyst to promote the isomerization of bound hydrogen peroxide. The binding of inhibitors to peroxidase activity in the distal pocket pushes the distal histidine out of the pocket and thereby significant decreases catalytic activity. While these aspects have been known for some time, the structural features that various substrate binding and the direct effect of substrates on the binding of oxygen and hydrogen peroxidase comprise a second type of control. The use of competitive binding equilibria to determine both the binding affinity and modes of binding has been demonstrated. X-ray crystal structures show at least two different modes of binding inside distal pocket, which appears consistent with the models proposed from the competitive binding equilibria. The combination of spectra and structural data will be used to elucidate the correlation small molecule binding and functional aspects of the protein for a range of substrates that now includes halogenated phenols, nitrophenols, halogenated indoles and pyrroles.

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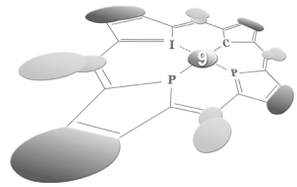

Targeted porphyrins and nanoparticles for both detection and photodynamic therapy

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Photodynamic therapy (PDT) is clinically used to treat different kind of cancers as well as age-related macular degeneration, acne… After excitation of a photo-activable molecule called the photosensitizer and energy transfer to oxygen, reactive oxygen species are produced leading to photooxidation reactions. One limitation of photodynamic therapy is the low selectivity of photosensitizers to tumor tissue compared to normal tissue. The synthesis of photosensitizers especially porphyrins or chlorins coupled with vectors specific of the membrane receptors over-expressed on neo-vessels or tumoral cells has become a center of interest.
The poor outcome of primary malignant brain tumors derives from local invasion and local recurrence. Standard treatment of high-grade astrocytic tumors usually consists of cytoreductive surgery followed by radiation techniques and chemotherapy; however these tumor types usually recur despite treatments. In most cases, curative resection is not possible due to infiltrating growth of the tumor into normal brain parenchyma. In this unfavorable context, PDT appears as an innovative technology being investigated to fulfill the need for a targeted cancer treatment that may reduce recurrence and extend survival with minimal side effects. We develop peptide-targeted photosensitizers[1,2,3] as well as peptide-targeted nanoparticles[4,5,6] to improve the efficiency of PDT to treat glioblastoma.
Ovarian cancer's prognosis remains dire after primary therapy. 60% of women with epithelial ovarian cancer considered in remission will develop recurrent disease within five years. Special attention to undetected peritoneal metastasis during surgery is necessary as they are the main predictive factors of recurrences. Folate Receptor α shows promising prospects in targeting ovarian cancerous cells and intraperitoneal PDT could be a solution in addition to macroscopic cytoreductive surgery to treat peritoneal micrometastasis.
We develop new folic acid targeted porphyrin[7,8,9]. The photodynamic activity of these targeted compounds are evaluated *in vitro* and *in vivo*.

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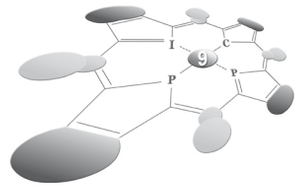

Solution-Processable Bulk-Heterojunction Solar Cells Utilizing Non-Peripherally Alkyl-Substituted Phthalocyanine-Tetrabenzoporphyrin Hybrid Macrocyles

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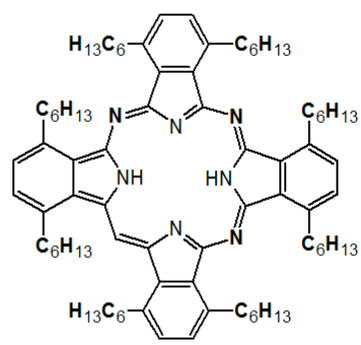
Liquid crystalline organic semiconductor is one of the promising materials for electronic device applications, because of the potentially high carrier mobility comparable to that of a-Si (0.1 cm^2/Vs). Non-peripherally alkyl-substituted phthalocyanines, such as, 1,4,8,11,15,18,22,25- octahexylphthalocyanine ($C6PcH_2$) are low-molecular-weight organic semiconductor and has high solubility in typical organic solvents due to the long substituents. $C6PcH_2$ exhibits liquid crystalline phase, such as, hexagonal disordered columnar mesophase between 161 and 170 °C.

Here, we report on solution processed small-molecule based organic solar cells (OSCs) utilizing phthalocyanine-tetrabenzoporphyrin hybrid macrocyles with alkyl-substituents at non-peripheral positions. By replacement of aza links at meso position in phthalocyanine core by methine groups, the optical absorption at B band of porphyrinoid complexes is enhanced, the energy bandgap is enlarged, and the packing structure of the discotic molecules changes. By controlling the numbers of aza links at meso position, that is, the energy diagram could be tuned, resulting in the modification of the electronic properties.

Utilizing the series of phthalocyanine-tetrabenzoporphyrin hybrid macrocyles as donor molecules in an active layer of bulk-heterojunction solar cells involving with a nanoscale phase separation, which could be fabricated by wet process, the photovoltaic properties depending on the number of methine groups could be obtained. In the case of solar cells with nonperipherally substituted octahexyltetrabenzotriazaporphyrin ($C6TBTAPH_2$), the external quantum efficiency at B band and power conversion efficiency are improved comparing with those with $C6PcH_2$, which was reported previously, resulting in 53% and 5.3%, respectively. The mechanism of the photovoltaic properties is discussed by taking the molecular packing structure in bulk heterojunction film and the charge transport properties into consideration.



$C6TBTAPH_2$

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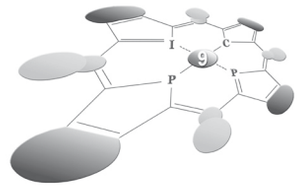

Observation of Low Energy π-π* Transitions in Oxidized Forms of Multi-Layered Phthalocyanines

Takamitsu Fukuda[a]

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The relationship between the stacked π-conjugation structures and resultant electronic structures is of great interest, since it is well known that electronic states of this type of molecules differ significantly from those of the corresponding monomer units. Since the HOMO of the typical phthalocyanine (Pc) is independent of the other MOs in energy, occupied frontier orbitals of multi-layered Pcs originating from HOMOs of the monomer units are useful probes for exploring the effect of π-stackings on their electronic structures, i.e. the splitting of the HOMO energy levels leads to a narrow energy gap between the resultant HOMO and HOMO−1 levels. Under ideal conditions and the infinite-chain limit, these HOMOs are anticipated to form the continuous band structure, while exceptionally small but discrete energy gaps between the HOMO and HOMO−1 levels are expected for multi-layered Pc complexes having finite number of Pc ligands.

We have so far successfully synthesized quadruple-decker type Pcs, $(Pc_2M)_2Cd$, by using double-decker Pc dimers (Pc_2M) as the building modules (Fig.1, left), and reported that the oxidized forms of the quadruple-decker exhibit the lowest energy π-π* transitions in the infrared region (Fig. 1, right).[1-3] Herein, we report our recent achievements for the synthesis of higher analogues of multi-layered Pcs, and discuss influence of the π-stacking on their electronic structures.

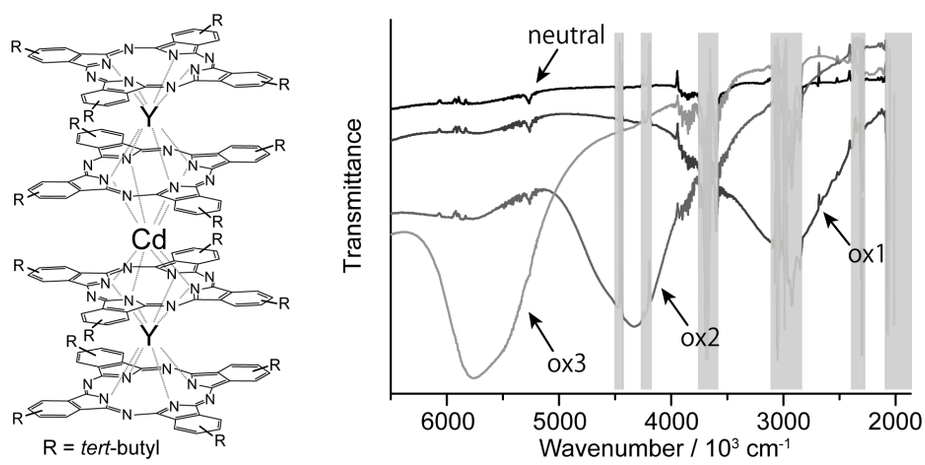

Fig 1. Structure (left) and π-π* transitions in the infrared region (right) of the oxidized forms of the quadruple-decker phthalocyanine.

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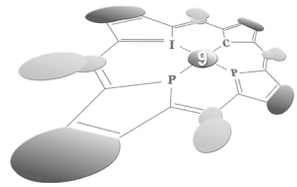

Electrocatalytic and Photocatalytic Reduction of CO_2 to CO with a Cobalt Chlorin Complex Adsorbed on Multi-Walled Carbon Nanotubes

Shunichi Fukuzumi,[a,b] **Shoko Aoi,**[c] **Kentaro Mase,**[c] **and Kei Ohkubo**[abc]

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The two-electron reduction of CO_2 to CO has merited significant interest, because CO can be converted to liquid hydrocarbon fuels with H_2 by Fischer-Tropsch processes.[1] Cobalt macrocycles are known act as good electrocatalysts for selective CO_2 reduction to CO in organic solvents.[2,3] In water, however, cobalt macrocycles have lacked selectivity for CO,[4,5] because cobalt complexes act as good catalysts for H_2 evolution.[6] We report herein selective electrocatalytic and photocatalytic reduction of CO_2 to CO using a cobalt(II) chlorin complex (Co^{II}(Ch)) adsorbed on multiwalled carbon nanotubes.[7]

The Co^{II}(Ch)-modified electrode was prepared by drop casting a sonicated acetonitirile (MeCN) solution containing Co^{II}(Ch) (1.0 mM), multi-walled carbon nanotubes (MWCNTs: 0.63 mg) as a support material and 5% Nafion (12 μL) as a proton exchange membrane and stabilization agent of Co^{II}(Ch) on MWCNTs to an glassy carbon electrode.[7] The electrocatalytic reduction of CO_2 on the glassy carbon electrode modified with Co^{II}(Ch) (0.01 μmol) adsorbed on MWCNTs (13 μg) in a CO_2-saturated aqueous solution containing Na_2SO_4 (5.0 mM) at an applied potential of -1.1 V *vs*. NHE afforded the current efficiency for CO production for the initial 2 h, which was as high as 89%, whereas that for H_2 production was 11%.[7] When MWCNTs were replaced by reduced graphene oxide (rGO), which is planar, as a support material of Co^{II}(Ch), the CO and H_2 yields became much smaller (TON = 300 for CO and 200 for H_2).[7] Thus, the three dimensional assembly of MWCNTs with Co^{II}(Ch) on the electrode surface may play an important role for the selective electrocatalytic reduction of CO_2 to CO.

Photocatalytic reduction of CO_2 and H_2O with triethylamine occurred efficiently using Co^{II}(Ch) adsorbed on MWCNTs as a CO_2 reduction catalyst and $[Ru^{II}(Me_2phen)_3]^{2+}$ (Me_2phen = 4,7-dimethyl-1,10-phenanthroline) as a photocatalyst in MeCN containing 5% (v/v) water to yield CO and H_2 with a ratio of 2.4:1 and the high turnover number of 710. The photocatalytic mechanism is clarified by examining each step of the catalytic cycle.

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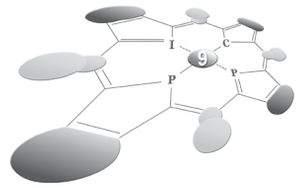

An Air-stable 19π Azaporphyrinoid Radical

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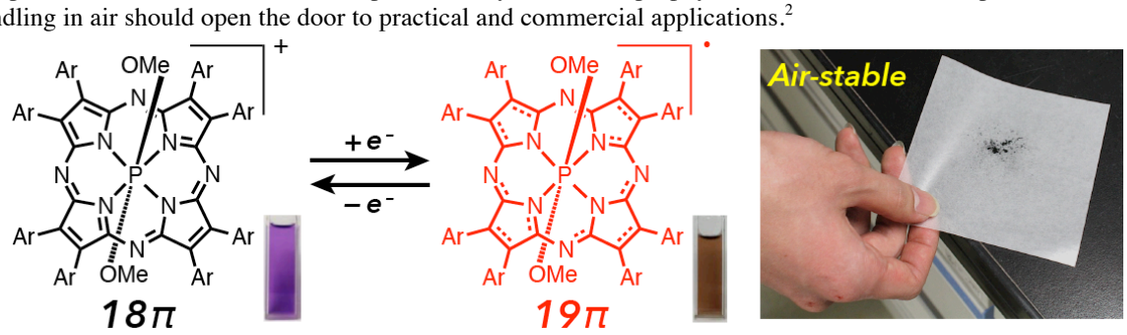
Azaporphyrin phosphorus(V) complexes show unique optical properties in spite of their simple 18π structures. The electron deficient phosphorus(V) ion is crucial for producing these properties. Recently we found that the optical properties of tetrazaporphyrin (TAP) phosphorus(V) complexes (PTAPs) had intense charge-transfer band between the Soret and Q bands.[1]

During the synthesis of PTAPs, we observed that the color of the crude solution of the octa-(*p*-tert-butylphenyl) PTAP changed from purple to brown on adding triethylamine. Finally, the brown compound was isolated as a stable solid by conventional Al_2O_3 open column chromatography with a basic eluent. The observed HR-MALDI-FT-ICR-MS spectrum and CHN elemental analysis data provided a reasonable match with a compound constituting a TAP phosphorus complex without any ion. The spectroelectrochemical switching between the original purple PTAP and the brown compound was completely reversible, supporting the premise that the brown compound is an air-stable one-electron reduced species of PTAP.

The solid state structure was unambiguously elucidated by X-ray diffraction analysis of single crystals. The EPR spectrum in degassed CH_2Cl_2 showed a singlet, characteristic of a delocalized radical having an unpaired electron (S = 1/2); no hyperfine coupling to nitrogen atoms was observed even in diluted degassed solution (as per similar $[\text{Phthalocyanine}]^{3-}$ systems). The ^{1}H VT-NMR spectrum showed broad signals at low-field, and reversible temperature dependence was also observed between 298 and 353 K.

Finally, analysis of absorption and MCD spectra, together with theoretical calculations concluded that the compound was isolable –3 TAP complex, namely, a 19π azaporphyrinoid radical. Such compounds with easy handling in air should open the door to practical and commercial applications.[2]



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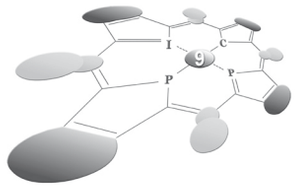

Bilin-binding photoreceptors as tools in fluorescence microscopy and optogenetics applications

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Bilin-binding photoreceptors, related either to the antenna type of cyanobacterial light harvesting systems or to phytochrome proteins, serve dual purpose in modern microscopic and optogenetics applications. Those proteins originating from the light-harvesting system (phycobilisomes) can be used as strongly fluorescent tags to follow in a time- and space determined manner physiological processes in living cells,[1] whereas the phytochrome-related proteins allow regulation of enzyme activities by selective irradiation.[2] Phycobiliproteins being normally membrane associated or –embedded proteins have been modified into soluble component of small size, ideally suited for protein tagging.[3] This presentation addresses preferentially phytochrome.related proteins. Most promising representatives of this protein class are the GAF domains of cyanobacteriochromes (CBCRs) that are found with absorbances virtually over the entire visible spectral range and even expanding into the near-UV and near-infrared range. GAF domains of CBCRs show photochromicity between their parental and photoproduct (=signaling) states. As signaling in many phytochrome(-related) proteins is accomplished through an up- or down-regulated enzyme activity, these proteins provide the potential to interfere with metabolic processes in a non-invasive manner, simply by wavelength-selective irradiation. Especially the phytochrome-related proteins share a structural motif that make them ideal targets to generate modified proteins: the light-sensing and the signaling functions are often located in separate domains of these proteins, being linked to each other through a structurally highly conserved coiled-coil motif. Such linker module now allows generation of proteins carrying a combination of sensing and signaling domains that do not exist (or have not been found so far) in nature.
An overview on structural and functional properties of CBCR-GAF domains is given together with applications of these proteins in living cells.

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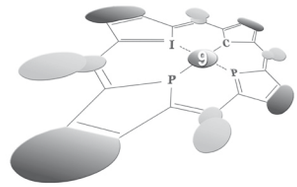

'*Totem*' C2-Symmetrical Iron(III) Porphyrin Complexes to Stereoselectively Promote Alkene Cyclopropanation

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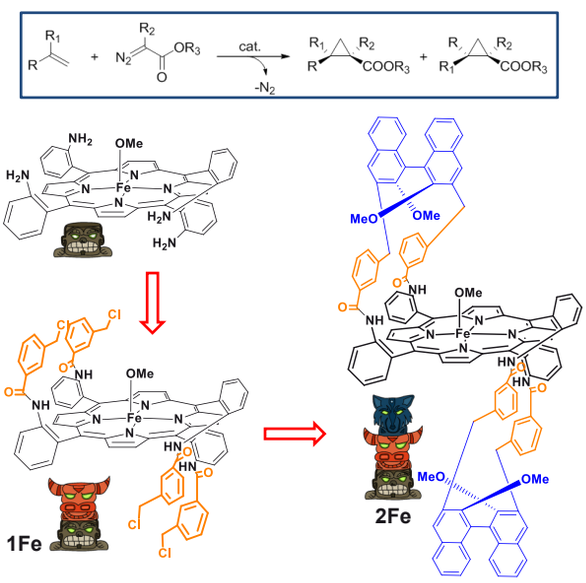
The stereoselective synthesis of cyclopropanes is an important issue in synthetic chemistry due to the relevance of the three-member carbon rings which often represent the active part in biological and/or pharmaceutical compounds.[1] The one pot reaction of diazo compounds with alkenes represents a sustainable methodology to achieve cyclopropanes due to the formation of N_2 as the only stoichiometric by-product. The reaction is efficiently catalysed by metal porphyrins which promote the synthesis of cyclopropanes with excellent diastereo- and enantioselectivities.[2] Considering the importance in developing eco-friendly catalytic procedures, we are currently studying the catalytic activity of iron porphyrins which display a cheap, efficient and low toxic metal centre.

The two iron complexes **1Fe** and **2Fe** are good catalysts for the alkene cyclopropanation, both of which have a C_2 axis within the porphyrin plane and exhibit an open space on each side for the substrate access. Complex **1Fe** displays a pre-organized structure responsible for excellent *trans*-diastereoselectivities (94-99%) in alkene cyclopropanations while the presence of chiral moieties in **2Fe** allowed to perform the reactions also with very good enantioselectivity (up to 87%).[3]

Experimental data disclosed that each '*totem*' portion of **2Fe** has a specific catalytic role: i) the porphyrin core containing the active iron centre is in charge of activating the diazo compound; ii) benzylic moieties are responsible for the reaction diasteroselectivity and iii) the two chiral binaphthyl groups allow the enantioselective synthesis of cyclopropanes. The study of the reaction scope revealed that both **1Fe** and **2Fe** catalysts were active in promoting the cyclopropanation of several olefins by differently substituted diazo compounds.



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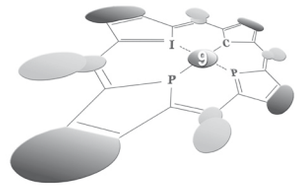
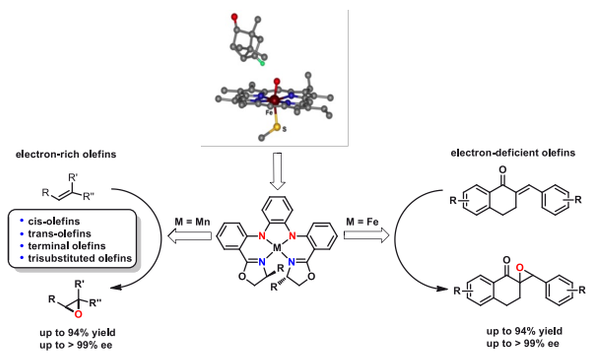


Design and Application of porphyrin-inspired ligands in asymmetric epoxidaion of olefins

Wen Dai,Shuang Gao*

Dalian Institute of Chemical Physics, the Chinese Academy of Sciences

The past decades have witnessed rapid progress in the asymmetric epoxidation of olefins with chiral organocatalysts[1] and metal-based catalysts.[2] In line with toughening environmental concerns, current challenges for asymmetric epoxidation lays in exploring more sustainable and efficient catalyst system. Consequently, the development of catalytic systems with high conversion and selectivity that utilize a readily available, cheap and non-toxic catalyst and environmentally benign oxidants is strongly desired. Inspired by the cytochrome P450 enzyme, substantial efforts have been focused on the development of asymmetric epoxidation methods based on metalloporphyrins which are the mimics of the cytochrome P450 active site.[3] However, no general approaches have been reported due to the challenges associated with the synthesis of chiral porphyrins and the environmentally unfriendly oxidant. With this background in mind, we have developed a new type of porphyrin-inspired N_4 ligands that fulfilled the structural requirements of the porphyrin ligand in some way. The porphyrin-inspired ligands have been successfully applied in the manganese-catalyzed asymmetric epoxidation of a variety of electron-rich cis-, trans-, terminal and trisubstituted olefins (up to 94% yield, >99% ee). To further extend the application of our strategy, we have also developed a highly enantioselective asymmetric epoxidation catalyst for electron-deficient olefins exploring the iron in combination with the porphyrin-inspired ligands (up to 94% yield, 99% ee) (Scheme 1).



Scheme 1. Strategy for the development of asymmetric epoxidation. page.

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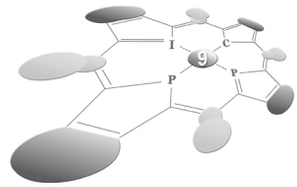

Photosensitizer-Modified Cellulose and Polyacrylonitrile Fibers as Anti-infective Materials

Reza A. Ghiladi[a], **Bradley L. Carpenter, and Sarah L. Stanley**

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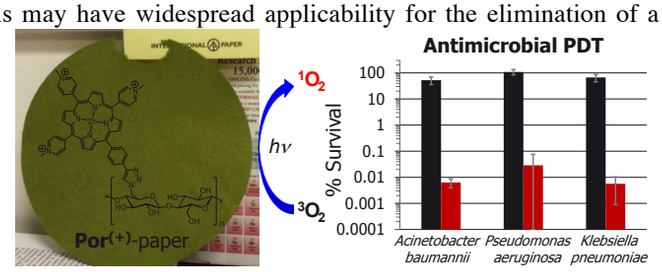
The transmission of pathogenic bacteria and fungi that adhere to surfaces poses an escalating threat to human health. Towards our overall objectives of developing potent antimicrobial materials to combat this threat, we have recently developed two innovative photoactive materials in which a porphyrin-based photosensitizer [Por$^{(+)}$] has been tethered to either cellulose nanocrystals[1] or cellulose fibers[2]. The cellulose nanocrystal-porphyrin materials were shown to be highly effective in the photodynamic eradication of a broad spectrum of bacteria, including eliminating 99.5+% of *Pseudomonas aeruginosa*, and upwards of 99.9999+% of multiple-drug-resistant *Acinetobacter baumannii* (MDRAB), *Staphylococcus aureus*, and MRSA after treatment with only 30 minutes of visible light. In other words, for MDRAB, *Staphylococcus aureus* and MRSA, if 100 million cells were present at the start, then fewer than 100 remained viable after 30 minutes of light exposure. The cellulose-porphyrin fibers, when pressed into sheets (see figure), were also found to be highly effective: *S. aureus*, *A. baumannii*, *P. aeruginosa* and *K. pneumonia* all exhibited inactivation by 99.99+%, as well as inactivation of dengue-1 virus (>99.995%), influenza A (~99.5%), and human adenovirus-5 (~99%). As an alternative strategy, we have also embedded the cationic porphyrin Por$^{(+)}$ into polyacrylonitrile nanofibers using electrospinning, and demonstrated that this non-covalent approach is also highly effective at mediating both antibacterial and antiviral activities via a photodynamic mechanism. As such, these materials may have widespread applicability for the elimination of a wide range of pathogens prior to infection. Thus, further research into alternative materials such as photosensitizer-cellulose conjugates may lead to their application in hospitals and healthcare-related industries wherein novel materials with the capability of reducing the rates of transmission of a wide range of bacteria and fungi, particularly antibiotic resistant strains, are desired.



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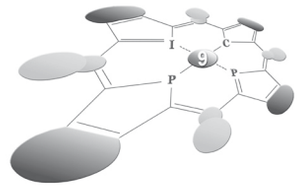

Comparative studies of 4d and 5d metallocorroles: New $Tc^{V}O$ and $Ru^{VI}N$ corroles

Abhik Ghosh,[a] Rune F. Einrem,[a] Abraham B. Alemayehu,[a] Hugo Vazquez-Lima,[a] Henrik Braband,[b] Roger Alberto[b]

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The insertion of large 4d and 5d transition metal ions into the sterically constrained central cavity of corroles is typically a considerable synthetic challenge, requiring careful optimization of reaction conditions. In this talk, we shall our describe our ongoing efforts to synthesize technetium(V)-oxo and ruthenium(VI)-nitrido corroles, the 4d analogues of the $Re^{V}O$ and $Os^{VI}N$ complexes recently reported from our laboratory. These studies allowed for some of the first detailed comparisons of 4d and 5d metallocorroles, affording key insights into the role of relativistic effects in shaping the spectroscopic and electrochemical properties of porphyrin-type complexes.

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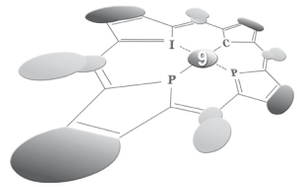

The effect of metal on the sonodynamic activity of cationic water-soluble porphyrin complexes

Francesca Giuntini[a], **Loredana Serpe**[b], **Ivana Fenoglio**[c], **Gianni Durando**[d], **Roberto Canaparo**[b]

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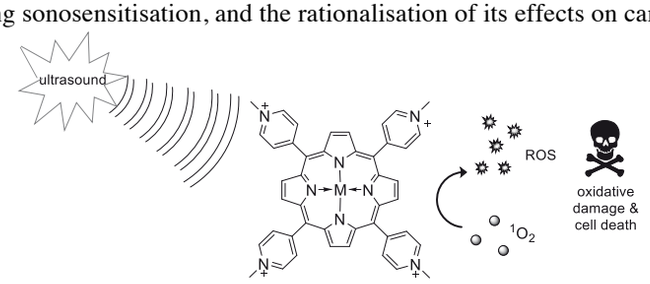
Sonodynamic therapy (SDT) is a therapeutic approach in which ultrasound irradiation is used to promote the generation of cytotoxic species *via* the excitation of particular chemical compounds (sonosensitizers). Similarly to photodynamic therapy (PDT), two individually non-toxic components initiate a process that culminates in the generation of reactive oxygen species (ROS), including radicals (hydroxy-, alkoxy- and peroxy-radicals) and singlet oxygen, causing rapid intracellular damages and leading to cell death *via* apoptosis and/or necrosis and/or autophagy.[1] The potential of this approach for the reduction of solid tumours has been shown, and its efficacy has been demonstrated at the preclinical level on some experimental tumour models.[2] A crucial difference between PDT and SDT arises from the different power of penetration of the activating radiation: while light has a relatively limited reach within tissue, ultrasound easily propagates through it, allowing the targeting of more deeply-seated lesions without the need of invasive devices such as implanted fibre-optics.[3] Despite these promising characteristics, the scarce reproducibility of the treatment outcomes and the poor correlation between the *in vitro* and the *in vivo* results hampered the development of a robust treatment protocol, preventing this approach from reaching clinical applications. Overcoming these disadvantages will require the elucidation of the molecular bases underlying sonosensitisation, and the rationalisation of its effects on cancer tissues.



M = $2H^+$, Zn^{2+}, Ni^{2+}, Pd^{2+}, Fe^{2+}

With this in mind, we undertook a study aimed at elucidating the effects of the presence and nature of the metal ion on the sonodynamic activity of a series of water-soluble porphyrin complexes. We will present the preliminary results of our investigation, concerning, in particular, the characterisation of the ROS produced by the complexes under sonication and the preliminary results of sonocytotoxicity on HT-29 cells.

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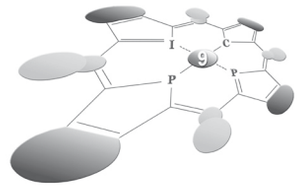

Insights into Structure and Mechanism of Cytochrome *c* Oxidase from Computer Simulations

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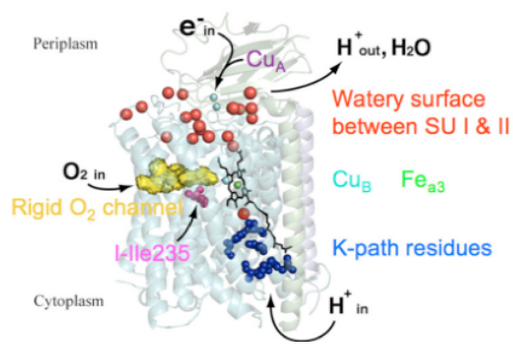
Cytochrome *c* oxidase (CcO) is the last enzyme in the respiratory electron transport chains of mitochondria and many aerobic bacteria. [1] Its function is to catalyze the reduction of molecular oxygen to water and utilize the resultant energy to pump protons across the inner mitochondrial or bacterial cytoplasmic membrane, forming an electrochemical potential that is utilized by the cell in numerous ways, most prominently for the synthesis of ATP. [2] The catalytic proton pumping cycle of CcO is driven by redox events, molecular oxygen binding, and O_2 activation in the dinuclear heme Fe_{a3}–Cu_B complex (DNC). We employ classical molecular dynamics (MD) simulations of the entire enzyme embedded in its membrane and density functional theory (DFT) calculations of large DNC cluster models to explore this redox-coupled proton transport mechanism. [3,4] Our focus is on B-type CcO from *Thermus thermophilus*, where X-ray structures and high quality spectroscopic and kinetic data are available. In this talk I will highlight DFT results for vibrational spectra and Mössbauer parameters that give insight into the spin and coordination states of the intermediates of the reaction cycle. In combination with experimental Mössbauer data [5] we were able, for instance, to determine the spin states of Fe_{a3} and Cu_B as well as the identity of the oxygen species in the DNC of CcO crystal structures in the reduced state and the oxidized state. [6]



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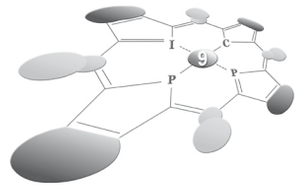

Using All the Isotopes of Hydrogen to Probe Mechanisms of Coenzyme B_{12}-dependent Radical Enzymes

Bernard T Golding

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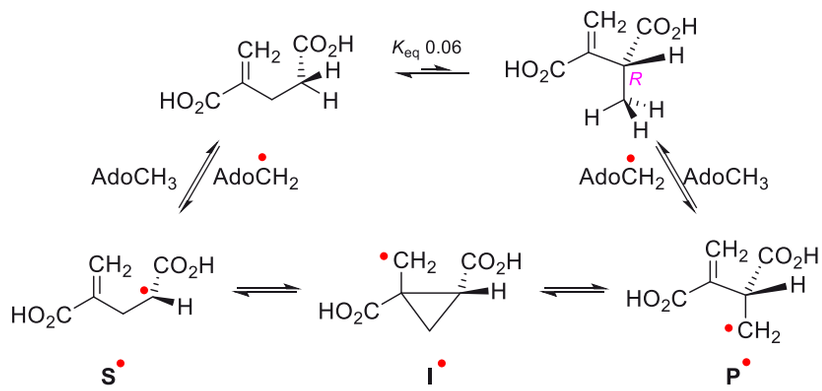
By substituting two hydrogen atoms in a methyl group with deuterium and tritium, a so-called chiral methyl group is generated. Methyl groups are ubiquitous in organic compounds ranging from simple hydrocarbons to complex antibiotics and vitamins. The action of enzymes on organic compounds, such as occurs for example in human metabolism, often involves initial attack on a methyl group. The chiral methyl group is a useful probe that enables the identification of intermediate radicals in enzymatic reactions at methyl groups, e.g. metabolism of toluene.[1] Radical enzymes catalyse reactions in which species with an odd number of electrons, classically described as 'free radicals', participate.[2] 2-Methyleneglutarate mutase is a coenzyme B_{12}-dependent radical enzyme isolated from *Eubacterium barkeri* that catalyses the equilibration of 2-methyleneglutarate ('substrate SH') with (*R*)-3-methylitaconate ('product PH'). Several mechanisms have been considered for the SH → PH conversion: organocobalt intermediates, carbocations, carbanions and radicals. Experimental and theoretical model studies, evidence from EPR spectroscopy and isotopic labelling support a mechanism via intermediate radicals (S•, I• and P•). The adenosyl radical ($AdoCH_2$•) from homolysis of the Co-C σ-bond of coenzyme B_{12} activates the substrate to S•, which is converted into product via an intermediate cyclopropylcarbinyl radical (I•) and P•:



The lecture will describe how a chiral methyl experiment validated this mechanism via a cyclopropylcarbinyl intermediate. This study is an exemplar for other coenzyme B_{12}-dependent mutases, the current mechanistic status of which will be critically assessed.

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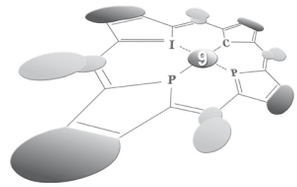

Polar Self-assembled Subphthalocyanine Materials

David González-Rodríguez,[a] Julia Guilleme,[a] Tomás Torres[a] and Maria Jose Mayoral[a]

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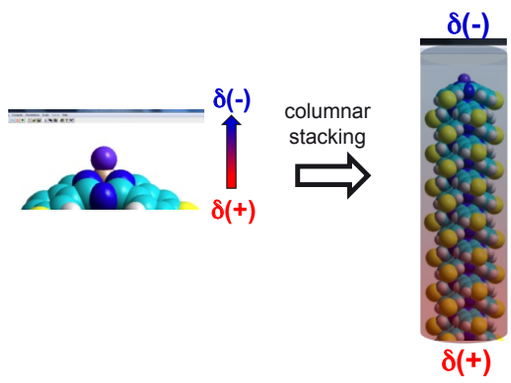
Subphthalocyanines (SubPcs)[1] are singular cone-shaped molecules with unique physicochemical properties that render them promising light-harvesting and/or donor units for photovoltaic and light-emitting applications. We were very interested in studying if such non-planar molecules with axial dipole moments could be self-assembled in columnar stacks, both in solution[2] and liquid-crystalline phases,[3,4] by hydrogen-bonding and π–π stacking interactions. The columnar aggregation of these molecules led to supramolecular chiral nanofibers and condensed phases that can be aligned in the presence of electric fields, yielding nanomaterials with permanent polarization and unusual ferroelectric and semiconducting properties.



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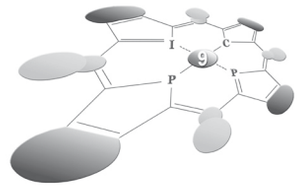

Effect of Heme Oxidation and Coordination State on the Conformational of P450cam Reaction Intermediates

David B. Goodin[a], Shu-hao Liou[a], Xiaoxiao Shi[a], Mavish Mahomed[a], Xu Cheng[a], William K. Myers[b] and R. David Britt[a]

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Recent evidence has suggested the peroxy-bond cleavage to form the reactive Compound I intermediate in P450cam occurs during a conformational shift of the enzyme from the closed to the open conformation. This transformation appears to be triggered in part by binding of putidaredoxin (pdx) to the enzyme and in part due to the change in oxidation/coordination state of the heme as it is reduced and proceeds through oxy- and hydroperoxo- bound states. Our results using X-ray crystallography [1,2] and Double Electron-Electron Resonance (DEER) [3,4] of spin-labeled forms of P450cam and pdx have allowed us to monitor these changes both in the crystal and solution states. We will discuss recent experiments that show that the conformation of P450cam upon binding putidaredoxin is dependent on the redox and/or coordination state of the system. This result offers a new understanding of the way in which pdx serves as a functional effector by triggering specific conformational changes required for peroxy bond cleavage and for product release in the enzyme cycle. In the oxidized state of the P450cam/pdx complex, the enzyme is in the open conformation, which converts to the closed conformation when reduced pdx binds to the enzyme in the ferrous/CO complex. In addition we will present data on samples in the ferrous-oxy intermediate to test ideas about the transmission of an effector signal from the proximal to distal heme face during Compound I formation.

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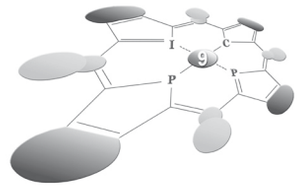

The Crucial Role of Self-Assembling in Nonlinear Optical Properties of Substituted Phthalocyanines

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Synthesis of compounds with nonlinear optical properties (NLO) is related to the search for the systems that limit the intensity of laser irradiation in nanoseconds and shorter time and thereby protect photosensitive devices and the eye from strong radiation. Among organic components of NLO materials, phthalocyanines (Pc) constitute one of the most attractive classes of photosensitizers. Variation of substituents at the periphery of the Pc macrocycle, as well as the metal ion in its cavity and axial ligands, results in the appearance of a huge family of compounds, affording thereby fine tuning of required physicochemical characteristics.

This report will demonstrate the possibilities of tuning NLO properties by means of supramolecular assembly of Pc molecules leading to extended aggregates. This effect appears both in solutions of aggregated Pc's and in films obtained by various techniques. Among the substituted phthalocyanines, crown-ether derivatives are very promising building blocks for assembly of molecules into cofacial and brick-wall supramolecular structures. It was found that the nonlinear response arises in solution and polymeric composites of crown-ether substituted phthalocyanines only after formation of supramolecular ensembles.[1-4] Such ensembles can be prepared through dissolution of molecular metallophthalocyanines in tetrachloroethane and subsequent treatment via multiple cycles of heating to 90□C and slow cooling to room temperature.

The z-scan method in femtosecond and nanosecond regimes was used for measuring nonlinear optical properties of phthalocyaninato In(III), Ga(III), Y(III) and Ru(II) in TCE solutions and polymer films. From the one side it was established that effect of heavy metal is basic factor which determines the quantum yield, photorefractive amplification of laser object beam, dielectric susceptibility of third order and nonlinear optical properties of metallophthalocyanines. At the same time, it was found that the nonlinear response of composites arises only after cyclic thermal treatment of the solution in tetrachloethane and storage up to 48 h. It has been demonstrated that the numerous weak contacts (CH…π, CH…N, CH…O, CH…Cl) in phthalocyanine lattice are responsible for the formation of nanoparticles in high-boiling solvents, as well as in polymeric films. Anisotropy of optical properties of these compounds is determined by architecture of ensembles and nanoparticles, whose size and geometry depend on the number and duration of heating/cooling cycles as well as aging time. Hence, it confirms that self-assembling has essential effect on the NLO behavior of the Pc polymeric composites.

It is expected that the developed methodology, can be used for preparation of novel efficient optical limiters starting from other substituted phthalocyaninates.

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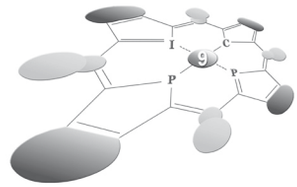

Functionalized Fluorinated Phthalocyanines

Hemantbhai H. Patel and Sergiu M. Gorun

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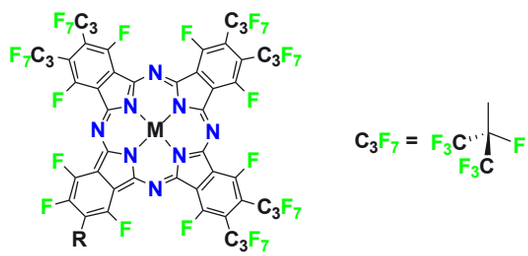
400 South Orange Ave., South Orange, NJ 07079, USA

Oxidation catalysts based on organic molecules are unstable due to the presence of labile C-H bonds. Replacing all C-H bonds of phthalocyanine by a combination of fluoro- and perfluoro-groups results in robust photochemical and chemical aerobic oxidation catalysts.
The inert C-F bonds, however, preclude the attachment of the organic scaffold to solid-state supports, except via weak van der Waals bonds, hindering the utilization of the heterogenized catalysts in solution and in the presence of organic reagents and products due to leaching of the phthalocyanine.
We report the synthesis of functionalized fluoro-phthalocyanines via grafting of functional basic groups, namely -NRR' (R, R' = H/CH_3).



R = -NH_2, -NHMe, -NMe_2; M = Co, Zn

The amino functionalized complexes retain their chemical oxidation catalytic activity of thiols to disulfides both in homogeneous solution, as well as when supported. No catalyst leaching was detected.

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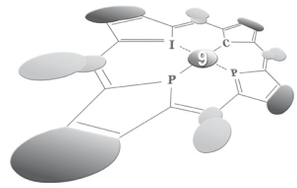

Selected Sulfur and Nitrogen Porphyrazines: from Synthesis to Physico-Chemical Properties and Biological Activity

Tomasz Goslinski

Department of Chemical Technology of Drugs, Poznan University of Medical Sciences, Grunwaldzka 6, 60-780 Poznań, Poland

Peripherally functionalized porphyrazines (Pzs) are compounds of potential applications in technology and medicine, especially photodynamic therapy, photodynamic antimicrobial therapy and photodynamic diagnosis. In recent years Pzs have been modified in the coordination center with metal cations and substituted in the periphery with groups containing hydrocarbons, halogens, oxygen, nitrogen, sulfur, oxygen and others [1,2].
In our research we focused on the following aspects of Pzs: (*i*) synthesis and physico-chemical properties of Pzs functionalized in the periphery with various pyrrolyl groups [3], (*ii*) synthesis and biological properties of diazepine annulated Pzs with nanomolar photocytotoxicity against oral cancer cells [4], (*iii*) studies on porphyrazine – nitroimidazole conjugates, (*iv*) synthesis and spectroscopic properties of sulfanyl Pzs of which some revealed moderate photocytotoxicity towards oral cancer cells, (*v*) research on hyperbranched dendrimeric sulfanyl Pzs and tribenzoporphyrazines with well-defined particle size and shape of potential applications in medicine and technology.
This study was supported by the National Science Centre under grant No 2012/05/E/NZ7/01204.

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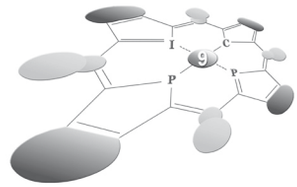

Manipulation of single porphyrin and porphycene molecules: Every atom counts

Leonhard Grill[a]

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The control of functional molecules on surfaces is a key challenge in nanotechnology. Molecular switches are a special class of functional molecules which are of interest in various fields from molecular electronics to molecular machines. Such molecules are characterized by at least two stable states, with different physical or chemical properties, that can be achieved reversibly by an external stimulus. Porphyrin and porphycene molecules can be considered as molecular switches since the hydrogen atoms in their cavity can move from one side to another in tautomerization processes. In this presentation, various recent examples of such molecules, studied by scanning tunneling microscopy (STM) under ultrahigh vacuum conditions, will be discussed.

An important issue for any functional molecule is the role of the direct environment for the molecular function. In a combination of tunneling spectroscopy and single-molecule manipulation, we could reveal how the characteristic appearance of single porphyrin molecules on a metal surface can be influenced by single metal atoms underneath their cavity [1]. Furthermore, we have studied the atomic scale surroundings of individual porphycene molecules and found that chemical processes within individual molecular can be controlled by single atoms. The rate of an intramolecular hydrogen transfer reaction [2] can be tuned up and down by only one single atom in the vicinity of the molecule [3]. The same effect is then extended to molecular assemblies where cooperative effects in single molecules are directly observed. On the other hand, it has been found that the hot carriers underneath the porphycene molecules can travel along the metallic surface and induce the tautomerization process remotely [4]. These different aspects of single porphyrin and porphycene molecules will be discussed together with more recent results that focus on the local environment.

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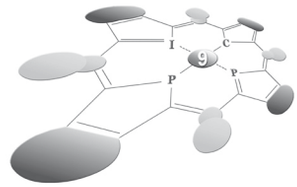

BODIPY-porphyrin and corrole dyads and polyads. Synthesis and antenna effects

C. P. Gros,[a] L. Bucher,[a,b] N. Desbois,[a] P. D. Harvey[b]

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BODIPYs (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene) and porphyrins are versatile organic dyes that can easily be functionalized to fine-tune their rich redox and optical properties (e.g. high extinction coefficient >80,000 $M^{-1}.cm^{-1}$ and high fluorescence quantum yield). When substituents yielding additional conjugation are added to the parent molecules, both the absorption and emission spectra of the resulting derivatives can shift to significantly longer wavelengths, with emission maxima greater than 750 nm. Red, green and blue BODIPY derivatives covering the entire range of the visible spectrum have already been reported in the literature as well as aza-BODIPYs. It includes fluorescent conjugates of a variety of antibodies, peptides, proteins, tracers, and amplification substrates optimized for cellular labeling, imaging and detection.
Different BODIPY and Aza-BODIPY-porphyrin dyads and polyads diversely substituted have been prepared (see some examples in Figure 1) as functional models of the photosynthetic center. We will discuss their synthesis and their photophysical properties. Interestingly, in some cases, an efficient energy transfer from the photoexcited singlet zinc porphyrin to the π-conjugated BODIPY moiety of the composites occurred in opposite direction.

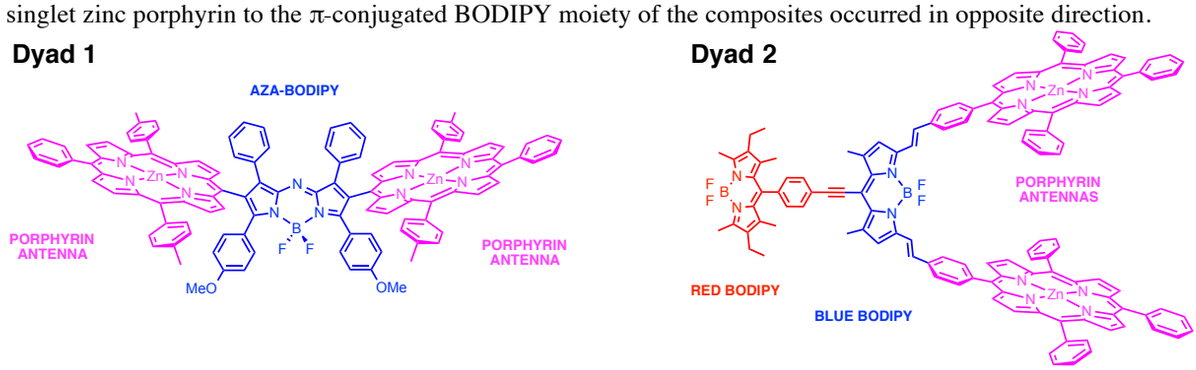

Figure 1: examples of BODIPY-dyads

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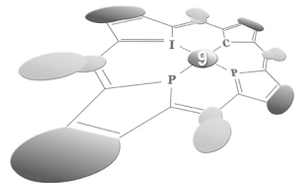

Tumor detection and elimination by targeted corrole metal complexes

Zeev Gross,[a] Jae Y. Hwang,[b] Lali K. Medina-Kauwe,[b] Ruijie D. Teo,[c] Harry B. Gray,[c] Punna Lim,[d] John Termini,[d] Matan Soll,[a] and Atif Mahammed[a]

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The first disclosure of corroles as anticancer agents appeared one year after the 1999 discovery of their first facile synthesis.[1] Large advances in understanding the fundamental coordination chemistry and other unique properties of corroles allowed for the significant breakthroughs in which the corresponding metal complexes were utilized instead of the initially used free-base derivatives.[2] The main focus was on post-transition metal complexes chelated by corroles that are substituted by two water-solubilizing sulfonic acid head groups on one pole of the macrocycle.[3] These derivatives have been used for both bioimaging (of cells, organs, and tumors) and cell killing; and their cellular penetration was found to be assisted by either native or specifically designed proteins to which they strongly bind.[4] The latter feature was used for selective targeting of tumors and even for specific types thereof;[5] and the already very large dark toxicity could be further increased via photoexcitation.[6]
Parallel efforts that were devoted to non-targeted metallocorroles uncovered many aspects regarding their mode of action, such as the late M phase arrest in several different cancer cell lines.[7] Another important outcome was the conclusion that gold corroles are more cytotoxic than all other previously investigated metal complexes.[8] *The contemporary research focuses on establishing the structure/reactivity profile for metallocorroles and on new tumor targeting approaches.*

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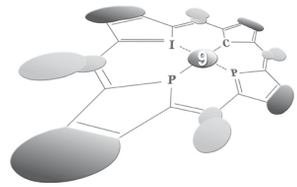
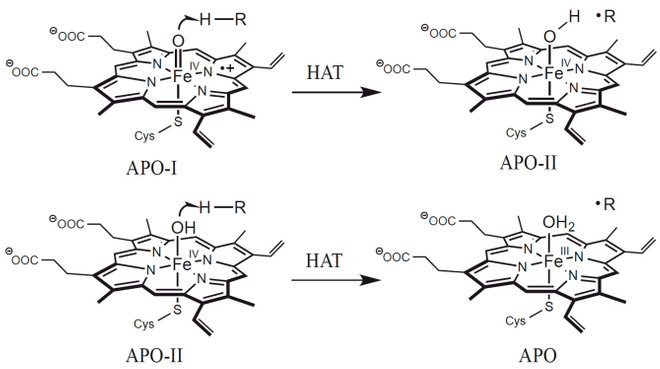


Exploring the reactivity of heme-thiolate oxygenases and peroxygenases – P450 vs APO

John T. Groves, Xiaoshi Wang, Christin B. Monroe and Kevin J. Speina

Department of Chemistry, Princeton University, Princeton, NJ 08544 USA

Known heme-thiolate proteins include cytochrome P450, nitric oxide synthase and chloroperoxidase. Recently, a new family of fungal heme-thiolate peroxygenases have been discovered. These proteins are novel biocatalysts that are capable of catalyzing the oxygenation of a variety of substrates using H_2O_2. Drug molecules are readily transformed into typical P450-type metabolites. We have found that the peroxygenase APO secreted by *Agrocybe aegerita* catalyzes the H_2O_2-dependent hydroxylation of simple alkanes and other organic substrates with high efficiency. Iron(IV) intermediates, compound I and compound II, of APO have been spectroscopically observed and kinetically characterized. The pK_a of compound II [Cys-S Fe(IV)-OH] has been determined by a novel reductive technique. The reduction potential and the O-H bond dissociation energy of Fe(IV)-OH have also been determined, thus accessing the reduction potential of compound I as well. APO-II is shown to have surprisingly high reactivity toward C-H and phenolic O-H hydrogen atom abstraction. The mechanism of C-H hydroxylation by APO will be compared and contrasted to those of other heme proteins and model porphyrin systems. Supported by the National Institutes of Health (2R37 GM036298-30).



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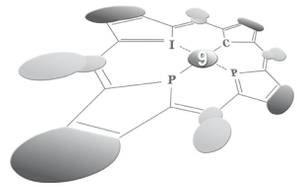

Exciton diffusion, singlet fission and photochemical upconversion in aromatic molecular crystals

Ferdinand C. Grozema[a], **Kevin Felter**[a], **Yaroslav A. Aulin**[a], **Maria C. Fravventura**[a], **Tom J. Savenije**[a]

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Perylene diimides (PDI) and phthaloncyanines (PC) are interesting materials that have favourable properties that make them suitable candidates for application in organic electronic devices. The properties of PDIs and PCs are complementary, which makes a combination of the two especially interesting. PDIs generally absorb between 400 and 600 nm and are very good electron acceptor, while PCs absorb at wavelengths longer than 600 nm and shorter than 400 nm with a gap in between and are very good electron donors. Interestingly, the electronic properties of solid state materials based on these molecules strongly depend on the way the molecules are organized in the crystalline state. This is true for the optical properties, but also for transport of charges, excited state diffusion and for less common photophysical processes such as singlet exciton fission.

In the work discussed here, we have characterized the photophysical properties of crystalline PDI derivative, in combination with PCs. Exciton diffusion is studied by unique time-resolved microwave conductivity measurements, which reveal that the exciton diffusion length in PDIs strongly depends on the crystal structure, which in turn is dictated by the substitution on the imid nitrogen. For the best PDIs values over 50 nm are reported.

In the same crystalline PDIs we have studied the occurrence of singlet exciton fission, which is a process by which a singlet excited state transforms into a combination of two triplet states that have roughly half of the energy of the initial singlet. An interesting aspect of singlet fission is that it is spin-allowed and therefore can be very fast. This process is particularly interesting for organic photovoltaics since it can potentially increase the efficiency with which high-energy photons are used in such devices. We have studied the formation of triplet in crystalline PDI film using fs-pump-probe transient absorption spectroscopy. Using these measurements, the formation of triplet excited states is shown to occur on a sub-picosecond times. This is much faster than can be expected for for instance intersystem crossing and the process is therefore attributed to fission. This is confirmed by estimating the yield of triplets per absorbed photon which is found to be close to 200%. We have investigated the dependence on the crystal structure.

Finally, in crystalline bilayers of PDIs with a PC derivative we have studied the upconversion of low energy photons followed by direct injection into TiO2. The upconversion involves the absorption of a low energy photon by PC, leading to an excited state that has too little energy to inject into a TiO2 substrate. This singlet state is rapidly transformed to a triplet state that subsequently transfers to PDI. This leads to a build-up of triplets in PDI where triplet-triplet annihilation can occur, resulting in the formation of a singlet state with higher energy than the original initial singlet state. This newly formed singlet has sufficient energy to inject into TiO2. This overall process is very interesting to improve the efficiency with which low energy photons are used in organic solar cells

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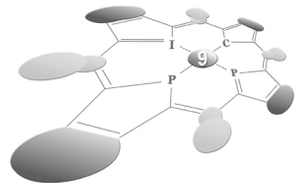

Self-assembling corroles

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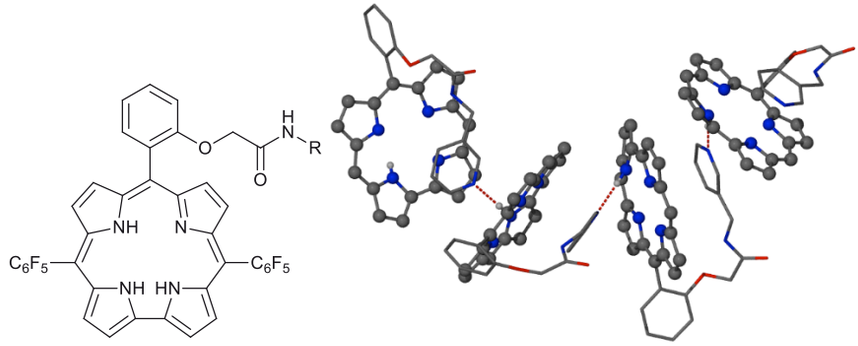
Trans-A_2B-Corroles[1,2] bearing $-OCH_2CONHR$ substituents at *ortho* position of the *meso*-phenyl substituent, undergo self-organization both in the solid state as well as in solution. The lack of additional donor atoms induces sheet formation, but if the pyridine unit is present in the structure, more complex helical forms are formed. The character of the internal NH at the corroles's core (serving as the hydrogen bond donor) is directly responsible for the strong self-organizing properties of these compounds. When combined with the special nature of the –CONH– group, these donating properties lead to the formation of aggregates in the solid state. In solution, UV-vis absorption and fluorescence analyses revealed the formation of large aggregates in methanol/water mixtures at a critical water percentage of about 40-50%. The formation of strong intermolecular hydrogen bonds is clearly visible in crystallographic structures as well as in ^{1}H NMR spectra as strong upfield shifts of the amide-arm signals.[3] The nature of hydrogen-bonded assembly can be regulated *via* the presence of an additional hydrogen-bond acceptor at the amide arm, opening interesting perspectives for the applications for the reported corroles.



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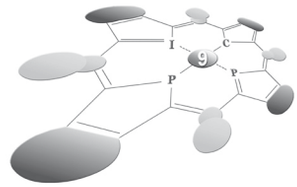

Porphyrins as Photocatalysts for Visible-Light induced Functionalizations of Aldehydes

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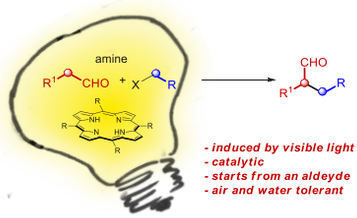
Porphyrins are natural functional dyes. They are utilized by Nature as prosthetic groups of various enzymes not *per se* because of their coordination characteristic, but due to the combination of other properties with absorption of light (which translates to color) being the most important.

Light is not only a cheap but a very powerful source of energy, a fact nature has exploited since the beginning.[1] Nowadays there are only few industrial, light induced processes.[2] However, organic chemists have only recently started to realize the potential of light induced transformations in effective photocycloadditions, rearrangements, cyclisation, alkylation, photooxidation, and photooxygenation reactions being already developed.[3]

Visible-light induced selective functionalization of aldehydes represents a significant challenge in organic synthesis. To date, only few photochemical transformations were accomplished: alkylation, arylation with ruthenium and iridium complexes.[4] This approach was subsequently advanced by Zeitler[5] and Melchiorre[6] who showed that organic dyes are also efficient photoredox catalysts for this reaction and what is more, in certain cases no photoredox catalyst is required. We wondered whether simple porphyrins could be used as photocatalyst. By being easily modified they give easy access to chiral catalysts. Herein, we demonstrate a successful application of these compounds as photocatalysts for visible-light induced hydroxylation and alkylation of aldehydes at the α-position. Reactions employ a dualcatalysis – merging photocatalysis with enamine-iminium catalysis.



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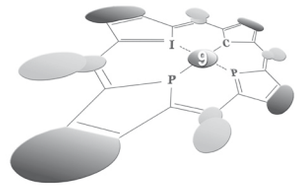

Integrating Porphyrins / Phthalocyanines and Nanocarbons into Novel Optoelectronic Materials

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Carbon is the key to many technological applications that have become indispensable in our daily life. Altering the periodic binding motifs in networks of sp^3-, sp^2-, and sp-hybridized C-atoms is the conceptual starting point for a wide palette of carbon allotropes. To this end, the past two decades have served as a test-bed for measuring the physico-chemical properties of low-dimensional carbon with the advent of fullerenes (0D), followed in chronological order by carbon nanotubes (1D), carbon nanohorns, and, most recently, by graphene (2D). These species are now poised for use in wide-ranging applications. Expanding global needs for energy have led to a significant effort to develop alternatives to fossil fuels. While alternative sources for energy are already in use, they comprise a small percentage of the energy demands needed to carry us through the 21st century. No single source will solve the global needs, but the development of photovoltaics has vast potential as a point-of-use power source.

I report on our efforts regarding a unifying strategy to use the unprecedented charge transfer chemistry of 0D fullerenes, the ballistic conductance of 1D carbon nanotubes, and the high mobility of charge carriers in 2D graphene, together in a groundbreaking approach to solving a far-reaching challenge, that is, the efficient use of the abundant light energy around us. For example, hybrid photoelectrochemical efforts with a percolation network of photon absorbers coupled to an electron/hole transporter in combination with advanced photon management are the ideal design for realizing breakthroughs in high photon conversion efficiencies suitable for the catalysis of water.

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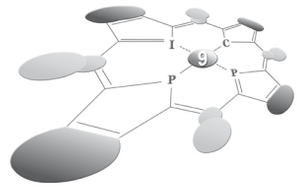

Bridged Bis-BODIPYs: Synthesis & Studies

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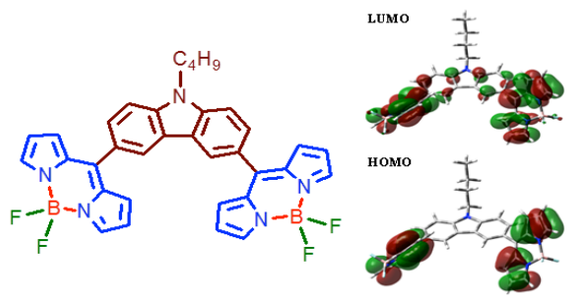
The boron dipyrromethenes (BODIPYs) are well known class of highly emissive molecules having variety of biological applications, e.g. biochemical labelling, photosensitizers for PDT (Photo Dynamic Therapy).[1] The electronic and photophysical properties of BODIPYs can be fine-tuned for different applications by structural modification of boron-dipyrrin core or by making their dimers and oligomers.[2] The Stokes shifts of BODIPYs can be increased by substituting the core with electron rich moieties.[3] The artificial BODIPY dimers have increased Stokes Shifts, broad absorption and red shifted emission for efficient light harvesting ability for solar cells and biological applications. Our group at IIT Gandhinagar is involved in the chemistry of BODIPY derivatives,[4] D-π-A type corroles and aza-BODIPYs. Here we present the synthesis, properties and DFT studies of thiophene, furan, N-butyl carbazole, triphenylamine, *p*- and *m*-phenylene bridged Bis-BODIPYs



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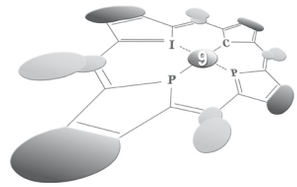

Phthalocyanine Complexes as Theranostic Agents for MRI and PDT

Ayşe Gül Gürek[a], Duygu Aydın Tekdaş[a], Veysel Koç[a], Aytaç Çavuş[a], Devrim Atilla[a], Eugeny Ermilov[b], Fabienne Dumoulin[a], Vefa Ahsen[a]

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Theranostics is one of the promising ways to personalized medicine, more especially against cancer, combining diagnostic and therapeutic effects. The third generation of photosensitizers combines imaging agents and photosensitizers to have the patient benefiting from a "see and treat" process, and theranostics quickly took place in PDT field. Among the different types of photosensitizers(PSs), consisting mainly of molecular tetrapyrroles of well-defined structures and tailorable properties; porphyrins and phthalocyanines are particularly employed. The porphyrins and phthalocyanines as tetrapyrrole derivatives have a unique theranostic role in disease therapy as third generation photosensitizers; they have been used to image, detect and treat a number of different cancer types.[1]

Although porphyrins and phthalocyanines share a tetrapyrollic backbone as PSs, there are literally unlimited variations on substituent components of porphyrins. In addition, by inserting a chelated metal within the porphyrin, even more possibilities exist. PSs have limited applications for detecting deeply seated tumors.[2] Therefore, the recent approaches for developing PS as bifunctional agents provides a unique approach for tumor-detection and therapy. The researches has focused on this approach in developing ''Multifunctional Agents'' for MR imaging-PDT and PET imaging-PDT. Advances steadily being made in the design of targeting vehicles used for delivery therapies could lead to the development of "Multifunctional Theranostics".Current focus is on the clinical imaging of tumor tissue; targeted delivery of photosensitisers and the potential of photosensitisers in theranostic platforms.[3] Finally, the synthesis and structural and spectroscopic characterization of tetrapyrrole derivatives in theranostic applications will be discussed as well.

Financial support by TÜBİTAK (the project 113R004 coupled to the COST Action TD1004) is gratefully acknowledged

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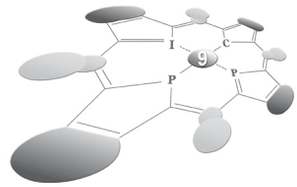

BODIPY-estradiol conjugates as multi-modality tumor imaging agents

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Introduction: In vivo imaging of estrogen receptor (ER) densities in human breast cancer is a potential tool to stage disease, guide treatment protocols and follow-up on treatment outcome. Among various techniques to detect ligand–ER interaction both positron emission tomography (PET) and fluorescence imaging have received ample attention. In this study we use 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY, λ_{em} = 510-638 nm) as a fluorescent probe to label estradiol-based ligands for ER.

Materials & Methods: The synthesis of these estradiol derivatives involves attachment of a BODIPY moiety to the C17α-position of estradiol using Sonogashira cross coupling reaction of iodo-BODIPY and various 17α-ethynyl estradiol (EE2) derivatives. Confocal laser scanning microscopy was used to monitor the cellular uptake of the EE2 conjugates after 1 h of treatment at either 10 or 100 nM with and without the presence of 1 μM of estradiol. Flow cytometric analysis was performed to determine the relative fluorescence in the nuclei.

Results & Discussion: The Sonogashira coupling reaction of **EE2** derivatives with iodo-BODIPY(1:1 molar ratio) in THF/toluene (1/2) and using $PdCl_2(PPh_3)_2$ as catalyst, NEt_3 as a base and CuI at room temperature gave the desired EE2-BODIPY conjugates in 45-86% yields after purification by silica gel column chromatography. In vitro fluorescence imaging of the basic EE2-BODIPY conjugate confirmed ER-mediated uptake by the nuclei of ER-positive MC7-L1 cells.

Conclusion: The synthesis of a series of EE2-BODIPY conjugates was achieved via Sonogashira cross-coupling in moderate to very good isolated yields. Our results warrant further in vivo studies to evaluate the potential of the EE2-BODIPY conjugates for PDT of breast cancer that overexpress ER. Also, selective localization in these tumors would render the conjugates good candidates for fluorescence and PET imaging via isotopic ^{18}F-^{19}F exchange in BODIPY dye.

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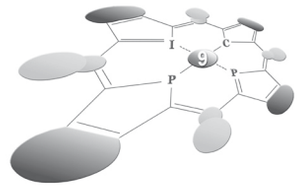

Photochemical mechanisms in antimicrobial photodynamic inactivation

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Antimicrobial photodynamic inactivation uses non-toxic photosensitizers (PS) and harmless visible light to generate reactive oxygen species (ROS) that damage biomolecules (proteins, lipids and nucleic acids) and kill all microbes including Gram-positive, Gram-negative bacteria and fungi. The principal types of ROS involved are singlet oxygen ($^1O_2$) and hydroxyl radicals (HO•). Singlet oxygen (Type II) is formed by energy transfer from the triplet state PS to ground state oxygen, while HO• (Type I) is formed by initial electron transfer to oxygen to form superoxide. Type I and Type II mechanisms can be usefully distinguished be employing commercially-available fluorescent probes that are specific for different ROS (Singlet Oxygen Sensor Green, SOSG, and Hydroxyphenyl-fluorescein, HPF). The particular features of the molecular structure of the PS are the principal factors that determine the balance between Type I and Type II photochemical pathways. The most important of these features are (a) the type of central metal in tetrapyrroles; (b) the redox potential; (c) the hydrophobicity of the PS and the microenvironment of the solvent. Our laboratory has studied several interesting groups of compounds where this balance between Type I and II pathways is important for aPDI, as microbial killing appears to be an ideal system for studying the relative cytotoxicity of different ROS. In the case of imidazole porphyrins and stable synthetic bacteriochlorins the central metal atom (2H; Zn; Pd; Ir) made a major difference with the Type II changing to Type I as in this order Zn > 2H > Ir > Pd. In the case of phenothiazinium dyes Type I mechanism appeared to depend on the degree to which the dye bound to the microbial cells. We discovered that sodium azide could be an interesting probe to distinguish between Types I and II mechanisms as azide quenches $^1O_2$ by a physical method, while on the other hand azide potentiates Type I pathway by reacting with HO• to form the long lived radical N_3• which can kill microbial cells better than HO•. Functionalized fullerenes are another class of PS that can efficiently carry out both Types I and II photochemistry depending on the exact structure and presence of internal electron donating groups. Finally titanium dioxide is a large-band-gap semiconductor which is excited by 360 nm light, and the aPDI effects can be dramatically potentiated by salts such as iodide and bromide.

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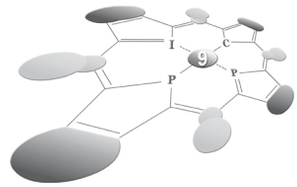

Synthesis and Photophysical Properties of Linear Cojugated Oligopyrroles

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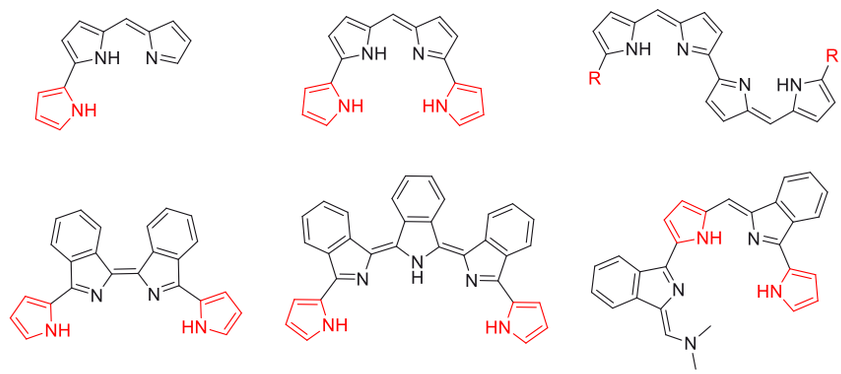
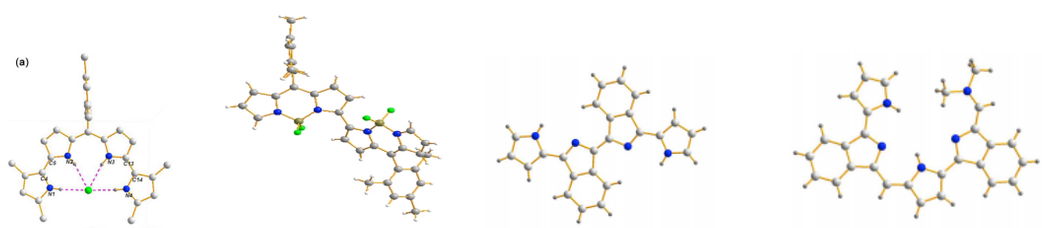
Conjugated oligopyrroles have found wide applications in organic synthesis, medicinal chemistry and material science. They also occur in nature and are key fragment of many synthetic porphyrinoids.[1] For example, pyrrolyldipyrromethenes are the core structure of prodigiosins and analogs, and have received wide attentions due to the wide range of important biological activities.[2] However, the synthesis of most conjugated oligopyrroles needs multiple-step synthesis and often gives low yields.[1-3] Herein, we present several new methods to prepare a series of conjugated oligopyrroles.





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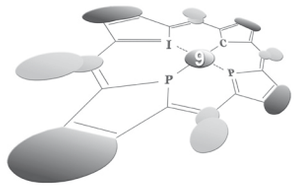

Isolation and Studies of Reactive Metalloporphyrin Species in Metal-Organic Frameworks

John S. Anderson, Audrey T. Gallagher, Jung Yoon C. Lee, Lujia Liu, Margaret L. Kelty, Jesse G. Park, and T. David Harris

Northwestern University

This presentation will outline our efforts to isolate, study, and explore the reaction chemistry of reactive chemical species in metalloporphyrin-containing metal-organic frameworks (MOFs). In particular, the chemistry of solids derived from the material PCN-224 with oxygen- and nitrogen-atom transfer agents will be detailed. This work has led to the structural characterization of several species that have proven to be unstable in related molecular complexes, including a five-coordinate oxyheme species, a manganese(IV) peroxo species, and a heme dintrosyl species. In addition to their structural characterization using single-crystal X-ray diffraction, these compounds have been subjected to an array of spectroscopic and magnetic analysis. For instance, Mössbauer, diffuse reflectance UV-visible, and extended X-ray absorption fine structure spectroscopies, along with variable-temperature dc magnetic susceptibility measurements, have been carried out in order to interrogate the electronic structure and local coordination environment of the isolated species. In addition, variable-temperature gas adsorption measurements have been carried out in order to elucidate the thermodynamics of binding between coordinatively unsaturated metalloporphyrins and small molecule substrates. Finally, this presentation will describe recent work to apply high-throughput synthetic approaches to the synthesis of nanocrystalline MOFs.

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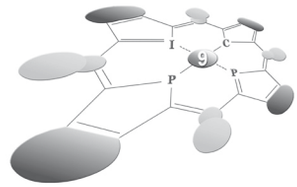

Photofunctional Supramolecular Architectures Composed of Porphyrin and Polycyclic Aromatic Hydrocarbon Derivatives

Taku Hasobe[a]

[a]*Department of Chemistry, Faculty of Science and Technology, Keio University, Yokohama, Japan*

One of the major challenges is to construct molecular architectures for electronic applicaytions. In particular, polycyclic aromatic hydrocarbon derivatives (PAHs) and porphyrin derivatives may be a good candidate to construct diverse supramolecular structures with considerable complexity by carefully adjusting intermolecular interactions such as hydrogen bonding, metal coordination, van der Waals and π–π interactions since electrochemical and photophysical proeprties can be systematically tuned by synthetic method. For example, Figure 1 shows the supramolecular charge-transfer (CT) π-complexes between planar porphyrins and 1,4,5,8,9,12-hexaazatriphenylene (HAT) derivatives for light energy conversion.[1] Our related molecular systems will be partially discussed in this presentation.[2]

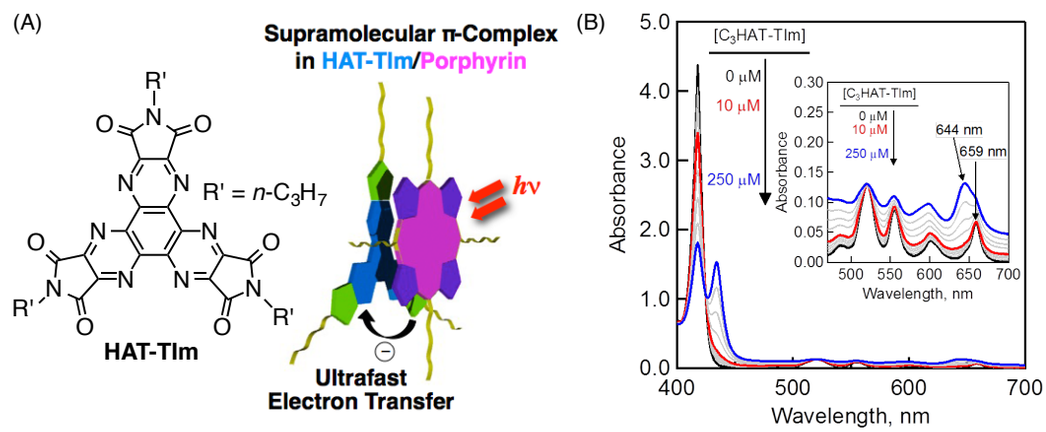

Figure 1. (A) A schematic illustration of CT π-complex formation between porphyrins and HAT derivatives. (B) Absorption spectral change of porphyrins (10 μM) upon addition of HAT derivatives in CH_2Cl_2. The inserted expandedfigure indicates a broad CT absorption of the porphyrin–HAT complex.

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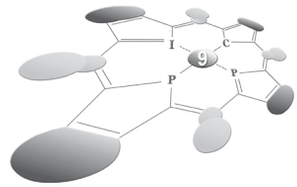

Hybrid Model of Cobalamin-Binding Domain in Methionine Synthase: Myoglobin Reconstituted with a Tetradehydrocorrin Cobalt Complex

Takashi Hayashi[a], **Yoshitsugu Morita**[a], **Koji Oohora**[a,b,c]

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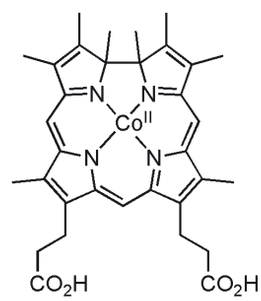
Methionine synthase, one of methyltransferases, is responsible for methylation of homocysteine to provide methionine. This enzyme consists of four large domains and one of them possesses cobalamin, a vitamin B_{12} derivative, as a cofactor. However, the precise 3D structure of the enzyme and the detailed reaction mechanism have never been completely clear. Therefore, our group has recently focused on the construction of a new enzyme model to understand the catalytic behavior of cobalamin in the protein.

It is known that the cobalamin-binding domain captures the cofactor via coordination of histidine as an axial ligand. Myoglobin, an oxygen storage protein, is a relatively small protein which has a histidine residue as an axial ligand to the heme cofactor in the heme-binding pocket, so we choose apomyoglobin as a substitute for the cobalamin-binding domain of methionine synthase. Furthermore, a tetradehydrocorrin cobalt complex was designed as an artificial cofactor to mimic the cobalamin moiety (see below), because native cobalamin consists of a corrinoid cobalt complex. The cobalt(II) complex was inserted into apomyoglobin to yield the reconstituted protein as a hybrid model of methionine synthase. The protein with the cobalt(II) complex was fully characterized by mass, UV-vis, and EPR spectroscopic methods. In addition, the x-ray crystal structure analysis of the protein reveals that the cobalt(II) complex is bound in the heme pocket with the axial ligation of the His93 residue.

Next, reduction of the protein by dithionite provided the cobalt(I) species and the tetra-coordinate complex structure via deligation of the His93 residue was determined by x-ray crystallography analysis. The addition of methyl iodide to the cobalt(I) species causes formation of a CH_3–Co bond in the heme pocket. Moreover, the mass study and trypsin digestion experiment show that the methyl group is then transferred to the Nε2 atom of the His64 imidazole ring quantitatively within 24 hours. Taken together, the present system demonstrates the model reaction of methionine synthase via the two key intermediates, cobalt(I) species and methylated cobalt(III) complex, in the protein matrix. In this presentation, we discuss the mechanism of the methyl transfer reaction.



tetradehydrocorrin cobalt complex

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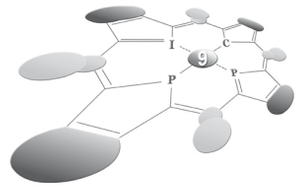

Porphyrin Clamp and Tripod for Surface Assemblies

Jonathan P. Hill[a], Yongshu Xie[b], Misaho Akada[a], Yutaka Wakayama[a], Katsuhiko Ariga[a]

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Supramolecular arrangement of porphyrins and other molecules has great potential in the fields of molecular information storage and sensing due to their ease of deposition and good chemical and thermal stabilities. In particular, porphyrins of relatively large molecular weights can be applied in thermal deposition while tetrapyrrole molecules have had an extensive synthetic chemistry developed, which enables synthesis of complex derivatives. In this work, we present complementary examples of porphyrin nanoarchitectonics. Starting from simple symmetrical phenol derivatives, we describe the effects of steric hindrance about the respective hydroxyl groups[1,2] and also the effects of conformational variation on the self-assembly structures.[3] We also investigated fabrication of binary molecular monolayers using two different porphyrin molecules *tetrakis*(3,5-di-*t*-butyl-4-hydroxyphenyl) porphyrin and *tetrakis*(4-pyridyl) porphyrin by deposition in ultrahigh vacuum.[4] This leads to two unusual heteromolecular monolayer structures were observed with one exhibiting good separation of molecules within the monolayer. Meanwhile, a synthetic nanoarchitectonic approach was used to prepare self-assembled molecular nanowires at a mica substrate. The nanowires could be observed growing using atomic force microscopy (AFM) and the network structures of the nanowires can be influenced by manipulation using the AFM probe tip.[4,5] Formation of molecular monolayers with chromophores positioned remote from the substrate surface will also be discussed.[6]

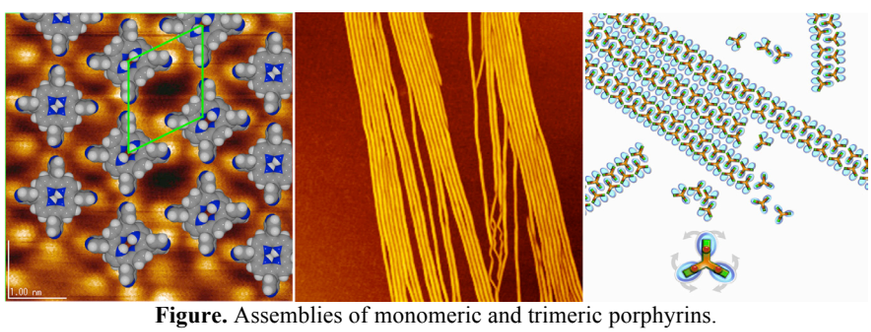

Figure. Assemblies of monomeric and trimeric porphyrins.

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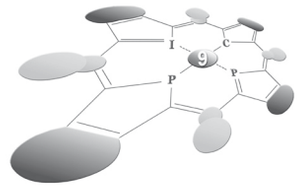

Computational Insights into Metal-Oxo Species in Heme and Nonheme Environments

Hajime Hirao[a]

[a] *School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 63737*

The mechanisms underlying the reactions of the $Fe^{IV}O$ species of cytochrome P450s supported by a porphyrin π-cation radical ligand ($Por^{+}\bullet Fe^{IV}O$), often called Cpd I, still provide a number of mechanistically interesting conundrums. Furthermore, Cpd I can be viewed as a reference point with which to compare the unique reactivity patterns of other metal-oxo species. Using computational approaches such as DFT and QM/MM, we have been studying Cpd I and many other metal-oxo species in different coordination environments. Thus, synthetic complexes, metalloenzymes, and metal-organic frameworks are all our research targets. Our computational studies identified clear distinctions between each species and Cpd I, which are brought about by different metals or ligands used.

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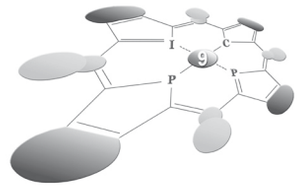

Phthalocyanines as Fluorescent Chemosensors for Cu^{2+}

Sevinç Topal[a], Vefa Ahsen[a], Catherine Hirel[a]

[a]*Gebze Institute of Technology, Department of Chemistry, P.O.Box 141, 41400, Gebze, Kocaeli, Turkey*

The determination of Cu^{2+} is important in environmental monitoring, industry, medical, biological and technical applications. Although the design and development of fluorescent chemosensor for the detection of Cu^{2+} is an important field of research, there is still necessary to develop new technologies and treatments in this field. Most of the reported Cu^{2+} fluorescent chemosensors are based on a quenching of the fluorescence emission in presence of the ions Cu^{2+} due to its paramagnetic nature. Recently chemosensors based on the fluorescence emission enhancement and sensitivity to Cu^{2+} have been also reported[1,2]. However, they mostly present a lack of selectivity and sensitivity. To overcome these major drawbacks, a phthalocyanine bearing nitroxide covalently link to the skeleton was designed to take advantage of the well-know high fluorescence quantum yield of phthalocyanines combined with the high selectivity and sensitivity of nitroxide moieties toward $Cu^{2+.}$ The current researches about the topic will be presented.

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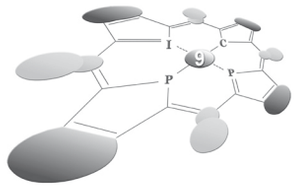

Domain Swapping of *c*-Type Cytochromes and Myoglobin

Shun Hirota[a], **Satoshi Nagao**[a], **Yugo Hayashi**[a], **Takaaki Miyamoto**[a], **Chunguang Ren**[a], **Masaru Yamanaka**[a], **Ying-Wu Lin**[a], **Hirofumi Komori**[b], **Yasuhito Shomura**[c], **Yoshiki Higuchi**[d]

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In domain swapping, a secondary structural region or a domain of one protein molecule is replaced with the corresponding region or domain of another protein molecule. We have previously shown that small spherical heme proteins form oligomers by domain swapping.[1] High-order oligomers of a thermostable *c*-type cytochrome (cyt), *Hydrogenobacter thermophilus* (HT) cyt c_{552}, increased as inserting more Gly residues at the major hinge loop of the wild-type protein.[2] N-terminal and C-terminal domain swapping were elucidated for the cyt c_{552} mutant.[2] Cyt c_{555} from hyperthermophilic bacteria *Aquifex aeolicus* (AA) possesses a unique long 3_{10}-α-3_{10} helix containing the heme-ligating Met61. AA cyt c_{555} formed dimers by swapping the region containing the extra 3_{10}-α-3_{10} and C-terminal helices.[3] *Pseudomonas aeruginosa* cyt c_{551} formed domain-swapped dimers by swapping the region containing the N-terminal α-helix and heme, which showed that the unstable loop region has a tendency to become a hinge loop in domain-swapped proteins.[4] Domain-swapped oligomers of HT cyt c_{552} were also formed in *E. coli* which expresses cyt c_{552}.[5] The amount of high-order cyt c_{552} oligomers increased in *E. coli* as the cyt c_{552} concentration was increased, whereas it decreased in the order of decrease in protein stability, indicating that domain swapping decreases in cells when the protein stability decreases.[5] This is an indication that exceedingly stable proteins may have disadvantages forming domain-swapped oligomers in cells. We also found that a four-helix bundle protein cyt cb_{562}, with the cyt b_{562} heme attached to the protein moiety by two Cys residues insertion, forms a domain-swapped dimer.[6] The heme coordination structure of the dimer was similar to that of the monomer. In the crystal, three domain-swapped cyt cb_{562} dimers formed a unique cage structure with a Zn-SO_4 cluster inside the cavity.[6] The Zn-SO_4 cluster consisted of fifteen Zn^{2+} and seven SO_4^{2-} ions. For myoglobin (Mb), the carbon monoxide binding rate constant of the domain-swapped dimer was about twice larger than that of the monomer, although the active site structure was similar between the monomer and dimer.[7] We also designed an artificial multiheme protein based on domain swapping of Mb.[8]

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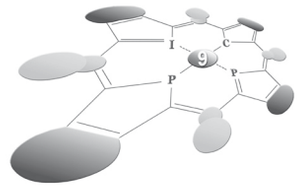

Highly-twisted porphyrin oligomers: Synthesis, characterization and applications

Satoru Hiroto, Satoru Ito, and Hiroshi Shinokubo

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Japan

Highly twisted π-conjugated molecules have been attractive and challenging targets in organic synthesis. Twisting away from the π-surface transforms the dimension of molecular geometries from 2D to 3D. The twisting induces anisotropic conformation, helicity, and dynamic motion. However, bending of π-conjugated plane often requires harsh reaction conditions to overcome high activation energy barrier due to its highly strained conformation.

Recently, we have found that the oxidation of 2-amino-5,10,15-triarylporphyrins proceeded selectively to provide planar pyrazine-fused diporphyrins in high yields.[1] In addition, the oxidation of 2-aminoanthracene proceeded selectively to provide highly distorted π-extended azahelicenes in one step.[2] This result has encouraged us to create other distorted π-conjugated molecules under mild conditions. Accordingly, we have succeeded in synthesizing highly twisted porphyrin dimers by using *meso*-tetraaryl substituted porphyrins. The structures of dimers have been unambiguously revealed by X-ray diffraction analysis. The twisting of the π-surface resulted in lowering of the HOMO–LUMO gap, which was confirmed by optical and electrochemical analysis. These results are promising for π-conjugated molecular wires, whose properties could be controlled by molecular twisting. In addition, we also succeeded in the synthesis of a twisted porphyrin tetramer by repeating use of the present amination–oxidation strategy. The structure was finally unveiled by X-ray diffraction analysis, exhibiting unidirectionally twisting conformation with the angle of 300° (Figure 1).[3]

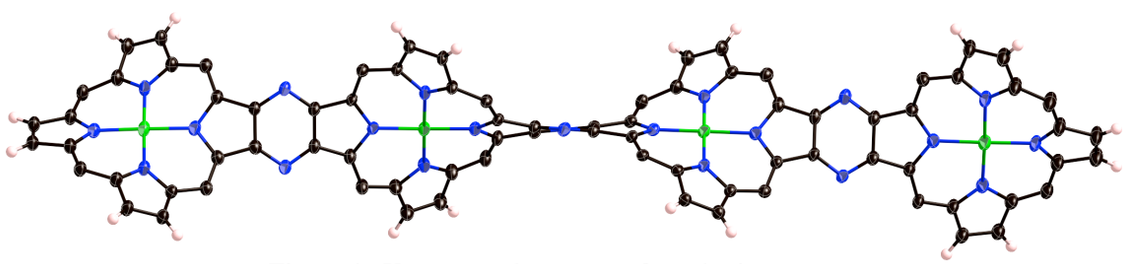

Figure 1. X-ray crystal structure of porphyrin tetramer.

Interestingly, Ni(II) type porphyrin dimers and tetramers exhibited weak but apparent CD signals in chiral amine solution. Such chiral induction behavior was also observed for Zn(II) metal complexes on addition of chiral amine ligands. According to the kinetic study, the activation barrier of racemization definitely proved dependent on *meso*-substituents. In this presentation, the synthesis, physical properties and dynamic motion of highly twisted porphyrin oligomers will be presented.

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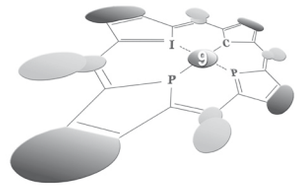

New hybrids consisting of tetraphenyl porphyrins covalently linked to C_{60} and graphene

Andreas Hirsch

Friedrich-Alexander University Erlangen-Nuremberg Department of Chemistry and Pharmacy, Henkestr. 42, Erlangen 91054, Germany (andreas.hirsch@fau.de)

We will present a series of new fullerene-porphyrin and graphene-porphyrin hybrids. For this purpose we have synthesized a variety of cascaded architectures that contain C_{60} as the central acceptor core. Using covalent addition chemistry we have prepared and isolated hybrid structures that are able to undergo photo-induced electron- and energy transfer processes. Using diazonium chemistry we have also covalently attached tetraphenyl-porphyrins to reduced graphene. Upon this process electrons were transferred from the graphenide to the tetraphenyl diazonium intermediate leading to N_2 extrusion and addition of the corresponding radicals to the basal graphene plane. In these new sheets architectures electronic communication between the corresponding building blocks was observed. These compounds were structurally characterized by state-of-the-art methods. In the case of the graphene-porphyrine hybrids statistical Raman spectroscopy provided very value information about the detailed materials composition.

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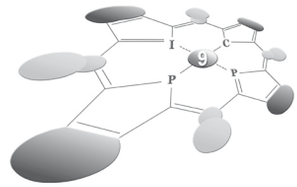

Bioinspired Catalysts based on Vitamin B_{12} Chemistry

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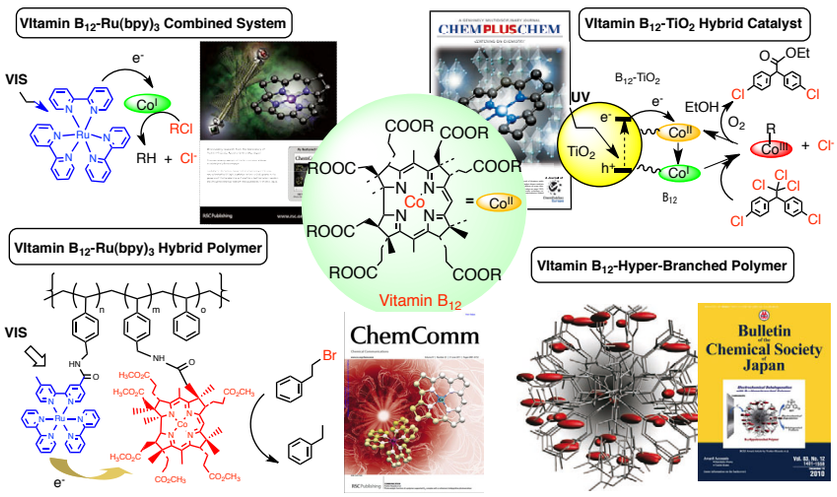
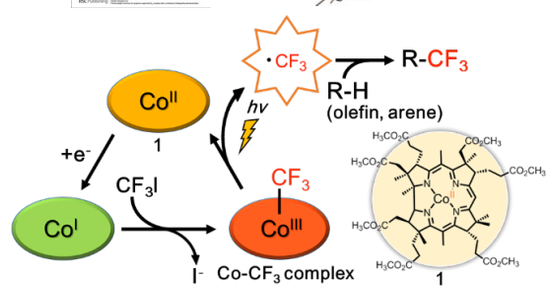


As part of a study directed toward design of good catalytic systems based upon a hydrophobic vitamin B_{12}, we reported preparation of various nanomaterials with the vitamin B_{12} derivative and photosensitizers. Examples include a vitamin B_{12}-titanium dioxide hybrid catalyst,[1] a vitamin B_{12}-Ru complex combined system,[2] and so on.[3] These bioinspired materials have potential as catalytic systems for degradation of organic halide pollutants and for molecular transformations via radical intermediates under irradiation with UV or visible light, and offer scope for applications that are of great interest in terms of green chemistry.[4]

Recently, we applied trifluoromethylation reactions catalyzed by vitamin B_{12} derivative (**1**) using electrochemical and photochemical activation. Details will be reported in this conference.



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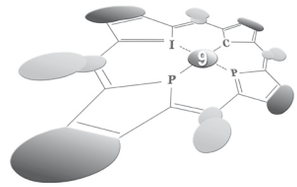

Synthesis of Edge- and Basal Plane-type NiTPP-Graphene with Directly Covalent C-C Bond via Diazonium Reation

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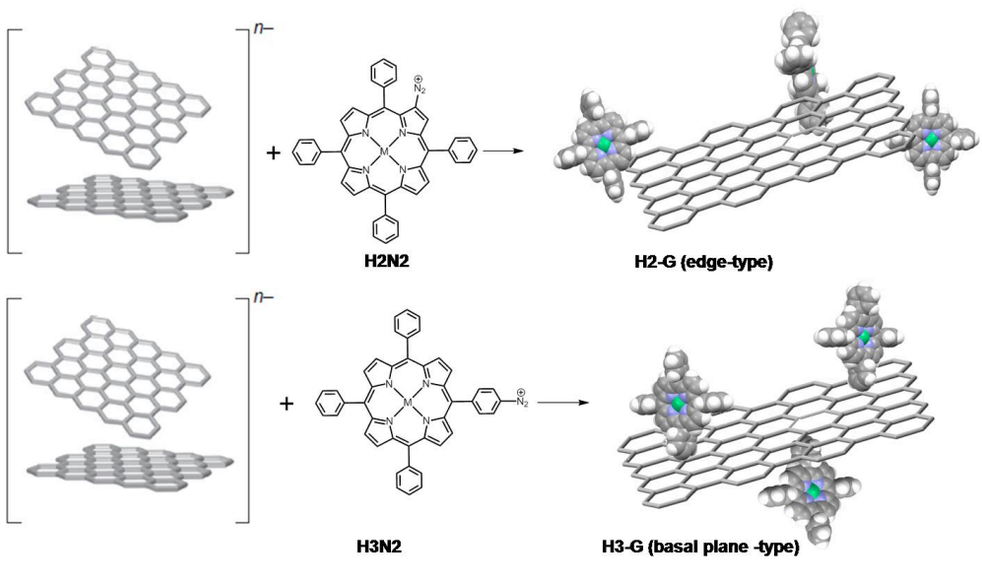
Porphyrin as planar, electron-rich, highly conjugated systems and typically intense absorption bands in the visible region, have been widely used for photo-harvesting and photoelectronic devices.[1] Graphene, an individual 2D structure consisting of single-atom-thick carbon atoms arranged in sp^2-hybridized, six-membered rings, has been intensively investigated in the family of carbon allotropes. Therefore, covalent attachment of optoelectronically active porphyrin molecules with the graphene to fabricate graphene-based hybrid material for researching their electronic and optica communication should be very of interesting, due to the interactions between the two components in the ground and excited states. [2]

Herein, we firstly describe the synthesis of two types of porphyrin-graphene hybrids: (i) edge-type β-NiTPP-graphene (**H2-G**, NiTPP = (tetraphenylporphyrinato)nickel(II)), and (ii) basal plane-type, NiTPP-graphene (**H3-G**) hybrid materials with only one covalent C-C bond via the reaction of reduced graphene and porphyrins diazonium salts (Scheme 1).



Scheme 1. Synthesis of two types of porphyrins-graphene hybrid materials.

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Application of Amide-linked Bisporphyrins and Trisporphyrins in Chirality Transfer

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Porphyrins have been intensively studied in chirality related fields in recent years. Many porphyrin systems have been developed for a variety of guests, such as diamines, diols, sugars, amino acids etc. But for monodentate chiral guests, such as monoamines, monoalcohols, it is very difficult to study without chemical modification. Recently, we have developed a series of amide-linked bisporphyrins.[1-3] All these hosts have amide groups which are localized at an appropriate position for potential hydrogen bonding interactions. We have also designed an amide-linked trisporphyrin. A series of chiral monoamines have been tested. For bisporphyrin, CD spectra show strong signals in the Soret band region. But to our surprise, when the substituent (R) is an aryl group, the signs of their CD signals are opposite to those when R is an alkyl group! We report further investigations on the possible mechanism in the molecular recognition process. For trisporphyrin, CD spectra show stoichiometry controlled supramolecular chirality transfer, which is caused by the corresponding 1:1, 1:2 and 1:3 host-guest complexes.

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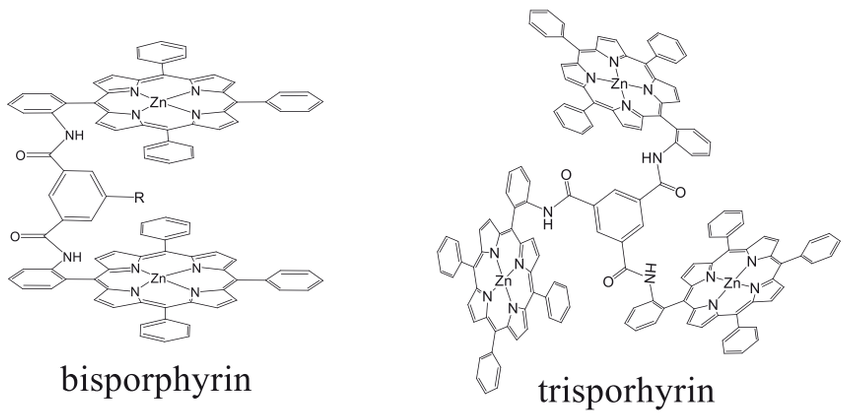

Fig. 1 The structural formulae of the designed bisporphyrins and trisporphyrin.

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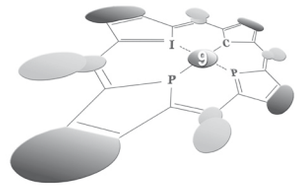

Albumin-embedding and tumor targeting of phthalocyanine photosensitizers

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Human serum albumin (HSA), a naturally abundant protein in blood plasma and tissue fluids, has an extraordinary ligand-binding capacity and is advocated as a drug carrier to facilitate drug delivery. To render it tumor targeting specificity, we generated a recombinant HSA fused with the amino-terminal fragment (ATF) of urokinase, allowing the fusion protein to bind to urokinase receptor (uPAR), which is shown to have a high expression level in many tumors, but not in normal tissues. This bifunctional protein (ATF-HSA) can then be used to embed drugs or photosensitizers inside the drug binding pockets of HSA. The embeding of hydrophobic phthalocyanine zinc (ZnPc) photosensitizer into HSA leads to dissociation of ZnPc aggregations and 100-fold enhanced fluorescence. Other aspects and additional examples using this strategy will be discussed in this presentation.

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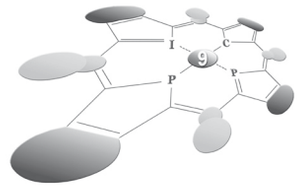

Oxasmaragdyrins as High-Efficiency Hole Transporting Materials for Perovskite Solar Cells

Chen-Hsiung Hung,[a] Sandeep Mane,[a] Chih-Fu Cheng,[a] Albertus Adrian Sutanto,[a,b,d] Shih-Chieh Yeh,[a] Eric Wei-Guang Diau,[c] Chin-Ti Chen[a]

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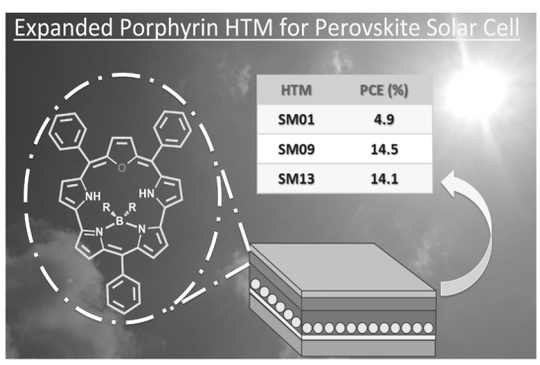
[c] *Department of Applied Chemistry and Institute of Molecular Science, NCTU, Hsinchu-30010, Taiwan*
[d] *Department of Chemical Engineering, NTUST, Taipei-10607, Taiwan*

In an earlier report, we have demonstrated that the boryl oxasmaragdyrins with terminal carboxylic acids as anchoring groups can function as a highly efficient sensitizer for DSSC. Analyzing the band gaps, we have also found that oxasmaragdyrins in theory can be a good hole transporting materials in n-type perovskite solar cells. We report herein the use of this expanded porphyrin as hole transporting materials for lead halide perovskite solar cells. Boryl oxasmaragdyrins, a family of aromatic core-modified expanded porphyrins with 22 π-electron conjugation, served as efficient hole transporters to achieve the power conversion efficiencies higher than 14% for mesoscopic perovskite solar cells (PSCs). This performance is near identical to the state-of-the-art hole transporting materials (HTM), spiro-OMeTAD. Moreover, with the addition of LiTFSI and tBP in measured HTMs, the zero field hole mobility (μ_h) of SBM09 is comparable to that of spiro-OMeTAD. These PSC devices with boryl oxasmaragdyrin HTMs are highly stable except the device using SBM01. The lower stability of SBM01 device is attributed to interactions of carboxyphenyl terminal on SBM01 with MAPbI3



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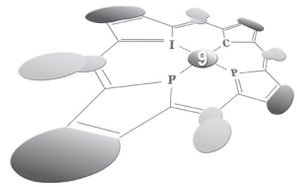

Modulating Bridge in Donor-Bridge-Acceptor Systems for Photoinduced Charge Separation and Solar Energy Conversion

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Photoinduced charge separation (CS) is one of the most fundamental processes in physics, chemistry, and biology. In the reaction center of natural photosynthesis, photoinduced electron transfer (ET) generates a long-lived CS state with ~100% efficiency, leading to light-to-chemical energy conversion. In contrast, photoinduced CS at the interfaces of organic photovoltaic cells and dye-sensitized solar cells generates an electron-hole pair, eventually achieving light-to-electricity conversion. However, the interfaces of semiconductor/dye and donor/acceptor (D/A) in artificial photosynthesis and organic photovoltaic cells often suffer from the partial or even large loss of the CS state at the early stage, which has still been controversial and not unveiled owing to inevitable inhomogeneous spatial distribution of D-A components.

In this context D-bridge (B)-A linked systems have generated remarkable interest for the last few decades. The covalent linkage between D and A with the bridge can eliminate complex factors arising from diffusion in solutions and assess the photoinduced CS precisely with the help of homogenous spatial distribution of the D-B-A components. So far these systems have provided fundamental information on photoinduced CS. Impact of various CS parameters, i.e., driving force (ΔG^0_{ET}), electronic coupling (V), reorganization energy (λ), and temperature (T), on ET rate has been evaluated by using elaborated D-B-A linked molecules. In particular, a well-defined D-B-A linked molecule with a rigid bridge has allowed us to shed light on photoinduced CS more accurately.

In this talk I will give an overview of our initiatives on the basis of D-B-A systems. In particular, I focus on photophysics of porphyrin-fullerene linked systems as well as photovoltaic properties of porphyrin-sensitized TiO_2 solar cells. Specifically, tropolone has been employed for the first time as the bridge between the porphyrin and TiO_2 electrode for dye-sensitized solar cells (DSSCs). The DSSC based on a push-pull porphyrin with the tropolone moiety exhibited a power conversion efficiency of 7.7%, which is almost comparable to a reference porphyrin with a conventional carboxylic group. More importantly, the former device was found to display the superior DSSC durability as well as binding ability to TiO_2 to the latter. These results unambiguously demonstrate that tropolone is the highly promising bridge of any dyes for DSSCs in terms of device durability as well as photovoltaic performance.

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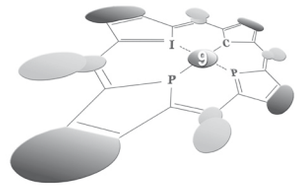

Porphyrinoids-resorcinarene cavitand hybrids: a strategy to maximize interactions between phthalocyanines and fullerenes

Zeynel Sahin,[a] Derya Topkaya,[b] Suleyman Gokhan Colak,[c] Mine Ince,[c,d] Vefa Ahsen,[a] Fabienne Dumoulin[a] and Umit Isci[a]

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Promoting the interactions between porphyrinoids and fullerenes is crucial to optimize photo-induced electron or energy transfers. Resorcinarene cavitands are known to be able to act as host for fullerene. This prompted us to design porphyrinoids-resorcinarene cavitand hybrids, with electron-accepting or electron-withdrawing substituents on the phthalocyanine. Such architectures are emerging as promising in numerous fields.[1,2]
Synthetic strategies will be presented. The effect of the phthalocyanine substitution pattern as well as the number of phthalocyanine units par resorcinarene cavitands will be investigated on a photophysical and photochemical point of view in the absence or in the presence of fullerenes.

ACKNOWLEDGEMENTS
The Scientific and Technological Research Council of Turkey (TUBITAK) is gratefully acknowledged for the funding of these works (project 114Z590 coupled to the COST Action CM1304)

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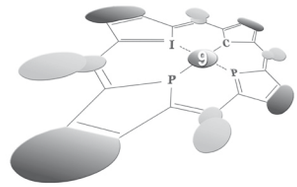

Doubly N-Confused [26]Hexaphyrin Bis-metal Complexes with Group 10 Metal Elements as Near-IR Dyes

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NIR responsible materials are designed as the substances that interact with NIR light absorption and emission under external stimulation such as photoexcitation, electric field, and chemical reaction. Tremendous endeavors have been devoted to the NIR dyes aiming for the applications such as organic semiconductor, bio-imaging, laser filter, and telecommunication.[1] Doubly N-confused hexaphyrin (**N_2CH**) is one of the synthetic NIR dyes based on expanded porphyrin analgoues containing two ''confused'' pyrrole rings.[2] Upon metal complexation of **N_2CH**, metal(II) centers are stabilized at the 26π-conjugated macrocyclic frameworks possessing different coordination environments, that is, *cis*-(*NNNN,NNCC*) and *trans*-(*NNNC,NNNC*). An example of bis-organopalladium(II) complex, ***cis*-Pd_2N_2CH** has been reported to be adopted a saddle shaped rectangular geometries and exhibits intriguing NIR absorption properties around 1500 nm.[3] In order to further elucidate the structural effects of **M_2N_2CH** on their photophysical properties, we have synthesized and characterized a series of bis-metal(II) complexes with group 10 elements. The detailed structures and photophysical properties of **M_2N_2CH** will be presented.

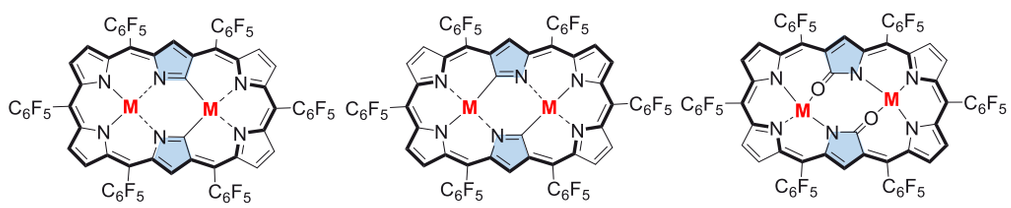

Figure 1. Chemical structures of ***cis*-M_2N_2CH** (left), ***trans*-M_2N_2CH** (middle), and **$M_2N_2CO_2$H**.(right)

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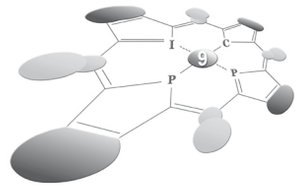

Functional and Structural Characterization of Heme Binding in Heme-regulated Proteins

Koichiro Ishimori

Department of Chemistry, Faculty of Science, Hokkaido University

Heme is a typical and common prosthetic group for various kinds of metalloproteins, but recent studies have revealed that heme can also function as a signalling molecule for many biological regulations including metal homeostasis, protein expression, biosynthesis of cofactors, and circadian rhythms. In these "heme-regulated" proteins, the heme binding is supposed to induce specific conformational and functional changes of the proteins[1], leading to inhibition or promotion of transcription, translation, or protein-protein interactions. In spite of such biological significance, the structural characterizations of the heme binding in heme-regulated proteins have not yet been done in detail and its functional significance is still unclear. Based on the spectroscopic data, we have already characterized the heme environmental structure of iron response regulator (Irr)[2,3], a key regulator protein for iron metabolism in a nitrogen fixing bacterium, showing the unique and specific heme environmental structure of heme bound Irr and the heme-induced inhibition of the binding to the target DNA in Irr. Here, we found that iron regulatory proteins, IRP1 and IRP2, which are the essential regulators for iron metabolism in mammalian cells and control the translation of proteins involved in iron uptake, storage and utilization, can specifically bind two and three equivalents of heme, respectively. The absorption spectra of these heme-bound IRPs showed a highly blue-shifted broad Soret peak around 370 nm as found for heme bound Irr, suggesting that the heme binding to the cysteine residue in the heme regulatory motif (HRM). To confirm the heme binding to the cysteine residue, we measured the resonance Raman spectra and observed a Raman line around 330 cm^{-1}. This Raman line showed the isotope shift by the substitution of ^{54}Fe-porphyrin for heme (^{56}Fe), confirming the stretching mode between the heme iron and cysteine. The Fe-Cys stretching mode appeared at 333 cm^{-1}, which is significantly lower than that of the typical cysteine-ligated protein and such a lower stretching mode was encountered for heme bound Irr[2]. These spectroscopic data indicate that the heme environmental structures in IRPs are quite similar to that of Irr, which would be a common heme environmental structure in the "heme-regulated" proteins. Quite interestingly, the gel shift assay revealed that the heme binding to IRP1 inhibits the binding of the target RNA, iron-responsive element (IRE). Using fluorescence labelled IRE, the specific decrease in the fluorescence anisotropy was detected for the complex formation of IRP1 with the IRE, showing that the dissociation constant is approximately 7 nM. In the presence of heme, the decrease in the anisotropy was not detected, corresponding to the heme-induced inhibition of the IRE binding in IRP1. Similar heme-dependent IRE binding inhibition was also detected for IRP2. These observations clearly show that the IRE binding in IRP1 and IRP2 is regulated by the heme binding to the HRM region, which is apparently distinct from the proposed mechanisms in these IRPs, and suggest that heme functions as the signalling molecule for iron homeostasis in mammalian cells.

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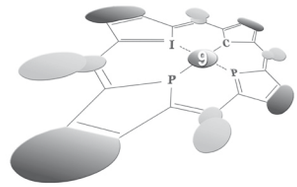

Synthesis, structure particularities and properties of hemihexaphyrazines and their metal complexes

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A crossover condensation of 2,5-diamino-1,3,4-thiadiazole with phthalonitrile, substituted phthalonitriles or their derivatives in organic solvents remains to be the main method of ABABAB-type macroheterocyclic compounds synthesis [1]. Their structure was proved by gas phase electron diffraction [2] and X-ray [3] methods. It was established that a flat macrocyclic core stabilized by inner tricentered hydrogen bonds forms an expanded coordination cavity which is able to hold three atoms of transition metals. But their structure remained unknown.
We succeeded in growing monocrystals of Cu-complexes of [30]trithia-2,3,5,10,12,13,15,20,22,23,25,30-dodecaazahexaphyrin bearing pentoxygroups in 3,6-positions (**I**).
It was shown for the first time that complex (**I**) contains 3 atoms of Cu and 2 atoms of halogens (Cl of Br) as counterions which form a trigonal bipyramid.

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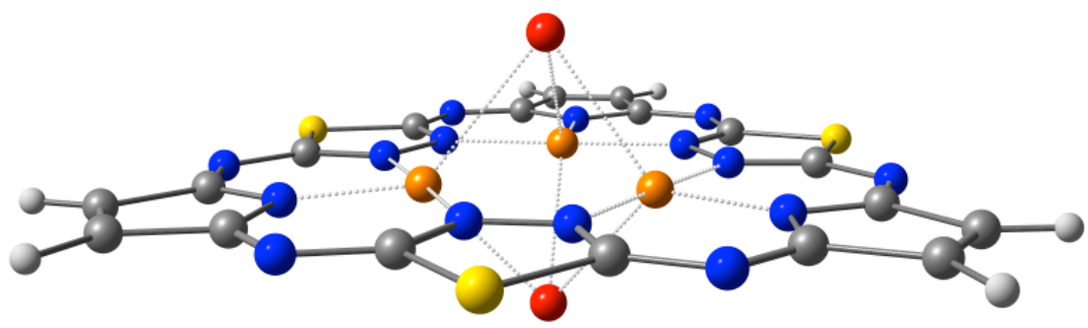

Fig. View of model of (**I**) optimized by DFT method

Acknowledgements
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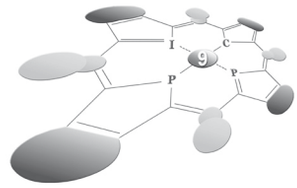

Mechanistic insights to the ferryl high-valent intermediates in peroxidases, KatGs and *de novo* mini-heme catalysts

Anabella Ivancich[a], **Toni Kühl**[a], **Kei Wada**[b], **Vincent L. Pecoraro**[c]

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Protein-based radicals, reacting in a concerted way with the metal active site of metalloproteins, are relevant to the enzymatic catalysis (1). In heme enzymes, Tyr and Tyr can play a crucial role both as true intermediates in their catalytic cycles, and in facilitating electron transfer between redox centers when behaving as transient radicals (2). Certain peroxidases, including cytochrome c peroxidase (3), lignin peroxidase (4), lactoperoxidase (5) and bifunctional peroxidases (KatGs) (6) stabilize [Fe(IV)=O Trp$^{\square+}$] and/or [Fe(IV)=O Trp$^{\square}$] species as catalytically-relevant intermediates, formed subsequently to the primary oxidizing intermediate, the [Fe(IV)=O Por$^{\square+}$] also known as "Compound I". We have shown that KatGs from *B. pseudomallei* and *M. tuberculosis* stabilize three different Trp$^{\square}$ as catalytic intermediates (6, 7), while the *Synechocystis* KatG has a unique Trp$^{\square}$ site (8). The recently reported structure of KatG from *Synechococcus elongatus* (9) does not reveal significant structural differences allowing rationalizing the stabilization of different Trp radical sites. We have then characterized the high-valent intermediates formed in *Synechococcus* KatG using multifrequency EPR spectroscopy. These results provide us with an overall picture related to high-valent intermediates and strategies for substrate oxidation in the bifunctional peroxidases (KatGs) family. Being the ancestors of mono-functional peroxidases, KatGs provide a rationale for the differences in intermediates observed among peroxidases. Our recent efforts towards using *de novo* designed heme proteins to better understand the physicochemical properties enabling formation of the high-valent intermediates in bifunctional peroxidases will be discussed.

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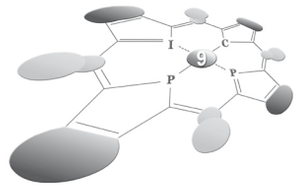

Multi-Chromophoric Architectures in Water: Constructed via Host-Guest Interactions

Janarthanan Jayawickramarajah[a], **Xiao Zhou,**[a] **Mengyuan Zhu**[a]

[a] *Department of Chemistry, Tulane University*

This presentation discloses our recent efforts on assembling multi-chromophore containing nanoarchitectures, with a particular emphasis on the supramolecular chemistry and photophysical properties of porphyrin-containing host-guest systems. These multi-chromophoric assemblies are judiciously prepared such that the individual porphyrin monomer units are (A) assembled—in a well-defined manner—in competitive aqueous media, and (B) do not undergo detrimental aromatic aggregation. The first segment of the talk will detail the preparation and photonic properties of porphyrin containing wires, spheres, and thin films constructed through, inter alia, cyclodextrin-driven host-guest chemistry. The second half of the seminar will discuss our recent forays into expanding the scope of the multi-chromophoric architectures by harnessing cucurbituril derived host-guest interactions, in addition to the unique self-assembly properties of synthetic oligonucleotides.

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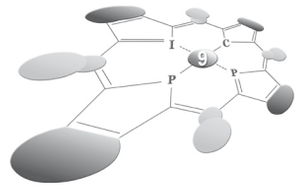

Combined Experimental and Theoretical Study on the Reactivity of Compounds I and II in Horseradish Peroxidase Biomimetics

Li Ji[a]

[a] *College of Environmental and Resource Sciences, Zhejiang University, Yuhangtang Road 866, Hangzhou 310058, China*

For the exploration of the intrinsic reactivity of two key active species in the catalytic cycle of horseradish peroxidase (HRP), Compound I (HRP-I) and Compound II(HRP-II), we generated in situ $[Fe^{IV}=O(TMP+C)(2\text{-MeIm})]^{+}$ and $[Fe^{IV}=O(TMP)(2\text{-MeIm})]^{0}$ (TMP=5,10,15,20-tetramesitylporphyrin; 2-MeIm=2-methylimidazole) as biomimetics for HRP-I and HRP-II, respectively. Their catalytic activities in epoxidation, hydrogen abstraction, and heteroatom oxidation reactions were studied in acetonitrile at −15 degree by utilizing rapid-scan UV/Vis spectroscopy. Comparison of the second order rate constants measured for the direct reactions of the HRP-I and HRP-II mimics with the selected substrates clearly confirmed the outstanding oxidizing capability of the HRP-I mimic, which is significantly higher than that of HRP-II. The experimental study was supported by computational modeling (DFT calculations) of the oxidation mechanism of the selected substrates with the involvement of quartet and doublet HRP-I mimics (^{2,4}Cpd I) and the closed-shell triplet spin HRP-II model (^{3}Cpd II) as oxidizing species. The significantly lower activation barriers calculated for the oxidation systems involving ^{2,4}Cpd I than those found for ^{3}Cpd II are in line with the much higher oxidizing efficiency of the HRP-I mimic proven in the experimental part of the study. In addition, the DFT calculations show that all three reaction types catalyzed by HRP-I occur on the doublet spin surface in an effectively concerted manner, whereas these reactions may proceed in a stepwise mechanism with the HRP-II mimic as oxidant. However, the high desaturation or oxygen rebound barriers during C–H bond activation processes by the HRP-II mimic predict a sufficient lifetime for the substrate radical formed through hydrogen abstraction. Thus, the theoretical calculations suggest that the dissociation of the substrate radical may be a more favorable pathway than desaturation or oxygen rebound processes. Importantly, depending on the electronic nature of the oxidizing species, that is, ^{2,4}Cpd I or ^{3}Cpd II, an interesting region-selective conversion phenomenon between sulfoxidation and H-atom abstraction was revealed in the course of the oxidation reaction of dimethylsulfide. The combined experimental and theoretical study on the elucidation of the intrinsic reactivity patterns of the HRP-I and HRP-II mimics provides a valuable tool for evaluating the particular role of the HRP active species in biological systems

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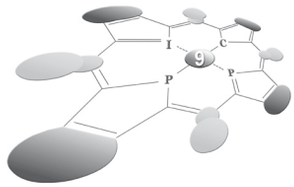

Sonodynamic Therapy for Treating Brain Stem Cancer

Ying Ji, Wangmin Che

[a] *Divisionof Neurosurgery Beijing Tiantan Puhua Hospital, China*

Sonodynamic therapy for treating brain stem cancer utilizes the good penetrative abilities of low-frequency ultrasound to activate the porphyrin photosensitizer accumulated within cancer cells to totally eradicate brain stem tumors and completely preserve the brain stem's neurological functions, thus serving as a successful treatment method.

Treatment method: Clinical MRI was used to diagnose brain stem cancer patients. 5 mg/kg body weight equivalent doses of "Sibofen" were intravenously injected. 24 hours after injection, the brain stem tumor was exposed, at its localized point, to ultrasound with frequency 450 KHz and sound intensity of 1 W/cm^2 to commence sound activation treatment. After treatment, the patient's situation was reviewed with another set of head MRI. After Sound Activated Cancer-Removal Treatment (SACT), patients were tracked for 12 months. 1, 2, 3, and 6 months after treatment, the patient underwent a series of MRI to observe the situation of tumor ablation.

Results: Brain stem tumors, 3 months after being exposed to sonodynamic therapy, became significantly ablated. 6 months after treatment, brain stem edema disappeared, and the original anatomy of the brain stem was restored. Patients' recovery from neurological damage varied to different degrees. Patients' progression-free survival (PFS) was about 12 months.

Conclusions: This research shows that SACT is a novel, breakthrough method for tumor treatment. It is a necessity for further clinical research exploring sonodynamic therapy's effects on other types of cancer tumors to be conducted, to thoroughly understand the weight and position of this technique in cancer treatment.

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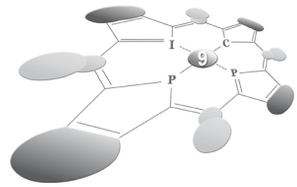

Macrocyclic Compounds-Driven Highly Active Electrocatalysts for Oxygen Reduction Reaction

Sang Hoon Joo[a]

[a]*School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST)*

The development of highly active, durable, and low-cost oxygen reduction reaction (ORR) catalysts is central to rendering polymer electrolyte fuel cells (PEFCs) and Li-air batteries commercially viable. In this context, tremendous recent efforts have been devoted to replacing expensive, scarce Pt-based electrocatalysts with non-precious metal or metal-free materials for the ORR. Among the classes of potential electrocatalysts, transition metal and heteroatom such as nitrogen co-doped carbon structures (M-N-C ; M=Fe and or Co) represent most promising catalytic activity, approaching that of Pt-based catalysts. In the M/N/C catalysts, active species are widely accepted as a porphyrinic M-N_x site. The design of high-performance M.N/C catalysts requires the generation of high density active sites, high electrical conductivity, and porous structures.

During the last few years, our group has endeavored to develop high-performance ORR electrocatalysts using macrocyclic compounds as precursors for M/N/C catalysts [1-7]. In this presentation, I will show some examples of M/N/C catalysts. We have prepared transition metal-doped ordered mesoporous porphyrinic carbons (M-OMPC) with high surface areas and tunable pore structures by nanocasting mesoporous silica templates with metalloporphyrins. Among the resulting catalysts, the FeCo-OMPC catalyst exhibited an excellent ORR activity in an acidic medium, which is higher than other non-precious metal catalysts. It showed higher kinetic current at 0.9 V and superior long-term durability and MeOH-tolerance than Pt/C catalyst. The use of Ni- and Fe-phthalocyanines as precursors during the nanocasting process yielded NiFe-doped graphitic nanoshell/mesoporous carbon compoiste structures, which show very high bifunctional catalytic activity both for oxygen reduction and evolution reactions. Finally, nanohybrid catalyst comprising CNT wrapped with porphyrinic carbon layer (CNT/PC) will be presented. The CNT/PC catalysts show very high activity for the ORR in both acidic and alkaline electrolytes. Significantly, they show record high performances in alkaline fuel cells among non-precious metal catalysts-based fuel cells.

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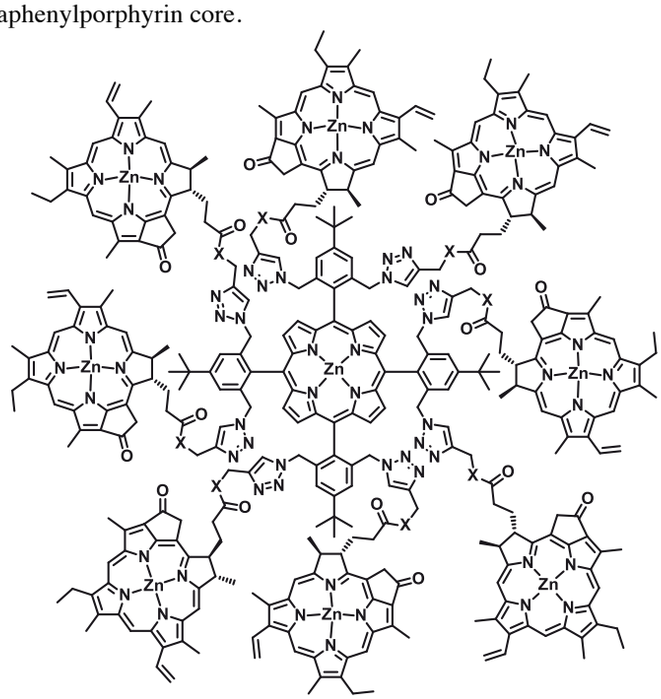
Novel pyropheophorbide a conjugates

Norbert Jux, Kathrin Eder, Helen Hölzel

Friedrich-Alexander-Universität Erlangen-Nürnberg, Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials

Oligoporphyrins have become of major interest due to their inherent photophysical and -chemical properties. We have synthesized series of oligo-pyropheophorbide systems with central [60]fullerene units,[1] including an antibody conjugate,[2] and studied their properties. Here, we wish to present a new series of compounds with a highly functionalized tetraphenylporphyrin core.



X = O, NH

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Electrochemistry of corroles. New insights into the redox reactions of a not so new molecule

Karl M. Kadish,[a] Xiangyi Ke,[a] Lei Cong,[a] Xiaoqin Jiang,[a] Wenqian Shan,[a] Yang Song,[a] Yuanyuan Fang,[a,b] Zhongpin Ou[a,b]

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Although the first electrochemistry of corroles was published more than four decades ago, it wasn't until recent years that numerous studies of these compounds began to appear in the literature. In general, corroles are harder to reduce and easier to oxidize than the structurally related porphyrin analogues but it is not clear if the two series of compounds should exhibit a similar HOMO-LUMO gap and a similar effect of substituents, for example when comparing derivatives of tetraphenylporphyrins and triphenylcorroles. There is also the question of how many reductions and how many oxidations might be expected to occur under optimum conditions in non-aqueous media. These questions are addressed in the current paper with examples being provided for several series of compounds, including those of the type shown in Chart 1.

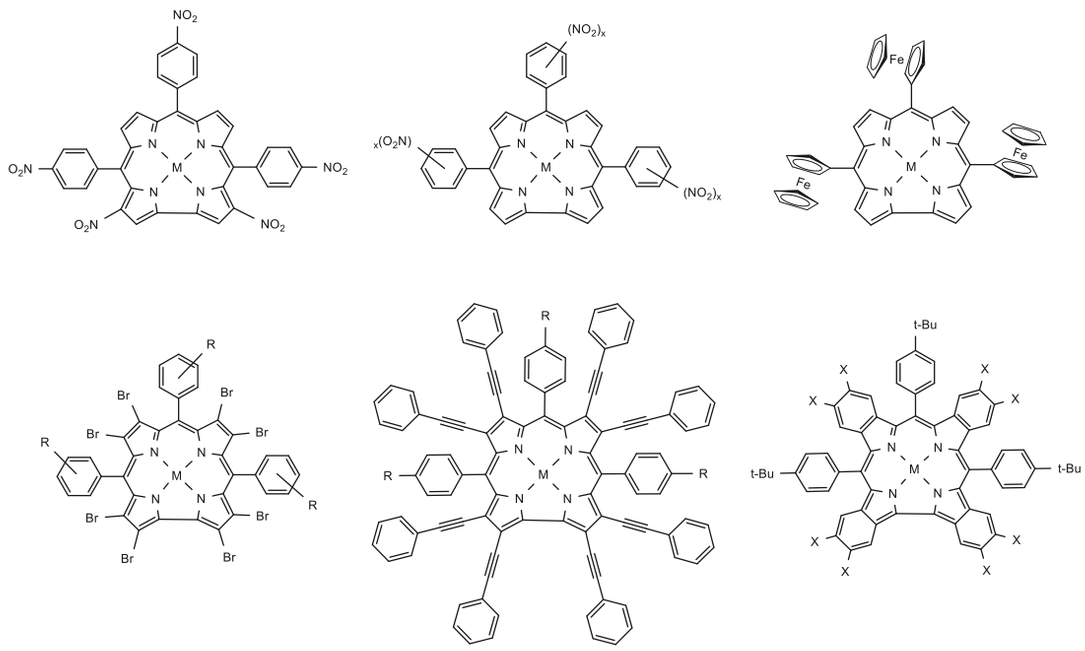

Chart 1. Selected structures of investigated corroles

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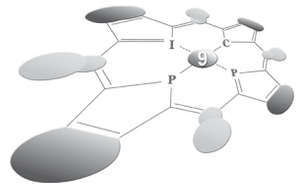

Redox-controlled molecular assemblies: a new porphyrin-based molecular tweezer

C. Kahlfuss,[a,c] E. Dumont,[a] E. Saint-Aman,[b] and C. Bucher [a]

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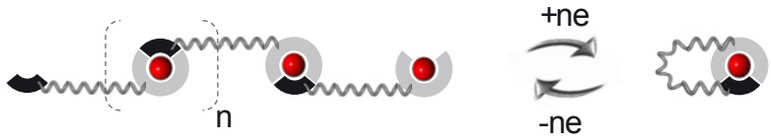
[b]*Département de Chimie Moléculaire (UMR5250), UJF/CNRS, Grenoble-France;*
[c]*Institut de Chimie de Strasbourg (UMR7177), UdS/CNRS, Strasbourg-France.*

The ability to control the structure and organization of molecular materials has emerged in the past decade as a major scientific objective that is mainly motivated by exciting foreseeable applications in nanoscience. Enormous technologic interests are indeed at stake in being able to devise molecular objects that could respond to external stimuli by changes in structure and function. These particular properties can lead to applications in various domains as (i) in molecular electronics, (ii) in analytic science, with switchable hosts allowing the controlled binding/release of pollutants or drugs, (iii) in materials science with the development of adaptive supramolecular polymers. One of our major research areas is focused on the use of π-radicals as building blocks for electron-responsive molecular materials and organized assemblies.[1-4]
In this lecture, the synthesis and detailed physico-chemical properties of a porphyrin based switchable molecular tweezer whose movements are triggered by electrochemically driven self-assembly of organic radicals will be presented. These molecular movements allowed to control both the binding/release of guest molecules and the degree of organization within self-assembled coordination polymers.[5,6] The dynamic properties of these redox-responsive molecular architectures and molecular materials will mainly be discussed on the basis of electrochemical, spectroelectrochemical and ESR experiments supported by quantum chemical calculations.



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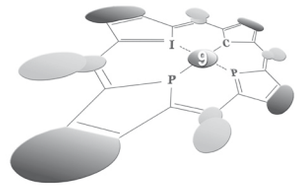

The Molecular Evolution of Heme: From Quantum Spin Crossover to Myoglobin in Diving Mammals

Kasper P. Kepp[a]

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The Porphyrin molecule is one of the most amazing accomplishments of molecular evolution, and the delicately tuned ligand works in a nearly perfect harmony with its central metal ions to fulfil some of the most difficult and vital processes of the biosphere [1].
The electronic properties of porphyrin and heme that produce the unique function of porphyrin are now well-understood; these properties are discussed, with special emphasis on O_2 binding and spin crossover, and the reasons for the success of this ligand system are explained [2−4]. Particular emphasis is given to the nature of the electronic FeO_2 adduct in oxyheme [5], and the "broad crossing mechanism" that explains how small ligands can bind fast and reversibly to iron porphyrins despite the small spin orbit coupling of iron [1,6].
At the end of the talk, the importance of porphyrin is exemplified by a recent case study on the role of myoglobin in deep-diving mammals such as whales [7,8].

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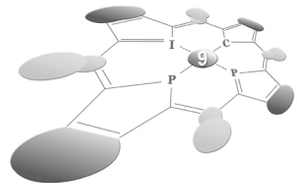

Synthesis, Spectroscopy and Nonlinear Optical Properties of Nickel Binuclear Phthalocyanine Complexes

Grace Ngubeni[a], Kapambwe Kabwe[a], Jonathan Britton[a] and Samson Khene[a]

[a]*Rhodes University, South Africa.*

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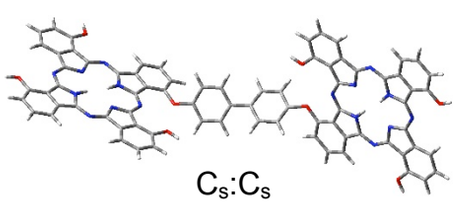

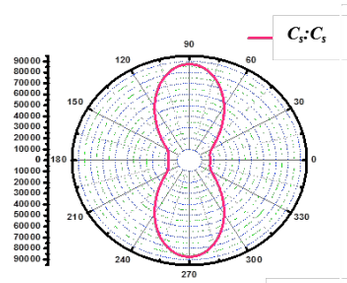

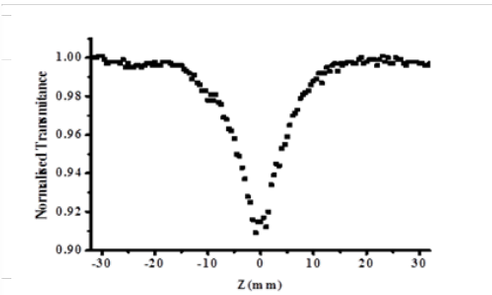

Considerable effort has been dedicated to the synthesis of novel phthalocyanines (Pcs), with the aim of improving their functional properties. Monomeric and low symmetry Pcs have been largely studied with the aim of optimising their second order nonlinear optical (NLO) properties for applications in practical area such as telecommunication systems, high speed electro-optic switching, data processing and optical limiting [1]. This work studies the second order hyperpolarizability (β) of binuclear phthalocyanines (Bi-Pcs) in order to further contribute to the study of NLO of Pcs in general. Multinuclear Pcs have shown potential of improving β values [2]. Furthermore low symmetry phthalocyanines are known to possess a variable dipolarity to octupolarity ratio [3], which contributes to the measured second order β values.

In this work the Z-scan technique has been employed to comparatively study the second order nonlinear optical (NLO) properties of nickel and metal free β and α -tert-butylphenoxy phthalocyanine (Pc) and their corresponding biphenyl bridged bis-β-tert-butylphenoxy phthalocyanine (β-BiPc) and biphenyl bridged bis-α-tert-butylphenoxy phthalocyanines (α-BiPc). This work shows that the presence of H-aggregation in metal free and nickel complex of β-BiPc and α-BiPc do not have a significant effect on second order nonlinear absorption coefficient (β) as compared to monomeric Pcs. Density functional (DFT) calculations of dipolar/octupolar contribution were performed, in order to explain the experimentally determined β value trend. Spectroscopic and photophysical properties of the synthesised compounds have been studied using a range of different spectroscopic techniques, including magnetic circular dichroism (MCD), time correlated single photon counting spectroscopy (TCSPC), and UV-visible absorption spectroscopy.

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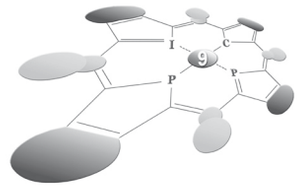

Real-time Intravital Imaging of pH Variation Associated with Osteoclast Activity Using BODIPY Based Two Photon Excitation Probes

Kazuya Kikuchi[a], **Hiroki Maeda**[a], **Toshiyuki Kowada**[a], **Junichi Kikuta**[b], **Masayuki Furuya**[b], **Shin Mizukami**[a], **Masaru Ishii** [b]

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[b]*Department of Immunology and Cell Biology, Graduate School of Medicine, Osaka University, Suita, Osaka 565-0871, Japan*

Intravital imaging by two-photon excitation microscopy (TPEM) has been widely utilized to visualize cell functions. However, small molecular probes (SMPs) commonly used for cell imaging cannot be simply applied to intravital imaging because of the challenge of delivering them into target tissues, as well as their undesirable physicochemical properties for TPEM imaging. Here, we designed and developed a functional SMP with an active-targeting moiety, higher photostability, and fluorescence switch, and imaged target cell activity by injecting the SMP into living animals. The SMPs are based on BODIPY structure which is optimized for photostability and for fluorescence wavelenghth overlap for multicolor imaging. The combination of the rationally designed SMP with a fluorescent protein as a reporter of cell localization enabled quantitation of osteoclast activity and time-lapse imaging of its *in vivo* function associated with changes in cell deformation and membrane fluctuations. Real-time imaging revealed heterogenic behaviors of osteoclasts *in vivo* and provided insights into the mechanism of bone resorption.

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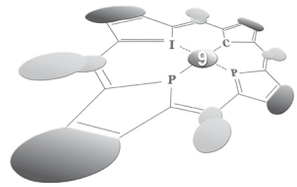

In Vivo Multiscale Photoacoustic Based Theraonstics

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[a]*Associate Professor of Creative IT Engineering (Primary), Mechanical Engineering, Electrical Engineering, Interdisciplinary Bioscience and Bioengineering, Pohang University of Science and Technology (POSTECH), 208 C5, POSTECH, Pohang, Gyeongbuk, Republic of Korea*

Abstract: High-resolution volumetric optical imaging modalities, such as confocal microscopy, two-photon microscopy, and optical coherence tomography, have become increasing important in biomedical imaging fields. However, due to strong light scattering, the penetration depths of these imaging modalities are limited to the optical transport mean free path (~1 mm) in biological tissues. Photoacoustic imaging, an emerging hybrid modality that can provide strong endogenous and exogenous optical absorption contrasts with high ultrasonic spatial resolution, has overcome the fundamental depth limitation while keeping the spatial resolution. The image resolution, as well as the maximum imaging depth, is scalable with ultrasonic frequency within the reach of diffuse photons. In biological tissues the imaging depth can be up to a few centimeters deep.

In this presentation, the following topics of photoacoustic imaging will be discussed[1-7]; (1) multi-scale photoacoustic imaging systems (i.e., Photoacoustic Nanoscopy, Optical-Resolution Photoacoustic Microscopy, Fast 2-Axis MEMS based Optical-Resolution Photoacoustic Microscopy and Endoscopic Probe, Intravascular Photoacoustic/Ultrasound Catheter, Virtual Intraoperative Surgical Photoacoustic Microscopy, Acoustic-Resolution Photoacoustic Microscopy, Clinical Photoacoustic/Ultrasound Scanner), (2) morphological, functional, and molecular photoacoustic imaging, (3) potential clinical applications, and (4) contrast agents for photoacoustic imaging.

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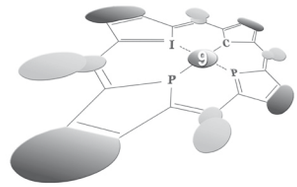

Spectroscopic Evidence for Baird's Rule: Janus-faced Hexaphyrins

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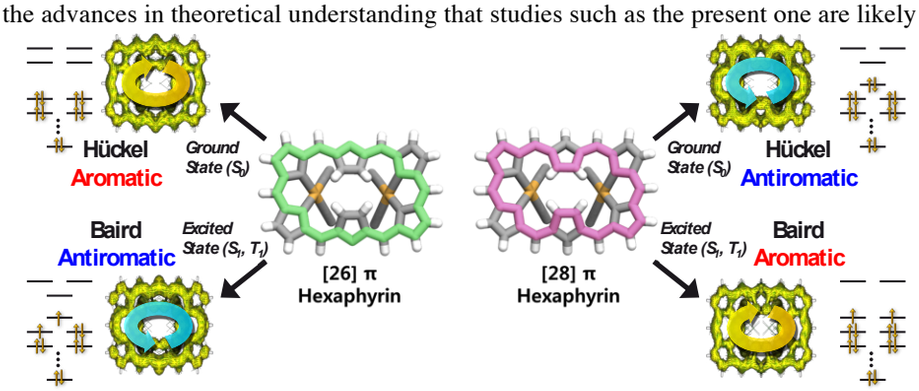
The presentation will demonstrate the spectroscopic evidence for reversal of aromaticity in the singlet excited state as well as the lowest triplet state. Reversal of aromaticity of annulenes in the lowest triplet state, or Baird's rule, one of the most interesting concepts in the field of physical organic chemistry, has been postulated for the past few decades with the aid of theory and quantum calculations, while its verification through experimental methods remains as a long-cherished goal for chemists. In this presentation we have illustrated aromaticity reversal of hexaphyrins in the first singlet excited state as well as the lowest triplet excited states (T_1-states) by means of various spectroscopic measurements. In the ground state, aromatic hexaphyrins exhibit a sharp Soret-like band and distinct Q-like bands characteristic of an aromatic porphyrinoid, while antiaromatic hexaphyrins exhibit a broad absorption spectrum without Q-like bands as typical for an antiaromatic porphyrinoid. In contrast, both singlet and triplet excited state absorption spectra of aromatic hexaphyrins exhibit broad and weak spectral features, while those of antiaromatic hexaphyrins display an intense and sharp Soret-like band. These spectral changes in the excited states provide direct experimental evidence of aromaticity reversal of hexaphyrins in the excited state. Furthermore, magnetic and topological indices of aromaticity such as nucleus-independent chemical shift (NICS) and harmonic oscillator model of aromaticity (HOMA) values for hexaphyrins also suggest that their aromaticity in the excited states become reversed. On the basis of the present findings, we suggest that the ability to manipulate (anti)aromaticity through selection of a desired electronic state, ground state or excited state, will provide a new tool for modulating the chemical features and reactivity of highly conjugated systems. Detailed studies of the modulation events are expected to provide additional fruitful insights into the relationship between (anti)aromaticity and electronic structure. Ultimately, this line of investigation could lead to the development of fast saturable absorbers, novel molecular magnets and photo-switchable devices that operate in both the visible and near-IR regions. To the extent this proves true, it could have far-reaching practical applications that complement the advances in theoretical understanding that studies such as the present one are likely to provide.



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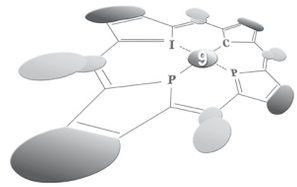

Z-form Poly[d(A-T)$_2$] Induced by a Cationic Porphyrin

Seog K. Kim[a] **and Yoon Jung Jang**[b]

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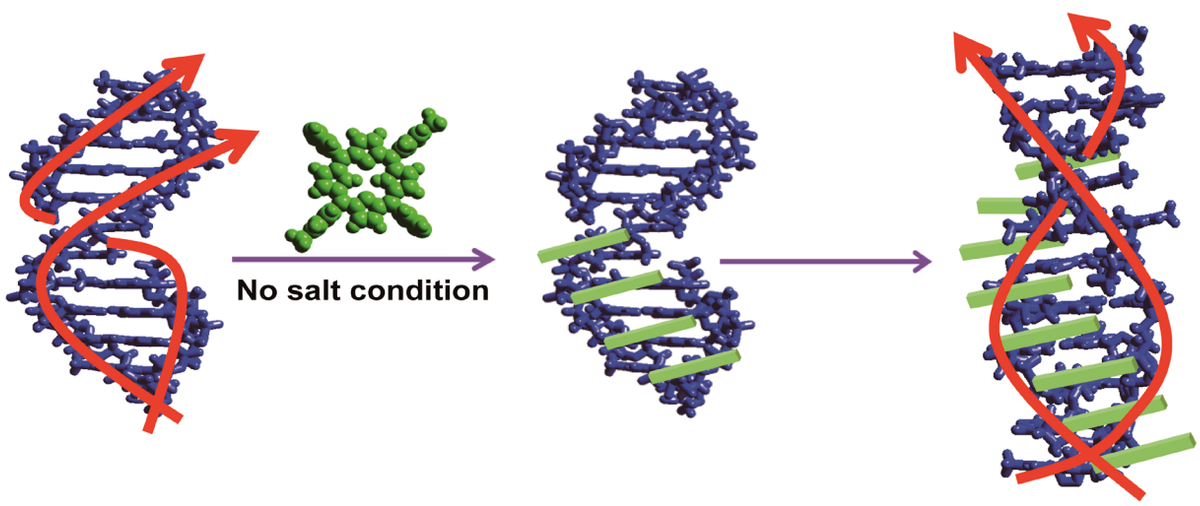
Trans-bis(*N*-methylpyrimidium-4-yl)diphenyl porphyrin (*trans*-BMPyP) induced the B-Z transition for alternated AT oligonucleotides. Typical CD spectrum of the right-handed poly[d(A-T)$_2$] was reversed when *trans*-BMPyP was bound. A single ^{31}P peak of B-form poly[d(A-T)$_2$] was split into two peaks, which is similar to the conventional B-Z transition of poly[d(G-C)$_2$]. All these observations indicated that the helicity of the polynucleotide was reversed to the left-handed form. The transition occurred simultaneously with appearance of the extensive stacking of porphyrin and complete B-Z transition required at least 14 base-pairs long. Insertion of one or two GC base pairs to AT oligonucleotide prevented the B-Z transition. The other polynucleotides, including poly[d(G-C)$_2$], poly(dG)·poly(dC) and poly(dA)·poly(dT) remained as the right-handed form in the presence of the same porphyrin. This observation suggests that the porphyrin array that was formed along the poly[d(A-T)$_2$] provides a template to which left-handed poly[d(A-T)$_2$] is associated with an electrostatic interaction.



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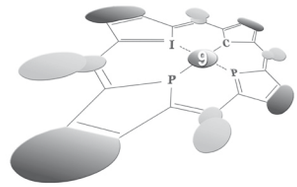

Structural characterization of Cytochrome P450 intermediates by Resonance Raman Spectroscopy

James R. Kincaid

Marquette University, Milwaukee, Wisconsin 53233

The mammalian Cytochrome P450 enzymes (CYPs) participate in a vast array of important physiological functions through the involvement of potent oxidizing intermediates capable of epoxidation or hydroxylation of even relatively inert substrates. Defining the structural dynamics of reactions involving these enzymatic intermediates continues to be one of the most challenging and important goals of heme protein research. In addition to the drug-metabolizing CYPs that metabolize most known pharmaceuticals and other xenobiotics, the steroidogenic CYPs collectively orchestrate the transformation of cholesterol into steroid hormones through the involvement of highly stereo- and regio-specific reactions ultimately yielding the corticoids, androgens, and estrogens. While many spectroscopic techniques have been effectively applied to study heme proteins, the impressive potential of resonance Raman (rR) spectroscopy for interrogating so many aspects of heme structure makes it a remarkably powerful technique to address many unresolved, but pressing issues related to these P450 enzymes. When coupled with the clever cryoradiolytic methods introduced by Symons and elegantly refined by Hoffman and coworkers, rR spectroscopy facilitates documentation of the essential nature of the terminal and intermediate states that arise during the course of an enzymatic pathway, revealing functionally significant structural changes induced by interactions of the enzyme with different substrates, effectors or redox partners. While these powerful techniques hold promise for the application to *mammalian* P450s, their study is sometimes compromised by the tendency of these membrane-bound enzymes to aggregate in solution in undefined and uncontrolled ways. However, such complications can be effectively eliminated by the application of the "nanodisc" sampling technology pioneered by Stephen Sligar and his group, an environment which closely mimics the native biological membrane. This presentation will focus on our most recent efforts, employing all of these powerful techniques, to characterize the structure and function of several physiologically important human cytochromes P450.

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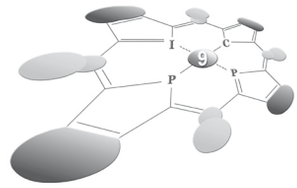

Tetrapyrrole-based Metal Complexes Designed for Bio-inspired Catalysis and Solar Fuel Production

Günther Knör

Johannes Kepler University Linz (JKU), Institute of Inorganic Chemistry, 4040 Linz, Austria

Light-induced substrate transformations in artificial photosynthetic devices and functional enzyme model systems strongly depend on the feasibility of multielectron transfer catalysis [1,2]. The crucial advantage of coupling multiple redox equivalents and proton transfer steps in photocatalysis is to avoid free radical reaction pathways and energetic constraints due to charge accumulation, as these processes can decrease both the long-term stability and the efficiency of the corresponding systems. In this context, certain coordination compounds including tetrapyrrole-based derivatives such as porphyrin, corrole and phthalocyanine complexes have been shown to achieve an efficient fusion of the complementary functions of a light-harvester, a photoredox interface, a substrate recognition site and a mediator for chemical reactions [3-6].

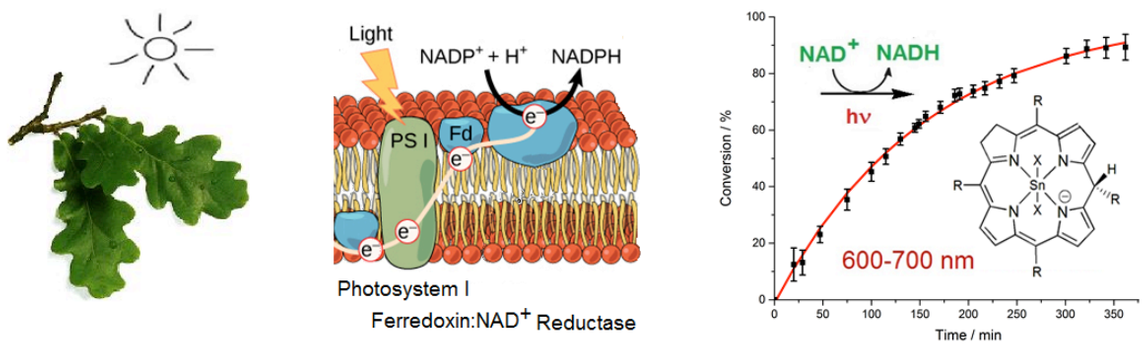

Fig 1. Artificial Photosynthesis: Functional replacement of the complete light reactions of natural PSI [2,4].

To further improve the performance of such systems, the design of long-term stable processes for artificial photosynthetic energy storage and green synthetic chemistry using artificial (photo)enzymes has to be achieved with sustainable, environmentally benign and earth-abundant bulding blocks. Another crucial aspect in the context of solar chemistry and catalysis is not only the requirement for using visible light, but also to shift the threshold wavelength of the photosensitizers as far as possible to the red and NIR-spectral regions. Some of our recent developments in this direction will be presented in this contribution.

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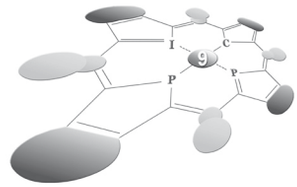

Investigation of the Dimerization Reaction of Phthalonitrile with Thiolate Anion and Its Application to the Synthesis of Expanded Phthalocyanines

Nagao Kobayashi,[a,b] Takehito Sato,[b] Taniyuki Furuyama,[b,c]

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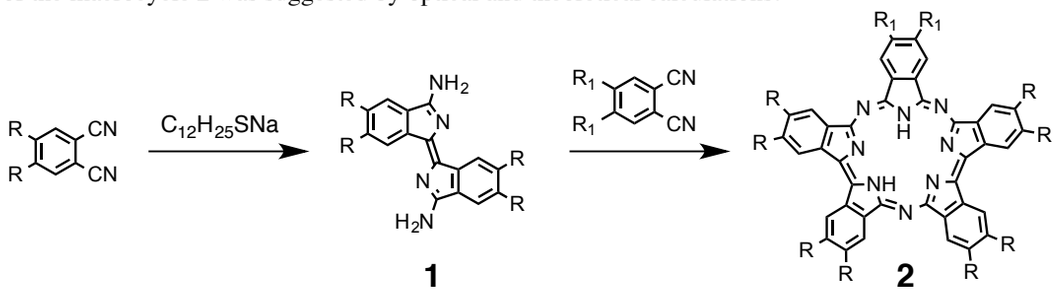
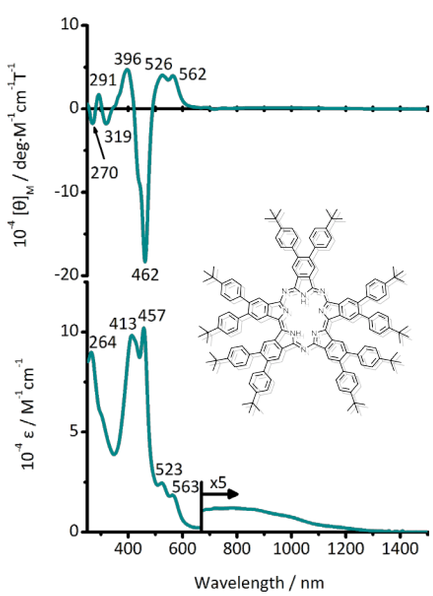
[c] *Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa, 920-1192, Japan*

Pentabenzotriazasmaragdyrin (PBTAS) **2**, the first example of an antiaromatic expanded phthalocyanine (Pc), classified as a norcorrole of a superphthalocyanine has been prepared and fully characterized.[1] The newly developped phthalonitrile dimerization reaction was a crucial step, which allowed for the bottom-up synthesis of expanded Pcs. Their structure was confirmed by single crystal X-ray difraction analysis. The 20π antiaromaticity of the macrocycle **2** was suggested by optical and theoretical calculations.





Thus, the thiolate anion, generated from dodecanthiol and sodium, was reacted with 4,5-disubstituted phthalonitrile, produced isolabile orange-colored dimeric **1** precursor. The condensation between **1** and phthalonitrile derivative gave **2** in ca. 14-20% yields depending on the substituent. The absorption spectrum of **2** (Fig. 1) is characteristic in that it has a very weak and broad absorption in ca. 700-1200 nm, two weak peaks in ca. 500-600 nm, and two intense bands in ca. 360-460 nm. These are interpreted using Michl's 4n-electron perimeter model, i.e. transitions between six orbitals from HOMO-2 to LUMO+2..[2]

Fig. 1. Electronic and MCD spectra of **2** (R=tBuPh) in CH_2Cl_2.

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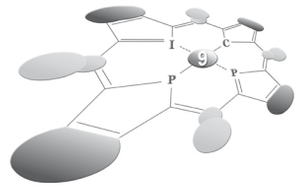

Diporphyrin Nanotweezers and Nanocalipers for Optical Resolution of Single-Walled Carbon Nanotubes

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We have been developing host-guest methodology for separation of single-walled carbon nanotubes (SWNTs). Tweezer- and caliper-shape host molecules, designated as diporphyrin nanotweezers and nanocalipers respectively, consist of two chiral porphyrins and rigid spacer in between (Fig. 1). They discriminate handedness, diameter, roll-up index, and even metalicity. Since the first report about optically active SWNTs [1], we have improved selectivity of the host molecules by changing the angles and distances of the two porphyrins [2-7].

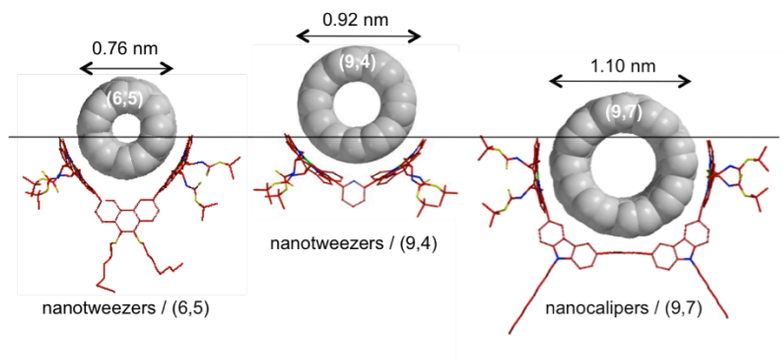

Fig. 1 SWNT complexes with nanotweezers and nanocalipers

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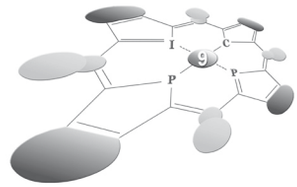

Electronic structure of metal-phthalocyanine and –corrole complexes from first principles

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Metal-porphyrins, - phthalocyanines, and –corroles pose significant challenges to first principles theory, often due to competition between different electronic configurations and the need to describe localized and delocalized electronic states on the same footing. Complexes based on such molecules pose additional difficulties, as weak dispersive interactions must also be accounted for. Here, I will present our recent progress on these issues, with an emphasis on quantities that can be verified experimentally via spectroscopy. I will focus on optimally-tuned range-separated hybrid density functionals, pair-wise dispersive corrections, and many-body perturbation theory. I will present applications to specific systems and discuss successes and remaining challenges.

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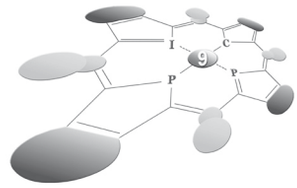

Optical properties of free base *meso*-triarylcorroles

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Corroles, contracted tetrapyrrolic macrocycles lacking one *meso*-carbon atom, have emerged as attractive porphyrinoid materials, notably during the past decade, in which novel synthetic pathways toward *meso*-triaryl-substituted corroles and numerous postmacrocyclization functionalization protocols have considerably extended the scope of available corrole structures and their potential applications. The absence of one *meso*-carbon bridge changes the bond alternation pattern in the corrole macrocycle. Noticeable distortions from planarity have been observed for free base corroles, even in the absence of overcrowding peripheral substitution, due to the decreased core size and steric hindrance preventing the three inner pyrrolic NH protons to be positioned in the same macrocyclic plane. These structural features result in a lower symmetry of the free base corrole macrocycle compared to porphyrins (C_s vs D_{2h}), and two corrole NH tautomers have been identified and characterized.
Free base corroles have remarkable optical properties [1-6]. The excitation energy deactivation rates and pathways were found to depend on the NH tautomerization process and acid-base equilibria, and can be tuned over a wide range by temperature and solvent. These features allow to designate corroles as macrocycles with flexible optical properties with respect to fluorescence and phosphorescence yields and rates, intersystem crossing yield, etc. In this presentation, a general overview of the optical properties of free base *meso*-triarylcorroles is presented and discussed.

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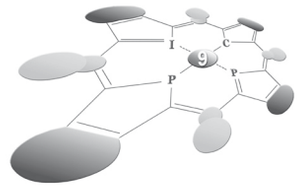

Novel Organometallic B_{12}-Chemistry

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Due to their exceptional structural properties and unique chemical reactivity [1-3], vitamin B_{12}-derivatives have always been fascinating. Amazingly, the important corrinoids are biosynthesized by certain procaryotes only [4]. Thus, the many B_{12}-dependent organisms have developed complex systems for B_{12}-uptake and cellular transport [5, 6]. The carriers and receptors involved here, may also help shuttling-in unnatural B_{12}-derivatives, such as those that eventually carry a toxic load and act as 'Trojan Horses' [7].
The cofactor roles of the natural B_{12}-derivatives are largely associated with their redox-properties and their organometallic reactivity [3,8]. Formation and cleavage of the organometallic bond of B_{12}-cofactors are essential for catalysis by B_{12}-dependent enzymes [3]. Enzymatic cleavage of the 'upper' axial group is critical for intracellular 'tailoring' of B_{12}-derivatives for their biological tasks [5, 9]. We have recently introduced organometallic B_{12}-derivatives that resist these latter processes [9,10] and that may, hence, act as 'antivitamins B_{12}' [11, 12].
This lecture will present synthetic approaches, structural properties and chemical reactivity of some novel organometallic B_{12}-derivatives that have been designed to explore B_{12}-biology in humans and animals.

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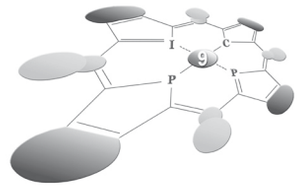

Porphyrin Dimers as Fluorescent Dual-Mode Viscosity and Temperature Sensors

Marina K. Kuimova[a]

[a]*Chemistry Department, Imperial College London, London, United Kingdom*

Viscosity is an important characteristic of a microenvironment, which determines properties of materials and controls the rates of processes on the microscopic scale. Detection of the fluorescence of molecular rotors has secured its place as a technique that allows imaging of viscosity in heterogeneous samples.[1] The viscosity sensitivity of such fluorophores is typically brought about by the interplay between 'bright' and 'dark' excited states, which is controlled by the rate of intramolecular rotation. We have established that porphyrin dimers, which are deep-red emitting molecular rotors, are capable of measuring changing viscosity in cells and in lipid membranes.[2-3] Furthermore, we have demonstrated that viscosity can be measured both ratiometrically by using its fluorescence spectra, as well as by its fluorescence lifetime.[3] Dual imaging probes are rare and offer several advantages while imaging.

We have also examined the effect of temperature on the photophysical behaviour of porphyrin dimers. We have confirmed that their ratiometric calibration in various viscosity mixtures at different temperatures is temperature independent. In stark contrast, their fluorescence lifetimes are dependent on both viscosity and temperature. Thus we provide a protocol whereby both ratiometric and lifetime measurements of a porphyrin dimer can be taken sequentially and used to determine simultaneously the viscosity and temperature of the system under study, in a spatially and time-resolved manner.[4] To the best of our knowledge, this is the only example of a fluorophore with dual functionality for imaging temperature and viscosity simultaneously.

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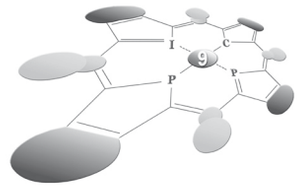


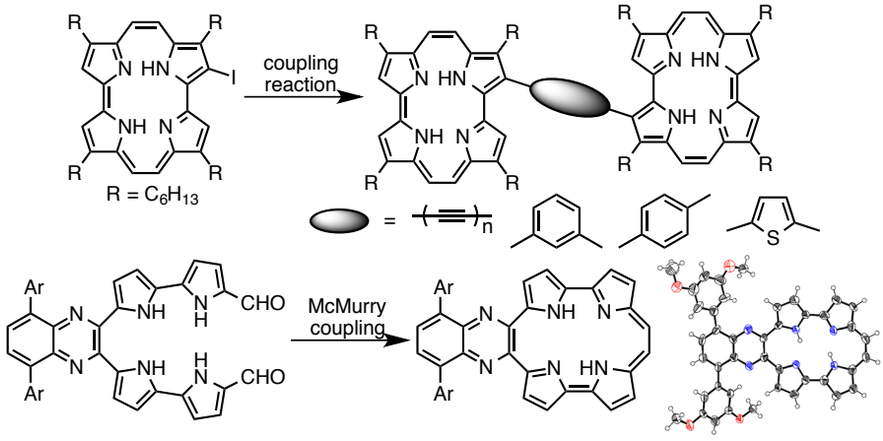
Functionalized Porphycenes for Organic Electronics

Daiki Kuzuhara,[a] Takuya Okabe,[a] Mika Sakaguchi,[a] Naoki Aratani,[a] Hiroko Yamada[a,b]

[a]*Graduate School of Materials Science, Nara Institute of Science and Technology, Japan*
[b]*CREST, JST*

Porphycene is a first reported constitutional isomer of porphyrin. The structure of porphycene consists of two direct bonds and two ethynyl bridges between neighboring pyrroles. Porphycene has characteristics of lower LUMO and narrower HOMO-LUMO difference compared with those of porphyrin, inducing intense absorption bands in the visible to near infra-red regions. This optical nature can be utilized for the multi-photon absorption for various applications and for photosensitizers of photodynamic therapy. On the other hand, we have developed the synthesis of functionalized porphycenes toward organic electronics. We realized that porphycenes have potentials to show ambipolar semiconductor characters. In this presentation we will present investigations of multi-porphycene systems and quinoxalin-attached porphycenes applied for the organic solar cells.

We have reported selective iodination reactions of porphycene with *N*-Iodosuccinimide (NIS) in the presence of additives to produce the mono- or di-iodinated porphycenes as useful building blocks.[1] The dimeric porphycenes with varied linkages were prepared from iodinated porphycene by cross-coupling reactions. In addition, we found that the dimeric porphycenes were employed as an n-type material for organic solar cells with p-type polymer materials. The other is quinoxaline-fused porphycene at *meso*-positions, since the quinoxaline-fused porphycene was predicted to significantly reduce the LUMO level by DFT calculation. The quinoxaline-fused porphycenes were prepared by an intramolecular McMurry coupling. In this presentation we will report the details of synthesis, optical and electrochemical properties, and device performances of these porphycene derivatives.



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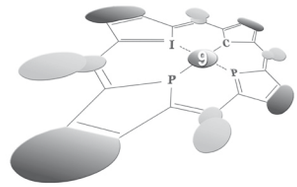

New Porphyrins for Solar Cells

Fernando Langa,[a] Susana Arrechea,[a] Pilar de la Cruz,[a] and Gabriela Morán[a]

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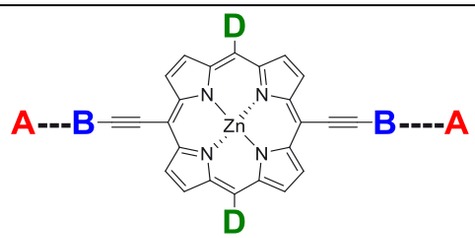
Along the last years, significant improvements have been made in the molecular design of porphyrins as small molecules for BHJSC and the devices have been optimized to enhance the power conversion efficiency,[1] therefore these cells have developed high JSC and high VOC.

Here, we will present the design, synthesis and characterization of new families of functionalized porphyrins with the configuration A-π-D-π-A, as well as the photophysical properties of these novel conjugates, to analyze their performance in Bulk Heterojunction Solar Cells (BHJSCs), and the effect in the performance devices, changing the porphyrin core, the acceptor and the π conjugation linker of the structures.[2,3]



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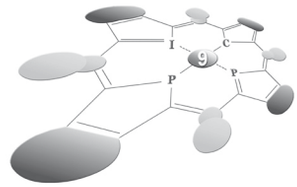
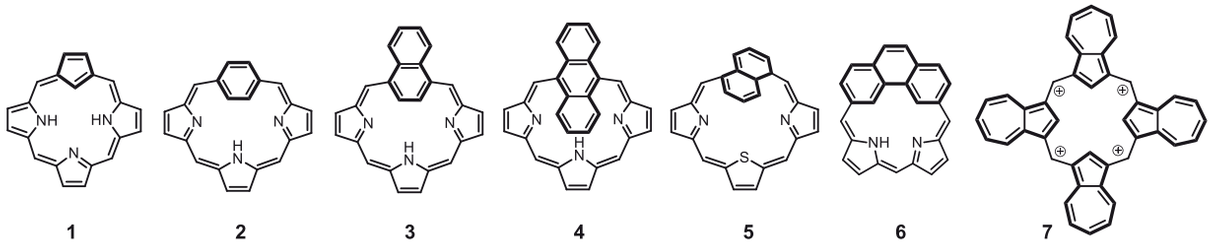


Aceneporphyrinoids: Synthesis and Transformations

Lechosław Latos-Grażyński

Department of Chemistry, University of Wrocław, POLAND

Redesign of archetypical porphyrin frame to create aceneporphyrinoids, realized through replacement of pyrrolic rings with other heterocycles or carbocycles, creates the innovative routes for exploration of coordination and organometallic chemistry confined in macrocyclic environments. Aceneporphyrinoids combine the structural features of polycyclic aromatic hydrocarbons and polypyrrolic macrocycles.[1] Here the hybrid compounds are exemplified by 21-carbaporphyrin **1**, *para*-benziporphyrin **2**, 1,4-naphthiporphyrin **3**, *meso*-anthriporphyrin **4**, 1,5-naphthiporphyrin **5** and phenathriporphyrin **6**. Polycarbocation confined in frames of thiatriazuliporphyrin or tetrazuliporphyrin **7**, treated as representative examples of tri- or tetracabaporphyrinoids, are also included into the analyzed class. In general such carbaporphyrinoids reveal peculiar electronic and molecular facets forcing atypical coordination modes and unique intramolecular reactivity.[1-5]



For instance a detected contraction of *m*-phenylene or *p*-phenylene to cyclopentadiene, triggered by insertion of rhodium(III) into *meta*- or *para*-benziporphyrins, affords rhodium(III) 21-carbaporphyrin (**1**-Rh) which incorporates and stabilizes the rhodacyclopropane motif. The reversible transformations of bridging methylene, provides an example of selective and reversible aliphatic C-H bond elimination. The contraction belongs to an exclusive group of reactions where the cleavage of aromatic structure is of fundamental importance.[4;5]

The amalgamation of phenanthrene moiety into porphyrin framework results in a hybrid macrocycle – antiaromatic phenanthriporphyrin **6** and related expanded carbaporphyrinoids.[1] The distinctive inner core of phenanthriporphyrin consists of two carbon donors prearranged for simultaneous coordination of phenanthrene and two pyrrolic nitrogen atoms as unambiguously demonstrated by insertions of small cations to form hypervalent organophosphorous or copper(III) derivatives. The activation of inner carbon atoms facilitates the transformation of **6** to pyreneporphyrin.

In more general terms aceneporphyrinoids are expected to generate an insight into a broad spectrum of fundamentally important molecular properties among which are nontrivial optical effects, electron transfer and redox chemistry or three-dimensional aromaticity.

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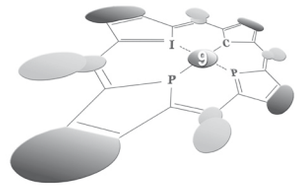

π-Conjugated Oligopyrrolic Macrocycles: Rare Classes of Porphyrinoids

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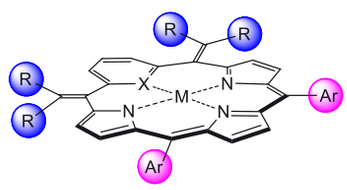
The porphyrinoids and core-modified porphyrinoids that bears exocyclic double bonds at meso-positions have not been well studied. So called, *meso*-alkylidenyl carbaporphyrins and their congeners are rather recently joined porphyrinoid family that have shown unique properties in prototropy, tautomerization, unusual protonation site selectivity and spectroscopic properties. With these regards, we have been working on these systems for the last few years and we here report the chemistry of *meso*-diethyl malonylidene-(m-benzi)porphyrin and *meso*-diethyl malonylidene-(m-benzi)pentaphyrins. The reaction with in-situ generated azomethine ylides and redox reactions. The 1,3-dipolar cycloaddition reaction has well documented and become an important alternative to the synthesis of pi-extended porphyrin analogs. The versatility and synthetic utilities associated with these reactions is useful in the synthesis of pi-extended analogs of the *meso*-alkylidenyl carbaporphyrinoids. The 1,3-dipolar cycloaddition of the corresponding Pd(II) complexes resulted in cyclized adducts which are resistant to DDQ oxidation. All adducts are liable to core N-methylation and all adducts displayed large bathochromic shift of absorption. The chemistry of the *meso*-alkylidenyl carbaporphyrins bearing various number of exocyclic double bonds will be presented.



X = CH, N
M = Pd(II), Ni(II), Ag(I),

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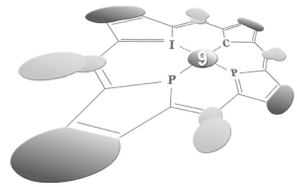

{FeNO}^{6}, {FeNO}^{7} and {FeNO}^{8} Porphyrinates – Structures and Vibrations

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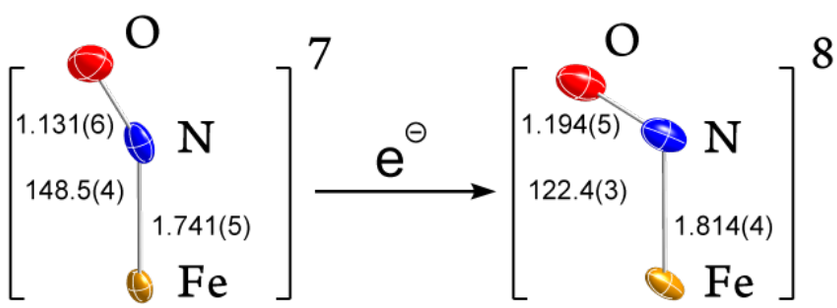
[a]*College of Materials Science and Opto-electronic Technology, University of Chinese Academy of Sciences, Yanqi Lake, Huairou District, Beijing, 101408*

Oriented single-crystal nuclear resonance vibrational spectroscopy (NRVS) has been used to obtain all iron vibrations in two {FeNO}^{6} porphyrinate complexes, five-coordinate [Fe(OEP)(NO)]ClO_4 and sixcoordinate [Fe(OEP)(2-MeHIm)(NO)]ClO_4. Single crystals of both complexes were oriented to be either parallel or perpendicular to the porphyrin plane and/or axial imidazole ligand plane. Thus, the FeNO bending and stretching modes can be unambiguously assigned. DFT calculations were also used to obtain detailed predictions of vibrational modes. Predictions were consistent with the intensity and character found in the experimental spectra. The NRVS data allow the assignment and observation of the challenging to obtain Fe–Im stretch in six-coordinate heme derivatives. NRVS data for this and related six-coordinate hemes with the diatomic ligands CO, NO, and O_2 reveal a strong correlation between the Fe–Im stretch and Fe–N_{Im} bond distance that is detailed for the first time.

The synthesis and X-ray structural characterization of the first, five-coordinate {FeNO}^{8} porphyrin structure $[Co(CP)_2]^+[Fe(TFPPBr_8)NO]^-$ and the five-coordinate nitrosyl precursor [Fe(TFPPBr$_8$)NO] are reported. The comparison of the two 100 K structures suggests significant differences on the axial Fe–NO bond distances and the Fe–N–O angles. The slightly shorter average Fe–N_p bond distance of $[Fe(TFPPBr_8)NO]^-$ is consistent with the DFT predictions and the singlet state of the iron center. Mossbauer measurements confirmed the low-spin state of the two complexes. IR and UV-vis spectra are also reported.



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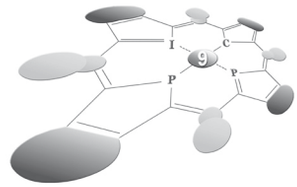


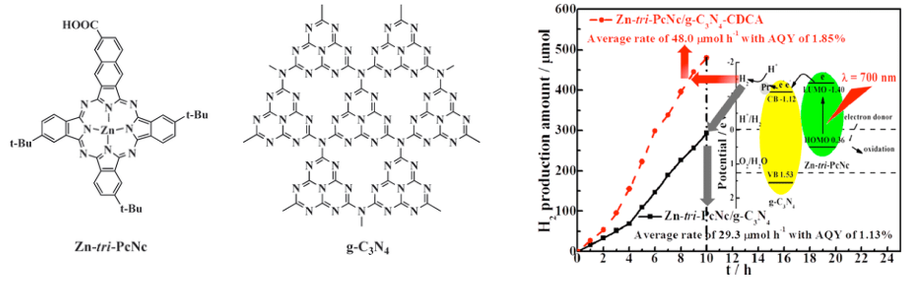
Asymmetric Phthalocyanine as a Sensitizer of Graphitic Carbon Nitride for Efficient Photocatalytic H_2 Production

Yingying Guo, Xiaohu Zhang, Renjie Li*

College of Chemistry and Molecular Science, Wuhan University, Wuhan, China (E-mail:lirj@whu.edu.cn)

In the past decades, enormous efforts have been focused on artificial photosynthesis for H_2 production over semiconductors, which could contribute to a sustainable energy supply and mitigate the increasing energy shortage due to its potential application in the direct production of clean hydrogen energy by using water and inexhaustible solar energy. Up till now, various semiconductors or their composite materials have been used as photocatalysts in order to solve the major problems (such as low visible-light utilization and quantum efficiency) of the promising but challenging technique. Recently, graphitic carbon nitrides (g-C_3N_4) as a novel polymer semiconductor have attracted numerous attentions due to its specific planar structure, physicochemical property and appropriate energy band positions for photosplitting water. However, g-C_3N_4 still has a bandgap as large as 2.70 eV with an absorption edge just at ~450 nm, which restricts the visible-light utilization. Although many efforts such as doping with a non-metallic element and co-polymerization of two or more precursors have been made to modify the physical and electronic structure of g-C_3N_4, the visible-light-responsive ability and photoactivity still need further improvement.

Among the various strategies for visible-light harvesting, dye sensitization is an efficient and widely used route to extend the spectral response region of wide-band-gap semiconductors. However, the mostly used Ru-complex and xanthene dyes hardly extend the spectral response region to longer than 550 nm. Phthalocyanines (Pcs) are a type of chromophore well-known for their intrinsic absorption in the UV/blue (Soret band) and the red/near IR spectral regions (Q-band, centred at □650–800 nm). By using the highly asymmetric Zn-tri-PcNc as a sensitizer of g-C_3N_4, it is found that the photogenerated electrons of the excited Zn-tri-PcNc can efficiently transfer to g-C_3N_4 based on the dynamic time-resolved photoluminescence spectra (TRPS) analyses. Zn-tri-PcNc/g-C_3N_4 with CDCA as coadsorbent exhibits a H_2 production efficiency of 125.2 μmolh^{-1} with a turnover number (TON) of □5008 h^{-1} under visible-light (above 500 nm) irradiation. Moreover, it gives an extremely high apparent quantum yield (AQY) of 1.85% at 700 nm monochromatic light irradiation, which has never been reached by the previous Ru-complexes and xanthenes dyes.



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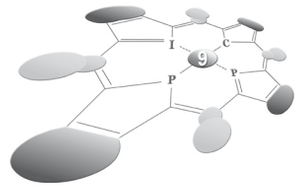

Porphyrins Bearing a Consolidated Anthryl Donor with Dual Functions for Efficient Dye-sensitized Solar Cells[1]

Chin-Li Wang,[a] Min Zhang,[b] Yu-Hsin Hsiao,[a] Chuan-Kai Tseng,[a] Chia-Lin Liu,[a] Mingfei Xu,[b] Peng Wang,[*,b] and Ching-Yao Lin[*,a]

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Three porphyrin dyes with different electron-donating groups were prepared to compare their photovoltaic performance in dye-sensitized solar cells. LWP12 is based on LD31 which has a complicated, piece-together electron-donating group, whereas LWP13 and LWP14 have merged substituents with electron-donating and absorption-broadening abilities. The results in this work suggest that consolidated anthryl donors may be used to design highly efficient photosensitizers.

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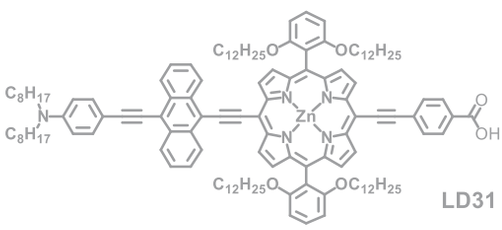

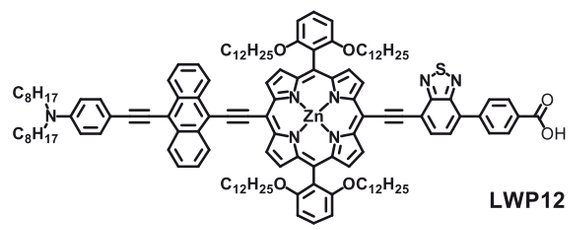

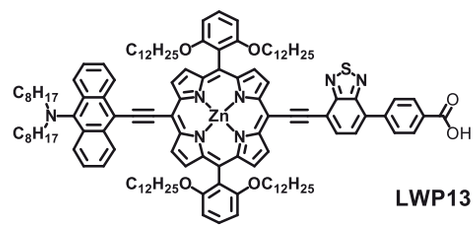

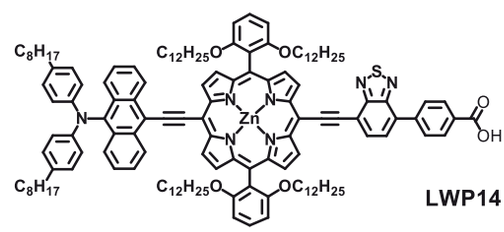

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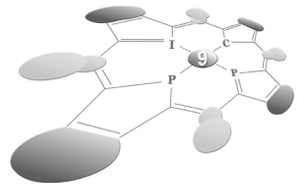

Custom design of novel porphycenes

Arkadiusz Listkowski,[a,b] Natalia Masiera,[a] Paweł Jędrzejewski,[a] Piotr Pawlak,[b] and Jacek Waluk[a,b]

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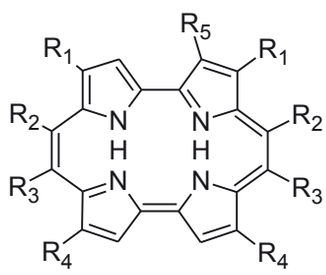
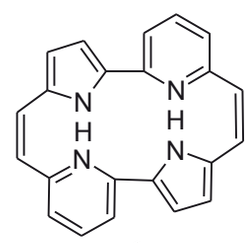
Porphycene is one of the most intensively studied constitutional isomers of porphyrin. In comparison with porphyrin, porphycene exhibits twentyfold larger absorption coefficients in the far-red region, which makes this compound and its derivatives attractive materials for many applications [1]. Their photophysical properties are known to be strongly dependent on the nature and localization of substituents. Some of these characteristics, like dependence of fluorescence intensity on the nature of substituents are so far not well predictable. Detailed investigations on a particular topic require designing of properly substituted derivatives, which allows tuning the electronic, spectroscopic, and photophysical features and affecting such properties like internal hydrogen bond strength or photostability [2,3].
In order to modify the potential governing the tautomerization in a controlled way, we have prepared a set of differently substituted porphycenes (see picture below for some selected examples). Initial studies confirm an astounding influence of the number of methyl substituents located at the *meso* positions on the photophysics. Other manipulations of electronic structure of porphycene led us to its first derivative bearing fluorine atom attached directly to the pyrrole ring. This type of substitution resulted in a strong change in the absorption spectra in comparison with bromine analog: an additional, fourth band appeared in the Q region.



1. R_1= R_2= R_4= R_5= H, R_3= Ph;
2. R_1= R_4= R_5= H, R_2= Me, R_3= Ph;
3. R_1= *t*-Bu, R_2= R_4= R_5= H, R_3= Me;
4. R_1= $(CH_2)_2OMe$, R_2= Me, R_3= R_4= R_5= H;
5. R_1= R_4= *t*-Bu, R_2= R_3= H, R_5= F;



6.

Combining our interest in the nature of hydrogen/proton transfer in porphycene and in such molecules like 2-(2'-pyridyl)pyrrole [4] we have made an additional attempt to obtain a new compound: $2^1H,6^1H$-2,6(2,5)-dipyrrola-1,5(2,6)-dipyridinacyclooctaphane-3,7-diene (**6**), which can be regarded as a non-aromatic dipyridineporphycene.

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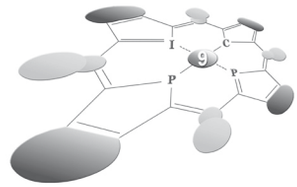

Photocytotoxicity and G-quadruplex DNA interaction of water soluble gallium(III) *tris*(N-methyl-4-pyridyl)corrole complex

Zhao Zhang [a], Jin-Yan Wen [a], Biao-Biao Lv [b], Xu Li [c], Xiao Ying [b], Ya-Jun Wang [c], Hai-Tao Zhang [c*], Hui Wang [d], Hai-Yang Liu [a,d*], C.-K. Chang [e*]

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[d]*State Key Laboratory of Optoelectronics Materials and Technologies, Sun-Yat Sen University, Guangzhou 510275, China.*
[e]*Department of Chemistry, Michigan State University, E. Lansing, MI 48824, USA*

A water soluble cationic gallium corrole, 5,10,15-Tris(N-methyl -4-pyridyl)corrolatogallium(III)(**3**), had been prepared and characterized. Photocytotoxicity of **3** was investigated using Hep G2 cancer cell line. Upon treatment with corrole **3** and irradiation, fragmentation of the tumor cell nucleus was observed, which leads to apoptosis. Flow cytometric analysis clearly showed the efficient induction of apoptotic cell death, and Gallium corrole **3** exhibited high photocytotoxicity towards Hep G2 cancer cells (IC_{50} = 60 nM). Furthermore, the binding behavior of corrole **3** with c-MYC G-quadruplex DNA, a potent target for antitumor drugs, has been investigated by spectroscopic methods and molecular docking simulation.

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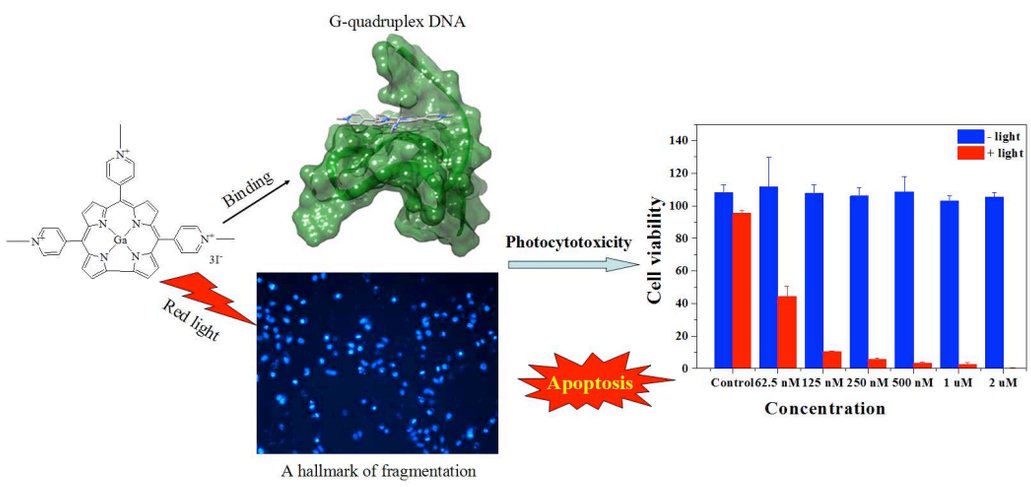

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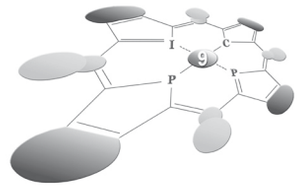

Synthesis, Self-assembly and Aggregations Nanostructures of Moleular Materials Based Porphyrin Unit

Huibiao Liu

CAS Key Laboratory of Organic Solids, Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

A series of molecules based on porphyrin unit are designed and synthesized. We have developed new methods to construct their aggregate nanostructures *via* self-polymerization and self-organization, and a combination of intermolecular interactions and self-assembly techniques based on covalent band, coordination, hydrogen band, π-π interactions.These methods are both facile and reliable, allowing us to produce ordered and aligned aggregate nanostructures, such as large-area arrays of nanorods, and nanoparticles. Large-area ordered aggregate structures exhibit interesting electrical, optical, and optoelectronic properties for applications in next-generation lithium-ion storgae, electronic and optoelectronic devices.

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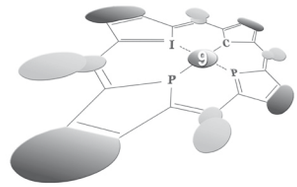

Bio-inspired Heme Model Compounds as Electrocatalysts for Oxygen Reduction Reaction in Polymer Electrolyte Fuel Cells

Jin-Gang Liu*, Ping-Jie Wei, Guo-Qiang Yu, Fei-Fei Wang, Ye-Min Zhao

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The oxygen reduction reaction (ORR) is one of the most important reactions in both life processes and energy conversion systems such as fuel cells.[1] The sluggish nature of ORR kinetics at the cathode is one of the key barriers for H_2–O_2 (air) polymer electrolyte membrane (PEM) fuel cells. The noble platinum (Pt)-based catalysts are predominantly used as the ORR catalysts in low-temperature fuel cells. Due to its high cost and, in particular, the constraints of the sustainable availability of Pt, it is highly desirable to develop earth abundant non-precious-metal catalysts (NPMCs) for the ORR, which is critical for large-scale commercialization of PEM fuel cells.
NPMCs for oxygen reduction have long been intensively investigated since the discovery of the capacity of metal complexes with macrocyclic N4 ligands to reduce oxygen electrochemically, however, NPMCs developed so far usually suffer from substandard stability in acidic environments. How to mitigating the performance loss that is ubiquitous among NPMCs is presently only based on trial and error.
Based on our biomimetic mechanistic studies on the binding/activating of O_2 by metalloenzymes such as heme-containing enzymes,[2] we recently developed a new class of high performance NPMCs for the ORR, wherein structure-defined biomimetic catalysts were covalently grafted onto the surface of carbon-based supports.[3] In this talk, we will present our efforts to improve the ORR catalyst's activity and stability via rational catalyst design, and demonstrate their applications to PEM fuel cells.

Acknowledgement: This work was financially supported by NSF of China (No. 21271072, 21571062, 21503080), the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning, and sponsored by Shanghai Pujiang Program (No 13PJ1401900).

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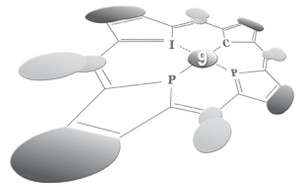

Supramolecular Chirality in the TPPS Assemblies

Minghua Liu, Li Zhang

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The water soluble meso-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) is of great interest due to its unique aggregation property and supramolecular chirality in the presence or absence of chiral species. Here, we will talk about the supramolecular chirality of the TPPS assemblies in various conditions, as summaries in Figure 1.

TPPS can form chiral assemblies through the air/water interface upon complexing with either chiral amphiphiles or achiral surfactants. With such property, TPPS can be used as the subphase to enhance the supramolecular chirality of the monolayer at the air/water interface detected by the SHG method.

The aggregation of the TPPS can be promoted when there is ionic liquid molecules existed in the aqueous solution. In this system, the supramolecular chirality can also be produced either in the absence or the existence of chiral species, during which the chirality was controlled by the chirality of the additional species.

TPPS can also undergo self-assembly in organic solvents. For example, in the mixed DMSO and alcohol solvents, TPPS can form aggregates, which could be controlled by the photoirradiation. Furthermore, TPPS was found to self-assemble into long nanofibers of ambiguous chirality in organic solvents, while mirror imaged chiral nanorods with controlled chirality were formed when (1R,2R)- or (1S,2S)- 1,2-diaminocyclohexane.

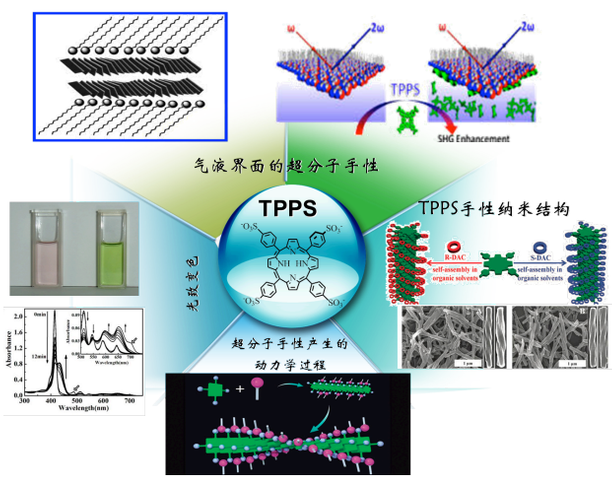

Figure 1. Self-assembly of TPPS into various chiral nanostructures. From the top-left and clockwise rotation: Chiral TPPS assemblies through the air/water interface, TPPS assemblies used as the enhancer for the supramolecular chirality detection in the interfacial films by SHG; TPPS chiral nanorods with diaminocyclohexane in organic solvents; Chiral TPPS assemblies promoted in ionic liquid; Chiral TPPS assemblies in mixed DMSO and ethanol under photo-irradiation.

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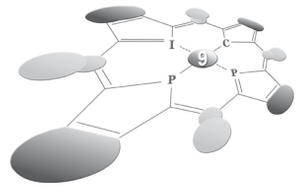

Porphyrin/Phthalocyanine Modified Inorganic Nanomaterials: Promising Peroxidase Mimetics for H_2O_2 and Glucose Detection

Qingyun Liu*[,a], Mingxing Chen[a], Lifang Sun[a], Miaomiao Chen[a] and Yanan Ding

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Porphyrin/phthalocyanine functionalized Inorganic nanomaterials have been prepared by a facile method and characterized by powder X-ray diffraction (XRD), transmission electron microscope (TEM) and Fourier transform infrared spectra (FTIR), respectively. Porphyrin-inorganic nanocomposites have been proven to function as peroxidase mimetics that can catalyze the reaction of peroxidase substrate 3,3',5,5'-tetramethylbenzidine (TMB) in the presence of H_2O_2 to produce a blue color reaction. Kinetic analysis indicated that the catalytic behavior was in accord with typical Michaelis–Menten kinetics. Porphyrin-inorganic nanocomposites/glucose oxidase (GOx)/TMB system provides a novel colorimetric sensor for glucose and shows good response toward glucose detection. Thus it may provide great potential applications in biomedicine, biotechnology and environmental chemistry.

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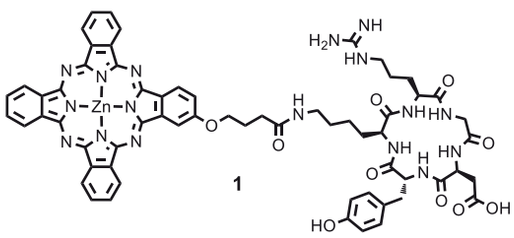
The Impact of Substituents on the Physicochemical and Photodynamic Therapy Properties of Phthalocyanine-cRGD Conjugates

Liqiang Luan, Wenjuan Fang, Wei Liu, Yuxing Ni, Xi Chen

State Key Laboratory of Crystal Materials, Shandong Univerisity

It was realized that the biological behavior of a photosensitizer is greatly determined by its structural characteristics. On the other hand, the efficiency of photosenitizers significantly relies on their tissue and intracellular localization. Herein, we describe the synthesis of two novel unsymmetrical phthalocyanine conjugates with a cyclic RGD (RGDyK) peptide, namely **1** and **2** (Fig 1), for the $\alpha_v\beta_3$ integrin-targeted photodynamic therapy (PDT). Their in vitro PDT efficacy, $\alpha_v\beta_3$ integrin bind specificity and the cellular uptake were investigated, and the two-photon absorption properties were also studied via excitation with fs laser plus, and their two-photon absorption cross section (TPACS) were calculated via comparison method at different laser wavelengths. Our results show that compound **1** is a promising photosensitizer for cancer-cell targeting PDT with an IC_{50} of 40 nM under the condition of our study. For comparision, compound **2** shows negligible photocytotoxicity, however, with enhanced cellular fluorescence emission in mitochondria, making it a promising one- or two-photon imaging probe for cancer cells. This comparative study further evidence the structure-activity relationship for Pc based photosensitizer.



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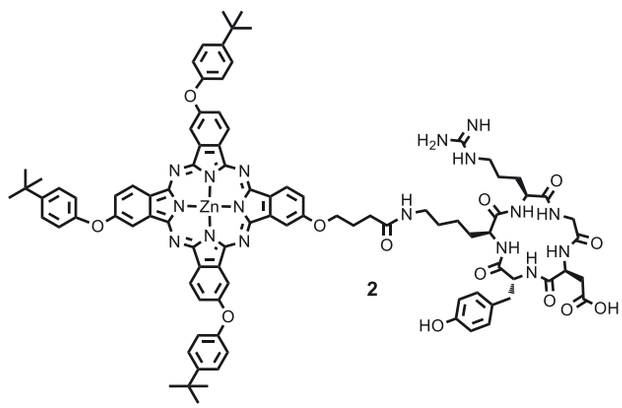

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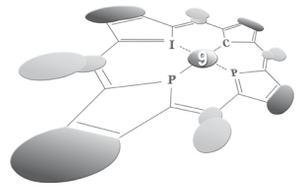

Nanotechnology to overcome tumor hypoxia for enhanced photodynamic therapy of cancer

Zhuang Liu[a]

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Hypoxia, severe oxygen starvation, has been considered to arise in solid tumors due to irregular cancer cell proliferation and distorted blood tumor vessel development. It is also recognized as one of the characteristic hallmarks in solid tumors with insufficient oxygen supply, directly contributing to the malignant properties of cancers. It is known that hypoxia plays essential roles in tumor angiogenesis and cancer metastasis. Moreover, hypoxia would also lead to resistance to medical therapies, such as radiotherapy, chemotherapy as well as photodynamic therapy (PDT), the latter of which is an non-invasive cancer treatment approach utilizing light to activate photosensitizers, generating singlet oxygen ($^1O_2$) and reactive oxygen species in the presence of oxygen to kill tumor cells. In this talk, I would like to introduce our latest efforts in the development of novel nanotechnology approaches to reverse the hypoxia state in the tumor, so as the overcome the hypoxia-associated resistant in the PDT treatment of cancer. Three strategies have been proposed : 1) Using tumor-homing H_2O_2-sensitive nanoparticles to in-situ produce oxygen inside the tumor ; 2) Challenging the tumor microenvironment with enzymes to improve the intra-tumoral blood perfusion and overcome hypoxia; 3) Using ultrasound responsive oxygen-delivery nano-carriers to locally deliver oxygen into tumors. Remarkably enhanced in vivo PDT efficacy in mouse tumor model experiments has been realized with all the above strategies. Therefore, overcoming tumor hypoxia with nanotechnology approaches may have a great potential to enhance current cancer PDT treatment.

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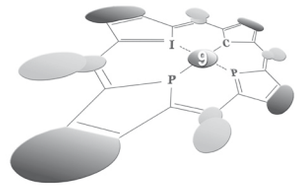

"Smart" Photosensitizers for Targeted Photodynamic Therapy

Pui-Chi Lo[a], Janet T. F. Lau[b], Xiong-Jie Jiang[b], Wen-Jing Shi[b], Qiong Wang[a], Hui He[b], Shi-Rui Zhao[b], and Dennis K. P. Ng[b]

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Photodynamic Therapy (PDT) has emerged as a clinical modality for treatment of some localized and superficial cancers.[1] Over the last two decades, significant advances have been made in the development of efficient photosensitizers based on various classes of functional pigments. However, the tumor selectivity remains as a major challenge. Various strategies have been explored to enhance the tumor-targeting property of photosensitizers, such as conjugation with targeting ligands and encapsulation into multifunctional nanocarriers. Apart from directing the photosensitizers to the cancer cells, controlling their photoactivity in a specific manner is another promising approach as it can minimize the photodamage of normal tissues in PDT. Recently, we have been interested in photosensitizers that can be activated by tumor-associated stimuli. In these smart theranostic systems, the photosensitizers are deactivated by the neighboring quenchers, such as 2,4-dinitrobenzenesulfonyl,[2] ferrocenyl,[3] and the newly developed ferrocenyl boron dipyrromethene (BODIPY)[4] moieties. Upon interactions with acid and/or thiols (e.g. glutathione and dithiothreitol), which can mimic the acidic and reducing environments of tumors, respectively, the photosensitizers are detached from the quenchers, resulting in restoration of their fluorescence and photosensitizing properties. The activation of these photosensitizers has also been demonstrated at the cellular level and in tumor-bearing nude mice. The results of these studies will be reported in this presentation.

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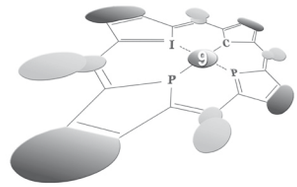

Design and Synthesis of Phthalocyanine and Porphyrin-based Conjugated π-Systems for Nonlinear Optical Imaging

Ismael López-Duarte, Luis Carlos Asensio, Tomás Torres

Departamento de Química Orgánica, Universidad Autónoma de Madrid, 28049-Madrid, Spain.
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Multiphoton imaging techniques based on nonlinear optical (NLO) phenomena such as two-photon excited fluorescence and second harmonic generation have revolutionized the field of microscopy in biological and biomedical research, providing non-invasive, high-resolution imaging of living samples in real time.[1]
In NLO microscopy, wavelengths of incident light in the near-infrared (NIR) range are employed to achieve deeper penetration through biological tissues, reduce scattering and diminish light-induced degradation of biological samples. Second-harmonic generation (SHG) microscopy, a form of NLO imaging, has recently attracted a great deal of interest.[2] SHG is only observed in non-centrosymmetric structures and therefore is a sensitive tool for providing information on complex biological structures such as lipid membranes. Furthermore, SHG microscopy has latterly become an attractive tool for mapping electrochemical activity in cells and cellular networks in real time.[2] Although great number of dyes have been developed for probing the structure and functions of complex biological systems, there is still an urgent need for new dyes to further exploit recent advances in nonlinear optical imaging techniques. In this talk, the synthesis of conjugated π-systems based on phthalocyanine and porphyrin units, together with an evaluation of their photophysical and photobiological characteristics pertinent to imaging membranes by SHG will be discussed, placing an emphasis on understanding the structure-property relationships that govern the nonlinear optical properties of these materials.[3]

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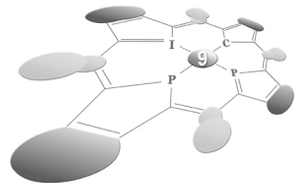

Porphyrin and Phthalocyanine Theranostic Agents

Jonathan F. Lovell[a]

[a]*State University of New York at Buffalo*

Porphyrins and pthlaocyanines have played unique roles in development of approaches to the diagnosis and treatment of diseases, in particular based on how these molecules interact with light. This lecture will cover some of our recent efforts to develop new self-assembled materials from porphyrins and related molecules and how these nanomaterials have potentially advantageous properties for disease diagnosis and therapy.

First, in relation to photodynamic therapy, nanovesicles containing small amounts of tetrapyrrolic lipid-conjugated photosensitizers (TLCP) have been developed that can release drugs in response to red laser irradiation, leading to enhanced drug deposition in irradiated tumors. Inclusion of 2 molar % TLCP imparts optimal near infrared (NIR) light-triggered release of doxorubicin (Dox) from conventional sterically stabilized stealth liposomes. Dox in stealth TLCP liposomes has a circulation half-life in mice of 21.9 hours and is stable in storage for months. Following intravenous injection and NIR irradiation, Dox deposition increases ~7 fold in treated subcutaneous xenografts. A low dose 3 mg/kg Dox phototreatment with stealth TLCP liposomes was more effective than a maximum tolerated dose of free (7 mg/kg) or conventional long-circulating liposomal Dox (21 mg/kg). To our knowledge, Dox-loaded stealth TLCP liposomes represent the first reported long-circulating nanoparticle capable of light-triggered drug release. Such a chemophototherapy paradigm provides an alternative to conventional photodynamic therapy.

Second, phthalocyanine and naphthalocyanine based imaging systems will be discussed that have been investigated preclinically. There is a need for safer and improved methods for non-invasive imaging of the gastrointestinal tract. Modalities based on X-ray radiation, magnetic resonance and ultrasound suffer from limitations with respect to safety, accessibility or lack of adequate contrast. Functional intestinal imaging of dynamic gut processes has not been practical using existing approaches. Here, we report the development of a family of nanoparticles that can withstand the harsh conditions of the stomach and intestine, avoid systemic absorption, and provide good optical contrast for photoacoustic imaging. The hydrophobicity of naphthalocyanine dyes was exploited to generate purified □20 nm frozen micelles, which we call nanonaps, with tunable and large near-infrared absorption values (>1,000). Unlike conventional chromophores, nanonaps exhibit non-shifting spectra at ultrahigh optical densities and, following oral administration in mice, passed safely through the gastrointestinal tract. Non-invasive, non-ionizing photoacoustic techniques were used to visualize nanonap intestinal distribution with low background and remarkable resolution, and enabled real-time intestinal functional imaging with ultrasound co-registration. Positron emission tomography following seamless nanonap radiolabelling allowed complementary whole-body imaging.

Additionally, the rational design of a stable phosphorus phthalocyanine (P-Pc) with a long wavelength absorption band beyond 1000 nm has been reported by Kobayashi's group. Here, we show that when dissolved in biocompatible liquid surfactants, P-Pc can give rise to formulations with intense absorption values of greater than 1000 at wavelengths beyond 1000 nm. This allows for exceptionally deep photoacoustic imaging.

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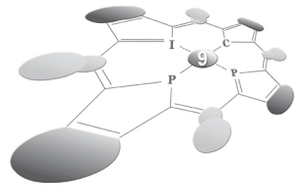
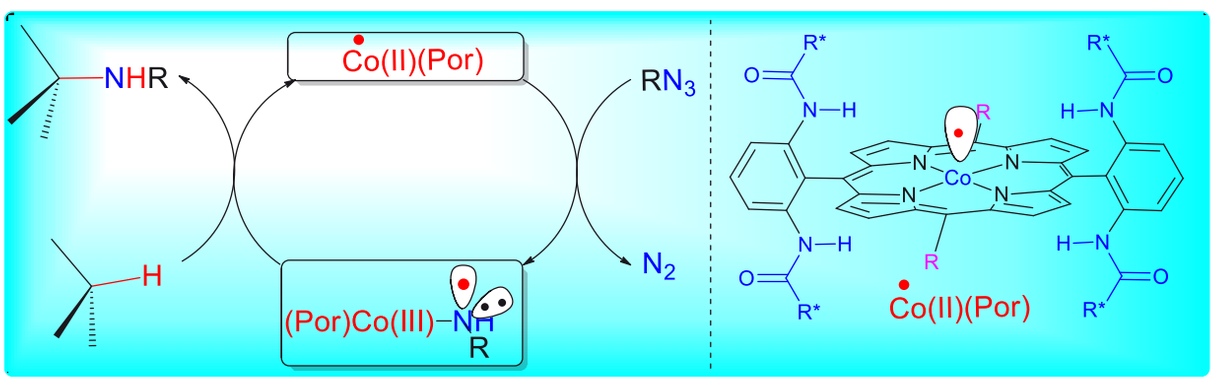


Stereoselective Radical C–H Amination via Co(II)-Based Metalloradical Catalysis

Hongjian Lu,[a,b] and Peter X. Zhang[b,c]

[a] *School of Chemistry and Chemical Engineering, Institute of Chemistry and BioMedical Sciences (ICBMS), Nanjing University*
[b] *Department of Chemistry , University of South Florida*
[c] *Department of Chemistry , Boston College*

Selective amination of omnipresent C–H bonds via metal-mediated nitrene insertion represents a powerful approach for direct introduction of valuable amino functionalities into molecules. As one of applications of the new concept of metalloradical catalysis (MRC) for achieving stereoselective radical processes, cobalt(II) porphyrin complexes ([Co(Por)]) were developed as metalloradical catalysts for C–H amination. Different from electrophilic metallonitrene systems, the Co(II)-based metalloradical amination has been demonstrated to proceed via a stepwise radical mechanism. Consequently, it possesses uncommon capability for efficient amination of challenging primary and electro-deficient C–H bonds and exhibits remarkable chemoselectivity toward allylic and propargylic C–H amination reactions. The [Co(Por)]-based metalloradical amination is unusual as it can effectively activate different kinds of organic azides as the nitrene sources under neutral and nonoxidative conditions, with the generation of nitrogen gas as the only by-product.



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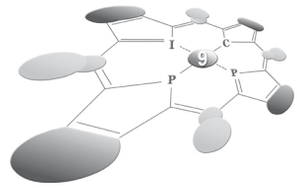

Rational design of tuned-wavelength BODIPYs: from blue to near infrared region

Hua Lu,[a] Zhen Shen,[b]

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Boron-dipyrromethene (4,4-difluoro-4-bora-3a,4a-diaza-s-indacene, BDP or BODIPY) fluorescent dyes, a structural analogue of the porphyrins, have been the focus of considerable research interest over the last three decades.[1] This has been related to (i) their facile synthesis and structural versatility, (ii) their excellent spectroscopic properties (narrow Gaussian-shaped absorption and emission bands, high molar extinction coefficients and Φ_F values, moderate redox potentials, negligible triplet-state formation and negligible sensitivity to solvent polarity, excellent photostability, and high solubility in commonly used organic solvents of differing polarities), and (iii) their wide range of potential applications in numerous research fields. A major drawback, however, is that the spectral properties of the classic BODIPY chromophore are typically lied in the 500–530 nm region, which limits their application in optoelectronic device and for biolabeling.[1]
Recently, we developed several synthetic methods for obtaining tuned-wavelength BODIPY derivatives covering the visible and NIR region.[2-8] My talk will focuse on the tuned-wavelength absorbing BODIPYs based on the wide range of structural modification methods that have been adopted by our research groups.

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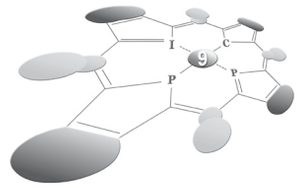

Bioinspired Catalytic Generation of High-valent Cobalt-oxo Species by the Axially Coordinated CoPc on Pyridine-functionalized MWCNTs

Nan Li, Tiefeng Xu, Zhenan Wang, Zhen Xu, Wangyang Lu,* Dongjing Ni, Xiyi Wang, and Wenxing Chen*

National Engineering Lab for Textile Fiber Materials & Processing Technology (Zhejiang), Zhejiang Sci-Tech University, Hangzhou 310018, China
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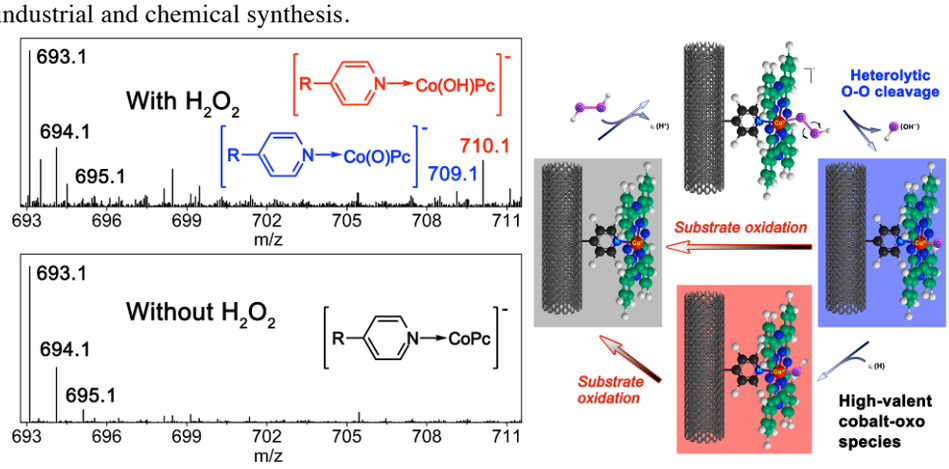
Enzymes have always been a source of inspiration for the design and improvement of catalysts. Many examples are occurring in heme/non-heme metalloenzymes with the generation of active high-valent metal-oxo intermediates that are controlled by the surrounding amino acids/protein and axial residue ligands, facilitating the efficient oxidation of substrates in biochemical processes. Here, the high-valent cobalt-oxo species have been formed during the heterolysis of H_2O_2 activated by the bioinspired catalyst, axially coordinated cobalt phthalocyanine (CoPc) on pyridine-functionalized multi-walled carbon nanotubes (MWCNTs-Py), characterized by ultraviolet–visible and X-ray photoelectron spectroscopy. Formation process of the active cobalt-oxo species has been further confirmed by electrospray ionization mass spectrometry analysis (UPLC Synapt G2-S HDMS) and the results from the density functional theory (B3LYP/6-311G) calculations. Such high-valent cobalt-oxo species exhibits a high reactivity and enough persistence for the oxidation of the target substrate, C.I. Acid Red 1. The oxidation products are nearly biodegradable small molecules identified by ultra-performance liquid chromatography/high-definition mass spectrometry. As a viable candidate species for catalytic systems based on transition metal complexes, high valent metal–oxo species hold great promise for selective oxidation via activating oxidant, which could ensure the effective catalytic system with enough durability and minimized deleterious side reactions, providing a strategy for highly reactive transition metal complex-based catalysts to practice in industrial and chemical synthesis.



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Anion-Exchanger Side-Substituted Metalloporphyrin Ionophores: Systematic Anionic Selectivity Tailoring

Larisa Lvova [a], Donato Monti[a], Corrado Di Natale[b], and Roberto Paolesse[a]

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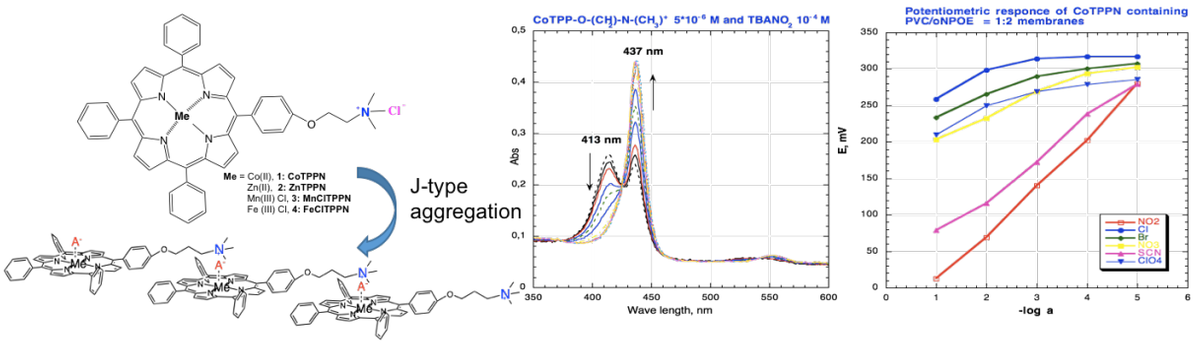
[b]*Department of Electronic Engineering, University "Tor Vergata", Rome, 00133, Italy*

The systematic way for tailoring an anionic selectivity of chemical sensors based on metalloporphyrin ionophores bearing anion-exchanger fragment incorporated in ionophore structure is represented. 5-[4-(3-trimethylammonium)propyloxyphenyl]-10,15,20-triphenylporphyrin complexes of Co(II), Zn(II), Mn(III) chloride and Fe (III) (TPP-$(CH_2)_3$-N-$(CH_3)_3$Cl) chloride, previously prepared and studied in our group [1], have been utilized as ionophores in PVC-based solvent polymeric membrane sensors. A plausible sensor working mechanism is related to the axial coordination of the target anion on ionophore metal center followed by the formed complex aggregation with the second ionophore molecule through positively-charged anion-exchanger fragment. The UV/Vis spectroscopic studies of developed sensing materials have revealed that increasing levels of primary anion induces the J-type porphyrin ionophore aggregation.



Solvent polymeric membranes showed close to theoretical Nernstian response towards those anions, preferably coordinated by the ionophore, depending on the central metal nature, ionophore percentage and the presence of additional lipophilic sites in the membrane phase; the resulting selectivity was a subject of specific interaction and/or steric factors. Potentiometric properties and selectivity of developed sensing materials and their applications for mult.trunsduction analysis will be discussed in detail in our presentation.

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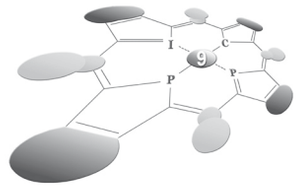

Metal–metalloporphyrin frameworks: from Design to Applications

Shengqian Ma

University of South Florida, Department of Chemistry, Tampal, Florida 33647, USA

Metal–metalloporphyrin frameworks (MMPFs) compose a class of coordination networks self-assembled via judicious selection of metal-containing secondary building units (SBUs) and custom-designed metalloporphyrin ligands. Some strategies to design MMPFs will be illustrated and their applications will be discussed.

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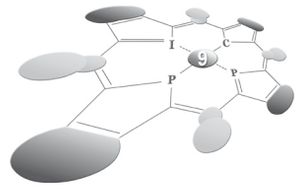

Rational design, synthesis and properties of non-benzo fused-ring-expanded phthalocyanines and aza-BODIPYs

John Mack[a], **Poulomi Majumdar**[a], **Jessica Harris**[a], **Lizhi Gai**[b], **Maohu Shi**[b], **Tebello Nyokong**[a], **Zhen Shen**[b]

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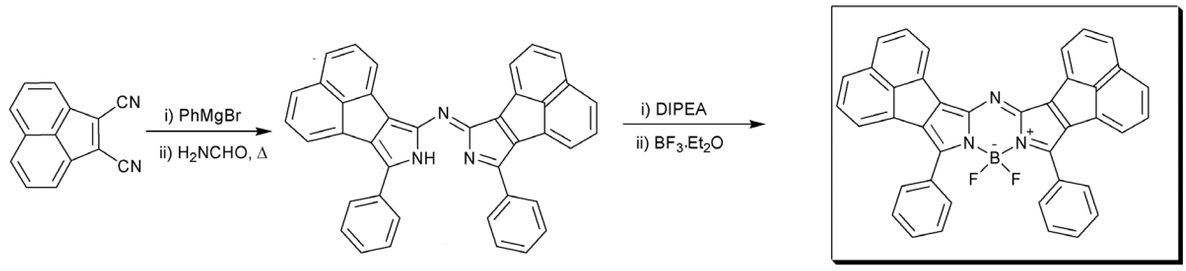
[b]*State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China*

The potential utility of non-benzo fused-ring-expanded phthalocyanine[1] and aza-dipyrromethene boron difluoride (aza-BODIPY)[2] analogues for photodynamic therapy and near infrared (NIR) region sensor applications is well-established. Attempts to prepare fused-ring-expanded aza-BODIPY analogues with benzene, pyrazine and naphthalene rings have demonstrated that their properties can vary markedly when different fused ring systems are fused on the β-carbons of the two pyrrole ring moieties.[3,4] It has been postulated that trends in the optical spectra, redox properties and electronic structures of aza-BODIPY dyes follow those observed for the phthalonitrile precursors and the analogous phthalocyanines despite the absence of a fully conjugated macrocyclic perimeter that obeys Hückel's rule.[3] Molecular modelling calculations have been carried out on series of fused-ring-expanded phthalonitriles, phthalocyanines and aza-BODIPY dyes and trends in their optical and redox properties have been analyzed to identify suitable target compounds on this basis for synthesis work.[4,5]



The synthesis of an NIR absorbing acenaphthalene fused-ring-expanded aza-BODIPY dye is reported.[6] 1,2-dicyanoacenaphthylene[7] was used as a precursor. To our knowledge, despite this phthalonitrile analogue being reported over 40 years ago, it has not been used previously to synthesize phthalocyanine or aza-BODIPY compounds. In contrast with the analogous naphtho-fused compound,[3] the acenaphthalene-fused analogue was found to be stable. Further progress on the synthesis and properties of non-benzo fused-ring-expanded phthalocyanine and aza-BODIPY analogues will be described.

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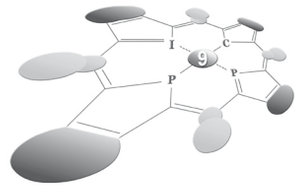

Push-Pull Porphyrins with Varying Donor Units for Bulk Heterojunction Organic Photovoltaics and Photodetectors

Mathias Kelchtermans[a], Jasper Deckers[a], Jurgen Kesters[a], Laurence Lutsen[b], Dirk Vanderzande[a,b], Jean Manca[c] and Wouter Maes[a,b]

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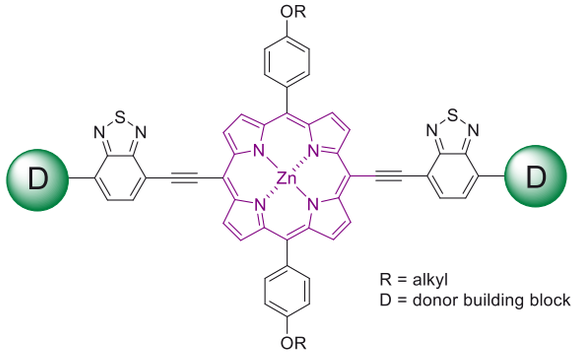
Organic photovoltaics (OPV) represent a thin-film PV technology offering attractive prospects toward low-cost and aesthetically appealing (colored, flexible, uniform, semi-transparent) solar cells printable on large surfaces. In bulk heterojunction (BHJ) OPV devices, organic electron donor and acceptor molecules are intimately mixed within the photoactive layer. Since 2005, the power conversion efficiency of said devices has increased substantially due to proceeding insights in the underlying physical processes, device optimization and chemical engineering of a vast amount of novel light-harvesting organic materials, either small molecules or conjugated polymers. As Nature itself has developed porphyrin chromophores for solar light to energy conversion, it seems reasonable to pursue artificial systems based on the same types of molecules. Porphyrins and analogues have indeed already been implemented successfully in certain device types, notably in dye-sensitized solar cells, but they have remained largely unexplored in BHJ organic solar cells. Very recent successes do show, however, the strong (latent) prospects of porphyrinoid semiconductors as light-harvesting and charge transporting materials in such devices.[1]

In this presentation, a number of advanced push-pull (low optical gap) porphyrinoid materials recently synthesized in our group will be presented. 2,1,3-Benzothiadiazole was combined with different electron donating building blocks and coupled to a central Zn-porphyrin moiety via Sonogashira cross-coupling. The influence of the various electron donor units on the optoelectronic properties and photovoltaic behavior of the porphyrin molecules will be discussed, with particular emphasis on homocoupling (structural) defects. An outlook to the application of similar materials in organic photodetectors will be provided as well.



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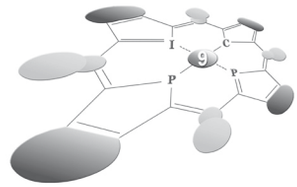

Physical Approach to Formation of Supermolecular Macroheterocyclic Nanomaterials

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Formation of porphyrin nanostructures is of great interest which is being driven mainly by advances in photonics, molecular electronics and biological applications. Langmuir-Blodgett (LB) technology provides possibility for self-organization of the molecules in one-, two- and three-dimensional nano- and microstructures of different size consisting of major nanoaggregates with diameter in the range of 5-15 nm (M-nanoaggregates) [1-3].
In the talk we will present our data on the aggregation process of some macroheterocyclic compounds at different stages ranging from formation of M-aggregates on water surface to nanocrystallization in thin films and formation of supermolecular materials. The structure of the floating layers is analyzed within the framework of an original model and method for quantitative analysis of compression isotherms of a monolayer comprised of 2D- and 3D-nanoaggregates. The method is based on the Volmer equation, generalized to the case when structural units of the layer are nanostructures. New parameters are used to characterize the structure and properties of the nanostructured monolayers. Thin films consisting of nanostructures of single type (supermolecules), including films with controllable orientation of main structural units for some compounds were prepared. Such results were achived due to specific physical conditions of controlled self-organization of organic molecules at air-water interface. Structure of the films formed under varied conditions was studied by spectroscopy and synchrotron X-ray scattering. The basic structure of the films is the layered packing of nanoaggregates. An approach to formation of such films and new supermolecular macroheterocyclic nanomaterials will be discussed.

The work is partially supported by the Russian Scientific Foundation (Project 14-23-00204 'New functional materials based on polyheterocyclic compounds: synthesis and applications'), Russian Foundation for Basic Research (Project N 15-42-03211a) and Ministry of Education and Science of RF (State task for ISUCT).

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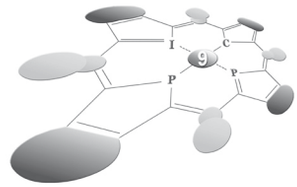

Vitamins B_{12} and C. Interplay in the Presence of Sulfur-Containing Compounds

S. V. Makarov[a], **I. A. Dereven'kov**[a], **D. S. Salnikov**[a], **and I. Ivanović-Burmazović**[b]

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Over the last decades, reaction of vitamins B_{12} (cobalamins, Cbls) and C (ascorbic acid, AA) have attracted intensive interest and been extensively studied [1]. It has been accepted that simultaneous presence of vitamins B_{12} and C results in irreversible modification of corrin ring of Cbl and oxidation of AA to dehydroascorbic acid (DHA). This report provides the kinetic and mechanistic data on the reaction between cob(II)alamin and DHA in the presence of biologically important compounds – glutathione (GSH) and thiocyanate. The oxidation of Cbl(II) by DHA in acidic and neutral solutions was monitored by UV/Vis spectroscopy under anaerobic conditions. AA and AA/DHA mixture do not modify corrin ring during the timescale of all measurements performed in this work. The pH dependence of the second order rate constants demonstrates substantial increase of the reaction rate upon a pH increase from 3.6 to 7.0 and is related to the deprotonation of GSH.
Importantly, reduction of DHA by Cbl(II)/GSH mixture proceeds much faster than direct reaction between DHA and GSH. Cryo ESI-MS was used to characterize reaction products. In this experiment no evidence of oxidation of GSH was found.
By way of comparison, we further investigated kinetics of the reaction in the presence of redox innocent S-donor, SCN^-. Thiocyanate also accelerates reaction of Cbl(II) and DHA, but rates are significantly less, than with GSH. Based on the saturation dependence of the rate constants on [GSH] and [SCN^-] and characterization of the GS^--Cbl(II) adduct by cryo ESI-MS, we can conclude that coordination of GS^- or SCN^- to initial five-coordinate Cbl(II) modifies redox properties of Co^{2+}-ion and activates an electron-transfer from Co^{2+} to DHA. We examined the redox behavior of the Cbl(II)/SCN^- and Cbl(II)/GSH systems by cyclic voltammetry. Addition of SCN^- and GSH, respectively, shifted the position of the oxidation wave of Cbl(II) to more negative values. GSH exerts stronger effect than SCN^-. In conclusion, for the fist time we have demonstrated that AA can be recovered from DHA within the process involving cob(II)alamin, but without depletion of GSH, which binding to the Co(II) center modulates the underlying redox mechanism.

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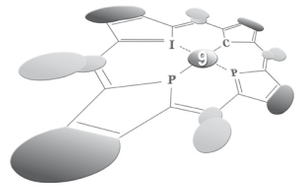

Modulating the Reactivity of Cytochrome P450 Ferryl Intermediates for C-C bond Scission

Thomas M. Makris[a], **Job L. Grant**[a], **Chun H. Hsieh**[a] **and Jose A. Amaya**[a]

[a]*Department of Chemistry and Biochemistry, University of South Carolina*

The metabolic diversity of cytochrome P450 (CYP) enzymes owes from sophisticated interplay of substrate molecular recognition and precise tuning of metal oxygen species formed at the enzyme active-site. OleT, belonging to the CYP152 family, metabolizes *n* chain length fatty acids to produce *n-1* terminal alkenes, utilizing hydrogen peroxide as a co-substrate in the reaction. This C-C cleavage reaction, in addition to its mechanistic peculiarity for a CYP, provides a potential means to convert a biologically abundant feedstock into a petrochemical and valuable synthetic precursor. In order to elucidate the chemical mechanism for OleT alkene formation, we have characterized its reaction with fatty acids. Isotope labeling studies indicate that the one carbon co-product of the alkene-forming reaction is carbon dioxide and that oxygen rebound is largely abrogated with a native chain length substrate. Benefitting from the high chemoselectivity of OleT and a facile means to rapidly trigger catalysis, we recently reported that a highly accumulating Compound I intermediate (Ole-I) could be isolated in single turnover reactions of OleT using the native H_2O_2 terminal oxidant and a bound deuterated substrate analog. The observation of a Compound I species in OleT, optically indistinguishable from oxoiron(IV) species that normally promote hydroxylations, suggests that the same P450 intermediate can be re-tuned to catalyze a fundamentally different reaction. Transient kinetics further reveal that Ole-I initiates the decarboxylation reaction sequence through substrate C-H abstraction, forming the iron (IV)-hydroxide species Compound II (Ole-II). The unprecedented stability of this intermediate provides direct insight into how metal-oxo reprogramming can be achieved by P450 cytochromes.

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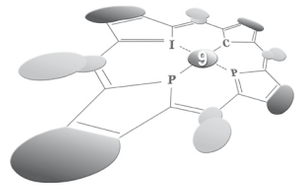

Fluorescent Boron Complexes of Dipyrrins and Expanded Porphyrinoids

M. Ravikanth

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Among the fluorescent dyes available, the BF_2 complex of dipyrromethene (BODIPY) dyes are becoming increasingly popular because the BODIPY dyes have remarkable characteristics such as high absorption coefficients, high fluorescence yields, long excited state lifetime, good solubility in organic solvents with excellent photostability and amenability toward chromatography.[1] BODIPY dyes have been used extensively as labeling reagents, fluorescent switches, chemosensors and as laser dyes. Recently, BF_2 complexes of expanded porphyrinoids such as smaragdyrin macrocyle were synthesized which are strongly fluorescent with interesting physico-chemical properties. Our group is involved[2-7] in the synthesis of various boron complexes of dipyrrin, azadipyrrin and expanded porphyrinoids which were appropriately functionalized and used for various applications. In my talk, I will present the synthesis, properties and applications of some selected fluorescent boron complexes of dipyrrins and expanded porphyrinoids (Chart 1).

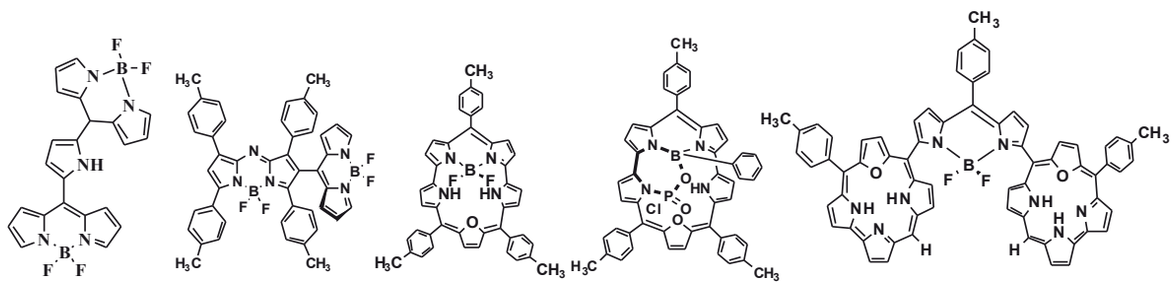

Chart 1

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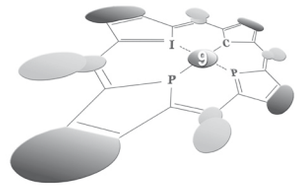
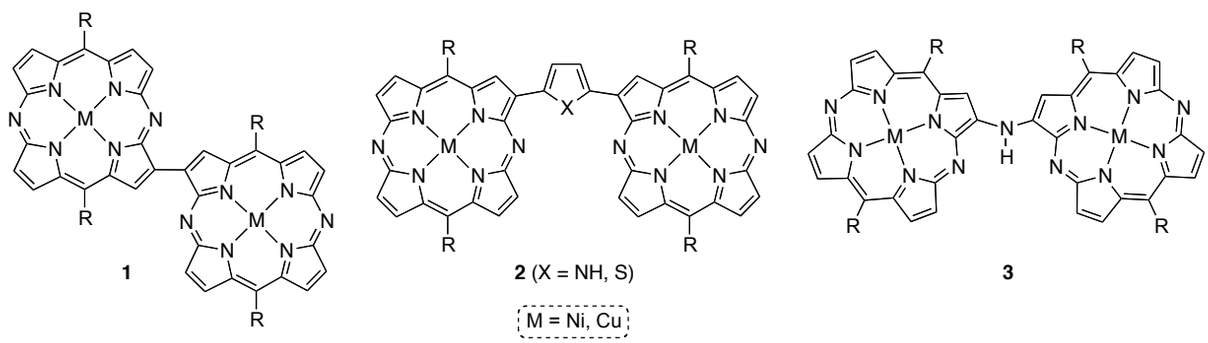


Covalently Linked Dimers of 10,20-Diaryl-5,15-Diazaporphyrin–Metal Complexes

Yoshihiro Matano

Department of Chemistry, Faculty of Science, Niigata University

5,15-Diazaporphyrin (DAP) is a structural hybrid of porphyrin and tetraazaporphyrin and contains an intrinsic D_{2h}-symmetric π-system with non-degenerate HOMO/HOMO-1 and LUMO/LUMO+1.[1] This gives rise to an intense HOMO-to-LUMO electronic transition when compared with a porphyrin analog. Therefore, the DAP π-systems are promising platforms for the development of new azaporphyrin-based sensitizers with high light-harvesting potential in the visible-near infrared (vis-NIR) region. Recently, we have reported several types of covalently linked DAP dimers (bisDAPs)[2] and their monomer reference compounds.[3] In marked contrast to the porphyrin counterparts, β–β directly linked bisDAPs **1** possess coplanar, *trans* geometries and narrow HOMO–LUMO gaps compared with acetylene- and butadiyne-bridged bisDAPs.[2a] These spectral features arise from the cooperative electronic and steric effects of the *meso* nitrogen atoms of the DAP ring. Moreover, pyrrole- and thiophene-bridged bisDAPs **2** exhibit a wide range of absorptivity because the heterole spacers are electron rich and polarizable.[2b] We also succeeded in preparing amino-bridged bisDAPs **3** and investigated their optical properties.[2c] In this presentation, the synthesis, structures, and optical/electrochemical/magnetic properties of these covalently linked bisDAPs **1**–**3** will be reported.



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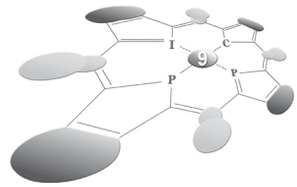

Unusual heme degradation achieved by unprecedented coupling of two distinct oxygenation modes

Toshitaka Matsui, Shusuke Nambu, and Masao Ikeda-Saito

[a]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University*

Heme degradation in bacteria is crucial to acquire iron from host heme molecules. An enzyme family termed heme oxygenase (HO) is known to degrade heme into iron, CO and biliverdin (Figure 1). Until recently, the HO family was thought to be the only heme degrading enzymes, however, a novel family of enzymes with heme degrading capabilities has been identified in *Staphylococcus aureus*. IsdG and its paralogue, IsdI, are heme degrading enzymes of *S. aureus* having distinct structures compared to the HO-family enzymes. Especially, heme bound to the IsdG-type enzyme exhibits severe distortion, best described as ruffled, in contrast to the flat heme in HO. This heme ruffling is expected to modulate the O_2 activation chemistry on the heme molecule, and in fact, a novel tetrapyrrole, staphylobilin, having an additional oxidation at a *meso* carbon is produced (Figure 1). Nevertheless, the unique reaction mechanism of the IsdG-type enzymes remains unclear.

In this study, we have examined heme degradation reactions by the IsdG-type enzymes, namely by MhuD from *Mycobacterium tuberculosis*. MhuD produces a novel tetrapyrrole product termed "mycobilin", which retains the *meso* carbon at the ring cleavage site as an aldehyde group (Figure 1). As expected from the mycobilin structure, the MhuD catalysis does *not* generate CO, indicating a unique mechanism for MhuD. In the heme degradation through reductive O_2 activation, MhuD accumulates an intermediate, which is identified by resonance Raman spectroscopy as an ferrous oxy-heme complex. Since the first oxygenation was successfully supported by H_2O_2, the reactive intermediate responsible for heme hydroxylation is suggested to be an iron-hydroperoxy species as in the canonical HO catalysis. Anaerobic reaction of heme-MhuD with H_2O_2 partially accumulates hydroxyheme, which was successfully converted into mycobilin. Further reaction analysis reveals the MhuD catalysis proceeds though a combination of two distinct modes of oxygenation. Detailed reaction mechanism of MhuD will be discussed at the meeting.

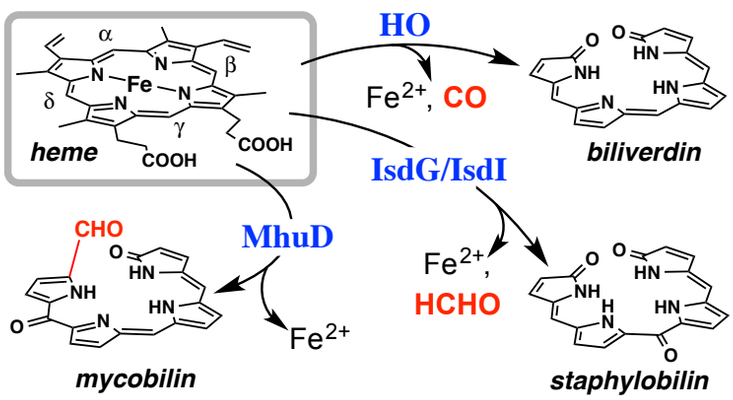

Figure Heme degradation products of the HO- and IsdG-type enzymes

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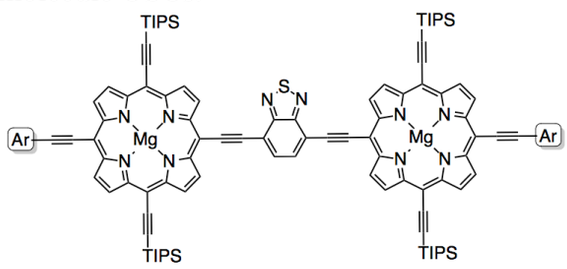
Magnesium Complex of Diporphyrins with Long-Wavelength Light Absorption for Organic Solar Cells

Yutaka Matsuo

Department of Chemistry, School of Science, The University of Tokyo

The porphyrin framework is used for photosynthesis in nature, and has advantageous photophysical and electrochemical properties. Porphyrins are good organic dyes possessing large absorption coefficient, high stability and high susceptibility in electron transfer reactions for organic photovoltaics. Soluble porphyrin derivatives as electron donor materials that have the long-wavelength absorption property are drawing much attention for high performance of small molecule organic solar cells (OSCs).

Herein, we report synthesis of the diporphyrin compound linked by an electron-withdrawing 2,1,3-benzothiadiazole unit for long-wavelength light absorption and photovoltaic performance in organic thin-film solar cells. A normal-structured bulk heterojunction device showed PCE of 2.75% with high open-circuit voltage (V_{OC} = 0.80 V) and near IR photocurrent conversion. These desirable features are attributed to low-lying energy levels, low-bandgap nature, and flexible diporphyrins structures. This molecular design will contribute to developing electron donor materials in small molecule OSCs.



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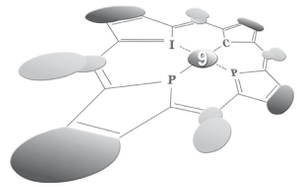

Azaphthalocyanine-Oligonucleotide Conjugates

Miletin M., Kopecky K., Novakova V., Zimcik P., Kucera R.

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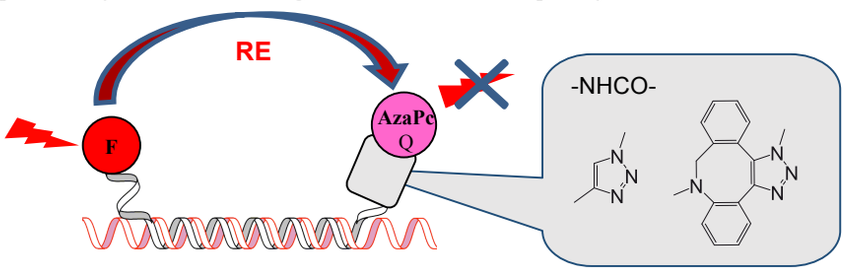
Chemically modified synthetic nucleic acids are used in many areas of both science and practical life including diagnostic and forensic methods as well as in therapeutic approaches (antisense and aptamer technology). Functionalization of oligonucleotides can be performed by several methods depending on the intended position of modifying molecule in the sequence and use of the conjugate.

Thanks to their excellence in fluorescence emission and/or its quenching ability, phthalocyanines (Pc) and their aza-analogues (AzaPc) are important candidates as diagnostic oligonucleotide probes modifying molecules, while AzaPc are the more powerful in these abilities.

Constructing oligonucleotide probes, a quenching molecule is preferably (but not solely) attached at 3´-end of the chain because of both synthetic and application reasons. The best way to attach a molecule there is to construct a modified solid phase support for oligonucleotide synthesis. AzaPc-bearing solid phases were prepared by employing two types of reactions: amide binding and standard Cu(I)-catalyzed azide/alkyne 1,3-cycloaddition, the second one achieving considerably higher loadings. To attach the AzaPc elsewhere than at 3´-end, improved Cu(I)-free azide/alkyne 1,3-cycloaddition on a cyclooctyne-modified oligonucleotide was found as the best choice. AzaPc-oligonucleotide conjugates were then prepared as mono- or dual-labelled (TaqMan) probes, purified by HPLC or cartridge methods, and subsequently tested in series of molecular biology experiments.



AzaPc Q = azaphthalocyanine quencher

F = fluorofore

Results:

- DNA hybridization assays confirmed high efficiency (QE>96%) of AzaPcs in quenching of six different most commonly used fluorophores ranging in emission maxima from 517 nm to 701 nm[1].
- AzaPcs were proved to be highly effective universal fluorescence dark quenchers in molecular oligonucleotide probes, comparable to or better than the standard commercial quenchers.
- AzaPc quenchers were better especially in experiments with dual-labelled probes, where Resonance Energy Transfer (RET) was the main quenching mechanism[2].

The study was supported by Czech Science Foundation, project No. 13-27761S

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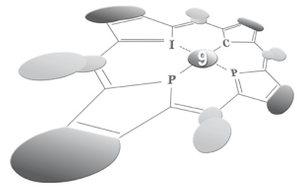

Functionalization of Naturally Occurring Tetrapyrroles – a Valuable Tool for Partial Synthesis of Artificial and Natural Porphyrinoids

Franz-Peter Montforts[a], Benjamin Gerlach[a], Nghiem Hai Vu[a]

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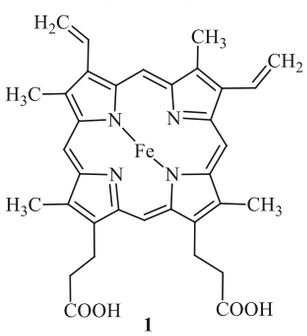
Naturally occurring linear and macrocyclic tetrapyrroles like heme **1**, chlorophyll **2**, and bilirubin **3** form an ideal platform for partial synthesis of artificial and natural porphyrinoid pigments for manifold applications.



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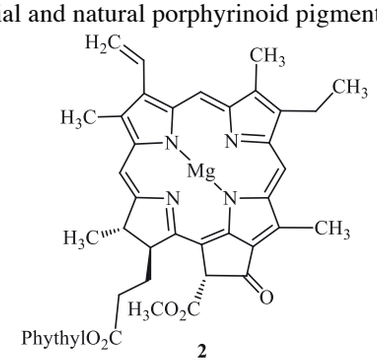

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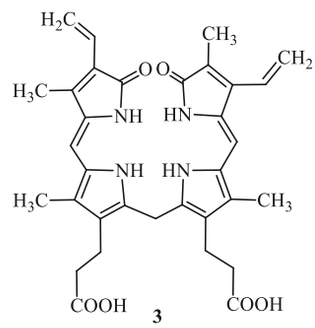
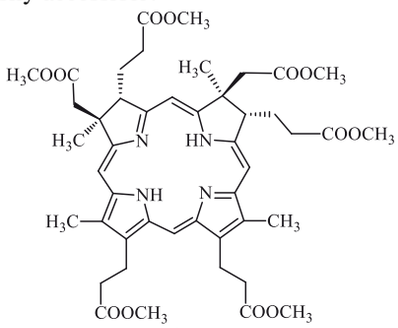


3

Consideration of particular reactivity and functionality as well as especial substitution patterns of the naturally available and renewable starting products allows selective synthetic transformations. This target oriented modifications make complex natural and artificial porphyrinoids like didecarboxy sirohydrochlorin **4** or azachlorin **5** easily accessible.



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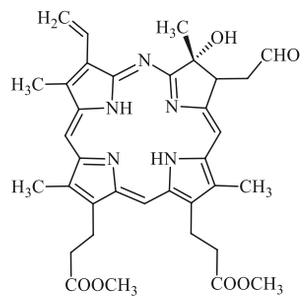

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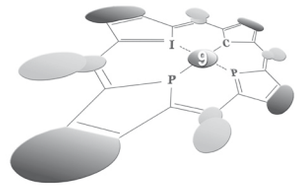

Synthesis and Properties of Bisporphyrins with Two Bicyclic Units

Shigeki Mori[a], **Naoki Kawamoto**[b], **Masayoshi Takase**[b], **Tetsuo Okujima**[b], **Hidemitsu Uno**[b]

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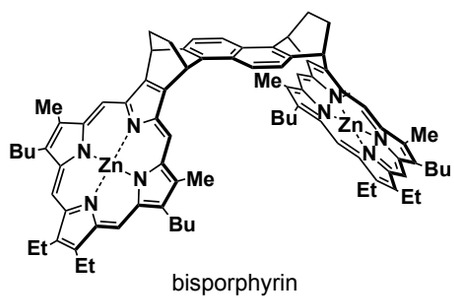
Porphyrins are macrocyclic molecules consisting of four pyrrole parts and characterized by their large π-conjugation system. Retro Diels-Alder reaction of bicyclo[2.2.2]octadiene (BCOD) framework is a promising method for constructing a novel π-conjugation network. We have developed the preparation of highly pure π-extended porphyrins and related compounds based on thermal conversion of BCOD moieties on the precursor in final step [1]. BCOD skeleton is also available as a connecting unit and thermal conversion affords two π-system-fused compound [2]. Non-covalent interaction by π-conjugated compound is of special importance due to the construction of host molecule. We have also reported the synthesis of bisporphyrins equipped two BCOD moieties in the spacer, which makes a cavity with defined size and shape [3]. In the cavity, the porphyrins can be expected to interact strongly with electron-acceptable molecules such as fullerenes [4].
In this study, we designed *syn*-oriented bisporphyrin bearing chrysene-like bridge unit. The inclusion behavior with fullerenes was examined by means of UV-Vis and fluorescent titration. We will discuss synthesis and properties of this bisporphyrin.



bisporphyrin

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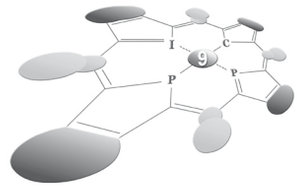

Molecular Design Guide to Achieve More than 15 % Energy Conversion Efficiency for Dye-Sensitized Solar Cells

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Dye sensitized solar cells consist of a porous semiconductor electrode, sensitizing dyes, electrolyte solution containing redox couples, and a counter Pt electrode. In the solar cells, charge separation occurs at TiO_2/dye/electrolyte interfaces. To achieve high separation efficiency, required energy differences are typically more than 0.2 eV between dye's LUMO and TiO_2 conduction band edge levels and more than 0.5 eV between dye's HOMO and electrolyte redox levels. However, the sum of the energy differences, 0.7 eV, is just used to separate the charges and cannot be used for external circuit. In other words, half of photon energy is used for the charge separation. If one can reduce the total energy differences down to 0.6 eV without decreasing the charge separation efficiency, 15 % energy conversion efficiency can be achieved.
To reduce the energy differences for dye regeneration process, facilitation of dye cation reduction kinetics is required. To find effective parameters influencing the reduction kinetics, we have measured the kinetics for dyes whose structures were systematically varied. One component of sensitizes is alkyl chains, which have been attached to dyes to reduce the undesired charge transfer from TiO_2 to acceptor species in the electrolyte. In view of reduction kinetics, we found that the alkyl chains reduce the kinetics of the reduction by donor species in the electrolyte [1]. This is because the alkyl chains can block not only the acceptor species but also the donor species from approaching to dye's HOMO. Another component of sensitizers is donor moiety. Even for porphyrin and phthalocyanine, recently designed sensitizers possess donor moieties. Here we studied the reduction kinetics for three dyes, whose differences were only the structure of donor moiety. We found that bulky donor showed fast reduction kinetics. We attributed the result to the larger scattering cross section of the sensitizers.
Facilitation of the reduction kinetics must be accompanied by the retardation of charge recombination. We found that three factors can explain the observed electron lifetimes in dye-sensitized solar cells [2, 3]. These three are physical blocking effect, electrostatic attraction by partial charge of dyes, and dispersion force of dyes. In the presentation, I will discuss how one can design dyes to facilitate the reduction kinetics at the same time with reducing recombination lifetime.

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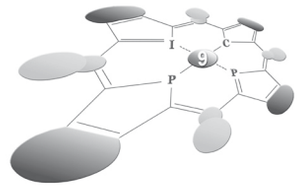

Synthesis and Electronic Properties of Benziphthalocyanines with a Cross-Conjugated 20π-Electron System

Atsuya Muranaka[a], **Shunsuke Yanagi**[b], **Naoyuki Toriumi**[b], **Masanobu Uchiyama**[a,b]

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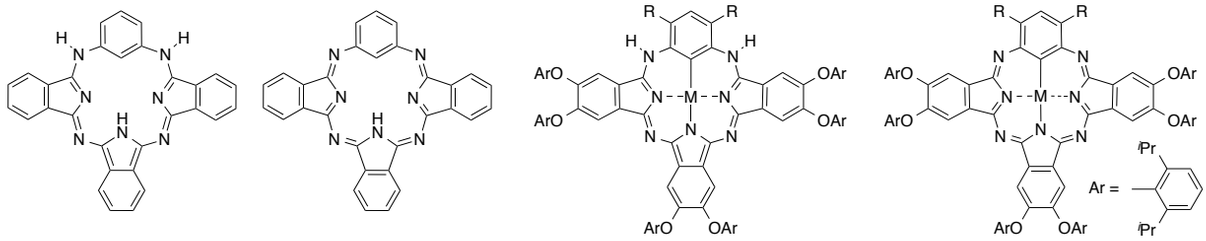
Benziphthalocyanines are cross-conjugated phthalocyanine analogues in which a single isoindoline of phthalocyanine is replaced with one benzene ring. Two different structures have been reported: one is the reduced form with a 20π-electron system,[1] and the other is the oxidized form with an 18π-electron system.[2] Although many benziphthalocyanines are known to adopt a cross-conjugated 20π-electron structure in the solid state, their electronic properties in solution have not been fully understood. In this presentation, we report the synthesis, spectroscopic characterizations, and quantum chemical calculations of 20π-electron benziphthalocyanines with bulky peripheral substituents ($\mathbf{1}_{red}$-$\mathbf{4}_{red}$). The 20π-electron macrocycles were successfully synthesized through hydrogenation of the corresponding oxidized forms ($\mathbf{1}_{ox}$-$\mathbf{4}_{ox}$). The ^{1}H NMR spectrum of $\mathbf{1}_{red}$ showed weak but distinct anti-aromatic paratropic ring current effects despite the cross-conjugated structure. Intense near-IR absorption bands ($\varepsilon > 10^4$ M^{-1} cm^{-1}) were observed for all the reduced forms. Molecular orbital analysis revealed that symmetry-lowering perturbation of the 20π-electron porphyrinoid skeleton enables the HOMO–LUMO transition to be electric-dipole-allowed. Low-lying triplet energy levels were calculated for the reduced forms, which would be related to a biradicaloid character of a cyclic 4*n*π-electron conjugated system.



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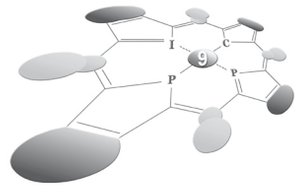

Crystal Structure of CYP90B1, Which Is Involved in Brassinosteroid Biosynthesis

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Brassinosteroids (BRs) are plant steroid hormones, which promote plant growth and development.[1] Several cytochrome P450s (CYPs) are involved in BR biosynthesis and they oxygenate the steroid core and its side chain. Many of these oxygen atoms are required for perception by the BR receptor and co-receptor. CYP90B1 catalyses hydroxylation at the C22 atom of campesterol (C_{28} sterol), which is the first and rate-determining step of BR biosynthesis. Although CYP90B1 exhibits higher hydroxylation activity for cholesterol (C_{27} sterol), the amount of cholesterol in plants is limited. In contrast, sitosterol (C_{29} sterol), which is very abundant in plants, is a poor substrate for CYP90B1. Therefore, CYP90B1 is the key enzyme in BR biosynthesis, and the enzyme's substrate selectivity (cholesterol > campesterol > sitosterol) and natural abundance of $C_{27\text{-}29}$ sterols (cholesterol < campesterol < sitosterol) leads to the production of brassinolide (C_{28} BR), which is the most potent BR in plants.[2] Uniconazole (UCZ), which is a gibberellin biosynthesis inhibitor, and brassinazole (BRZ) bind and inhibit CYP90B1. We determined the crystal structure of UCZ-bound CYP90B1 at 1.9 Å resolution. The overall structure of CYP90B1 has a P450 fold and shows substantial similarity to CYP120A1 and CYP46A1, which catalyse hydroxylation of retinoic acid and the C24 atom of cholesterol (RMSD 1.70 and 2.12 Å), respectively. The UCZ triazole coordinates to the heme iron and the chlorophenyl ring fits snugly into the hydrophobic pocket. We also determined the crystal structure of the BRZ-bound form at 2.3 Å resolution. Although the structures of UCZ and BRZ are similar, the conformations of these inhibitors bound to CYP90B1 show substantial differences. Moreover, significant conformational changes of CYP90B1 are found around the substrate binding pocket. A long loop before the A-helix moves further away from the active site and a C-terminal loop is relocated closer to the active site. Owing to these conformational changes, BRZ has a larger contact area with the enzyme than UCZ; therefore, BRZ has a higher affinity for CYP90B1 than UCZ. To obtain insights into the substrate binding mode and substrate selectivity, we performed a substrate docking simulation in CYP90B1. The docking simulation showed that the side chains of cholesterol and campesterol fit into the narrow pocket, and the C22 atom, which is the hydroxylation site, is located close to the heme iron. However, because sitosterol has a larger substituent on the side chain than cholesterol and campesterol, the side chain of sitosterol cannot fit into the narrow pocket and the C22 atom of sitosterol is far from the heme. The docking simulation also showed that the hydroxyl group at the C3 atoms of cholesterol and campesterol probably form a hydrogen bond with His386. Several hydrophobic residues interact with the steroid core of the substrates. To verify the binding mode of cholesterol and campesterol suggested by the docking simulation, mutagenesis studies were performed on this enzyme. Replacement of most of residues that are expected to interact with the substrate resulted in the loss of hydroxylation activity, indicating that the substrate binding mode in CYP90B1 is similar to that suggested by the docking simulation. Details of regiospecific and stereospecific hydroxylation at C22 and its implications for BR perception are discussed.

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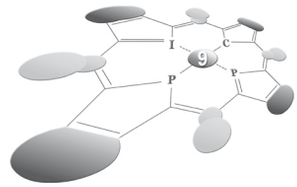

Synthesis and Design of Corroles Endowed with Electron Withdrawing Groups: Examples of Applications

Mario L. Naitana[a], Nicolas Desbois[a], Stéphane Brandes[a], Franck Gallardo[b], Xiaoqin Jiang[c], Karl M. Kadish[c], Virginie Blondeau-Patissier[d], Claude P. Gros[a].

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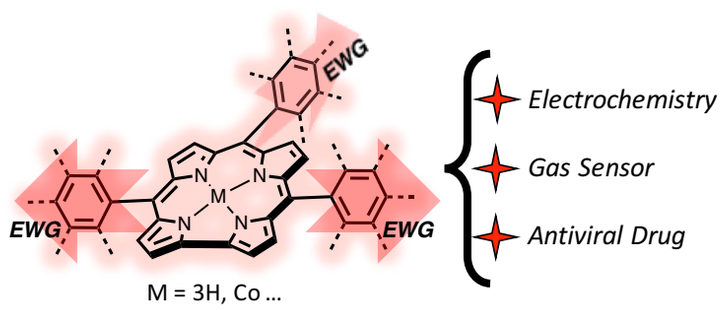
Among porphyrinoids, corroles display unique structural, spectroscopic and photophysical properties, as well as distinctive coordination chemistry and chemical reactivity. All of these features can result in molecular performances, which can be advantageously exploited in many applications ranging from material science to medicinal chemistry. In the present paper, we will focus on the synthesis and design of free-base and metallocorroles bearing electron withdrawing groups (EWG) at the *meso* positions of the macrocycle. From the physical-chemical point of view, the interesting electrochemical features of these derivatives[1] were characterized in order to correlate the redox reactivity and potentials with the number and positions of the EWG substituents. One main goal of the syntheses involves the preparation of cobalt complexes which have applications as sensors, for example, as devices for carbon monoxide detection.[2] We have also examined the *in vivo* activity and cytotoxicity of the newly synthesized corroles as antiviral agents against Human Cytomegalovirus (hCMV) infection,[3] paying particular attention on the relation between the position of the functional groups and their efficiency as virus inhibitors.



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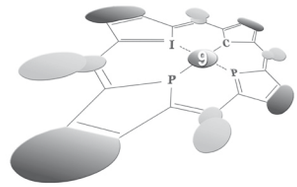

The Coupling Mechanism Between Proton Pumping and Oxygen Reduction Reaction in Cytochrome *c* Oxidase

Satoru Nakashima, Chen Li, Tatsuhito Nishiguchi, Kyoko Shinzawa-Itoh, Sinya Yoshikawa, Takashi Ogura

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Cytochrome *c* oxidase (CcO) is the terminal enzyme of respiratory chain, which catalyses the oxygen reduction reaction coupled with proton pumping across inner membrane. To achieve this efficient function, multi parts of the protein cooperate each other spontaneously and sequentially. Especially the coupling between oxygen reduction site (heme a_3 with Cu_B) and the proton pump pathway is the most crucial point that should be clarified in detail. To elucidate these proton transfer dynamics, IR spectroscopy, which can detect C=O stretching of carboxyl groups and amide bands, is considered to be an ideal tool. We recently have developed new time-resolved IR (TRIR) spectrometer that can detect the enzyme reactions dynamics in water solution in physiological condition.[1] By using this apparatus we succeeded to observe the time-resolved IR absorption spectra of CO photolysis of CcO.[1,2] From the observed results, dynamical complete loading of four pumping-proton equivalents to the network in each catalytic turnover through a water-channel is found to be followed by O_2 binding. This binding triggers the channel closure for blockage of spontaneous proton-back leak during the pumping process. The timely channel closure determines the pumping direction giving efficient energy transduction.

Moreover, to apply TRIR spectroscopy to the oxygen reduction reaction of CcO, we also have developed a new flow system. Since the reaction turnover is within a few ms even in 5ºC condition, the system must have μs order time-resolution. CO photolysis from CO bound CcO in O_2 saturated buffer is one of the methods to initiate the reaction in such fast time-resolution. The flow system contains syringe pumps, oxygen supplied system (oxygen lung) and thin (< 50 μm) water flow cell where the observing point is located. In the system, the syringe pump pushes CO-CcO to oxygen lung where the enough amount of oxygen is injected, and the sample is transferred to the observing point and is stopped. Then visible laser light pulse (5 ns) is irradiated to start the reaction by the photolysis of CO from CcO, and next IR laser pulses are irradiated to monitor the IR spectral changes after certain delay times (100 ns – 5 ms). All these apparatus are synchronously controlled. By using this system, oxygen reduction reaction of CcO was observed by time-resolved visible and IR spectroscopy. From visible absorption measurements, it was confirmed that the flow system worked properly, and the intermediate states, R, A, P, F and O were observed sequentially. In the initial stage of this series of reactions, during R (fully reduced) to A (oxygen-bound) form, a new intermediate was found. This intermediate can be assigned to O_2 bound to Cu_B form that influences the electronic state of heme a_3. Furthermore, in TRIR measurements, protein part dynamics could be observed successfully. The transient structures of protein were altered with the electronic state of heme a_3.

All these observed results, especially from TRIR measurements, exhibit that the proton pumping mechanisms are strongly correlated with the state of oxygen reduction reaction in heme a_3. The details of the coupling mechanisms between the reaction on heme a_3 and proton pumping will be presented.

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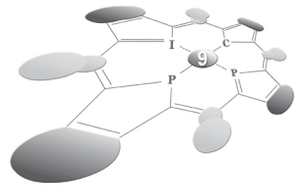

Biomimetic Metal-Oxygen Intermediates in Dioxygen Activation Chemistry

Wonwoo Nam

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Dioxygen is essential in life processes, and enzymes activate dioxygen to carry out a variety of biological reactions. One primary goal in biomimetic research is to elucidate structures of reactive intermediates and mechanistic details of dioxygen activation and oxygenation reactions occurring at the active sites of enzymes, by utilizing synthetic metal-oxygen complexes. A growing class of metal-oxygen complexes, such as metal–superoxo, –peroxo, –hydroperoxo, and –oxo species, have been isolated, characterized spectroscopically, and investigated in various oxygenation reactions. During the past decade, we have been studying the chemical and physical properties of various reactive intermediates in oxygenation reactions, such as high-valent iron(IV)- and manganes(V)-oxo complexes of heme and non-heme ligands in oxo-transfer and C-H activation reactions, non-heme metal-peroxo complexes in nucleophilic reactions, and non-heme metal-superoxo complexes in electrophilic reactions. The effects of supporting and axial ligands on structural and spectroscopic properties and reactivities of metal-oxygen adducts have been extensively investigated as well. In this presentation, I will present our recent results on the synthesis and structural and spectroscopic characterization of mononuclear nonheme metal-dioxygen intermediates as well as their reactivities in electrophilic and nucleophilic oxidation reactions.

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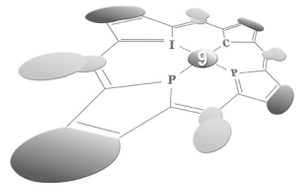

Hydrogenation of Calix[4]pyrrole: Creating and Studying Novel Ligands from a Macrocycle Known for 130 years

Reinhard Neier,[a] Guillaume Journot,[a] William Maupillier,[a] Christophe Letondor,[a] Valeria Blangy,[a] Helen Stoeckli-Evans,[b] Andrea Gualandi,[c] Lucia Cerisoli,[c] Diego Savoia[c]

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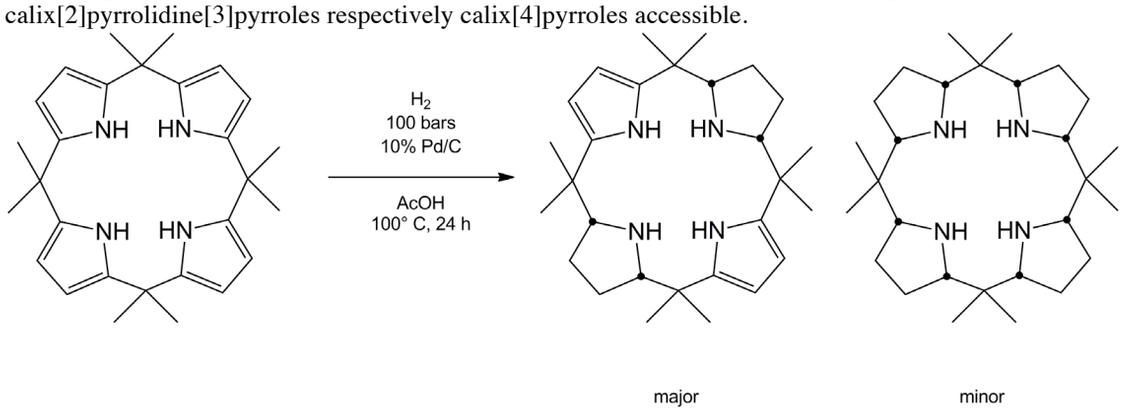
Calix[4]pyrroles, first synthesized by Adolf von Bayer 130 years ago, can be transformed only under forcing condition into transition-metal complexes. Reducing the macrocycle creates a ligand that easily forms classical Werner complexes with many transition metals. The totally reduced calix[4]pyrrolidines are offering four amino-nitrogen atoms in a geometry resembling the arrangement of ligand atoms in porphyrins. The calix[4]pyrrolidines are therefore ideal compounds for studies identifying and exploring the importance of the π-system on the properties of the metal complexes. Conceptually the transformation of calix[4]pyrroles into the calix[4]pyrrolidine is a simple hydrogenation. Our recent studies made for the first time the partially and totally reduced calix[2]pyrrolidine[3]pyrroles respectively calix[4]pyrroles accessible.



The effort invested by our group to develop the hydrogenation from the first successful trials to a reliable process will be presented. The metal complexes obtained will be described and in the case of the manganese complex the catalytic activity will be described. In parallel we developed an approach to the mixed calix[n]furan[4-n)pyrrole macrocylces. The hydrogenation of these mixed compounds gave new insights into the special properties of these new ligands. Our NMR studies revealed a process of slow equilibration between "locked conformers.

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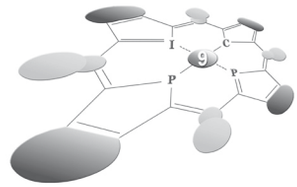

Synthetic strategies for preparation of ferrocene-containing BODIPYs and azaBODIPYs by core modification reactions

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A large number of ferrocene-containing BODIPYs, azaBODIPYs, and BOPHYs (with representative examples given in Figure 1)[1,2] have been prepared by stepwise modification of the parent BODIPYs, azaBODIPYs, and BOPHYs. Both methyl-group activation and chemical modification at the central boron atom were used as synthetic strategies for preparation of the final products. UV-Vis-NIR, NMR, HRMS, and X-ray crystallography were used for identification of the target compounds, while their redox properties were investigated by electrochemical and spectroelectrochemical methods as well as by the chemical oxidation approach. The experimental electronic, spectroscopic, and geometric parameters of the organometallic BODIPYs, azaBODIPYs, and BOPHYs were correlated with DFT and TDDFT calculations.

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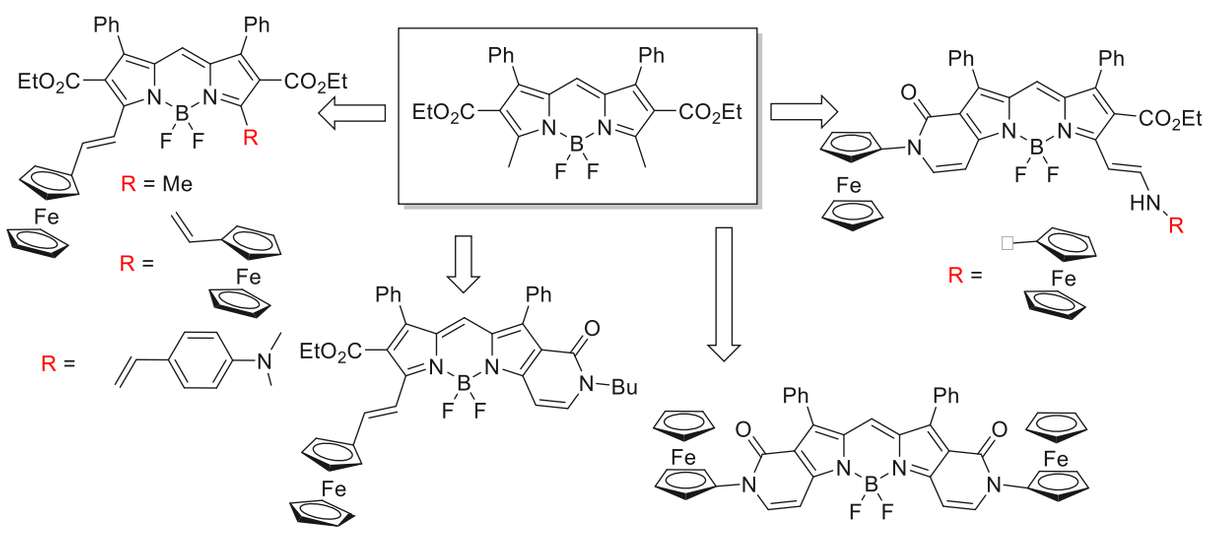

Fig. 1. Representative examples of ferrocene-containing BODIPYs.

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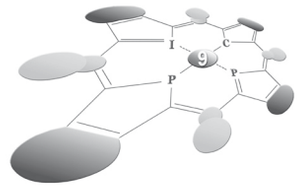

Practical Synthesis of Symmetric Isomers of Diacetyl-, Hemato-, and Protoporphyrins

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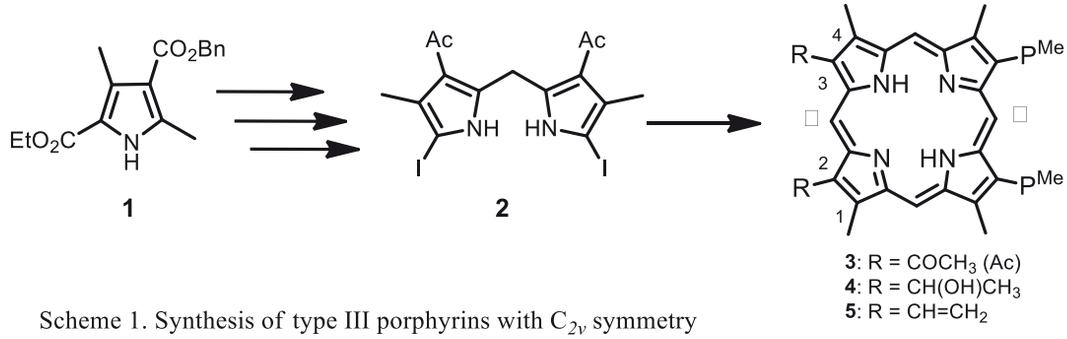
Iron porphyrin is important for various biological processes such as oxygen storage, electron transfer, and degradation of hydrogen peroxide. Protoheme IX with two vinyl groups at peripheral 2,4-positions is asymmetric about the α,γ-meso carbon axis, existing in two orientations rotated about the axis in protein. Owing to the presence of two components of the natural heme, the physicochemical analysis of hemoprotein is seriously complicated in several cases.

Symmetric protoheme is necessary to characterize rigorously hemoproteins without the heme disorder. Since protoheme III bearing two vinyl groups at 2,3-positions is symmetric about the α,γ-meso axis, it is an ideal material for such a purpose. For the synthesis of protoheme III, a pyrrole with acetate group is necessary as the starting material. This pyrrole is derived from methyl 3-acetyl-4-oxopentanone which is not readily available. Accordingly, the reported protoheme III synthesis is not easy to perform. We have devised an improved procedure for protoporphyrin III, starting from a readily available Knorr type of pyrrole, 4-benzyloxycarbonyl-2-ethoxycarbony-3,5-dimethylpyrrole (**1**). Scheme 1 shows the reaction pathway to protoporphyrin III. Pyrrole **1** was self-coupled into a dipyrromethane, and then converted to 3,3'-diacetyl-4,4'-dimethyl-5,5'-diiodo-2,2'-dipyrromethane (**2**) after several steps. Each of the steps proceeded in high-yield. Coupling of **2** with the diformyl counterpart with propionate groups gave symmetric diacetyldeuteroporphyrin III (**3**). Porphyrin **3** was subsequently reduced into hemotoporphyrin III (**4**). Dehydration of porphyrin **4** afforded protoporphyrin III (**5**). The visible absorption spectrum of **5** was closely similar to that of protoporphyrin IX. In the ^{1}H-NMR spectrum of **5**, three meso-proton signals with 1:2:1 intensity ratio were observed, and only two types of peripheral methyl peaks were found, supporting the type III symmetry.

It is notable that starting pyrrole **1** is prepared from inexpensive commercial diketones. The conversion of diacetylporphyrin **3** to protoporphyrin **5** is easily carried out. The 2,3-substituents in porphyrins **3**, **4,** and **5** have electronic influence to different extent against the chelating metals. These results taken together demonstrate that Scheme 1 provides very practical access to the type III isomers, which are essential for the structural characterization of hemoproteins without the heme disorder.



Scheme 1. Synthesis of type III porphyrins with C_{2v} symmetry

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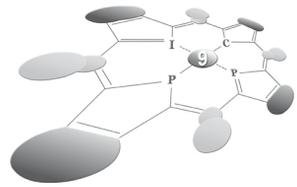

Self-Quenched Phthalocyanines as Smart Photosensitizers for Photodynamic Therapy

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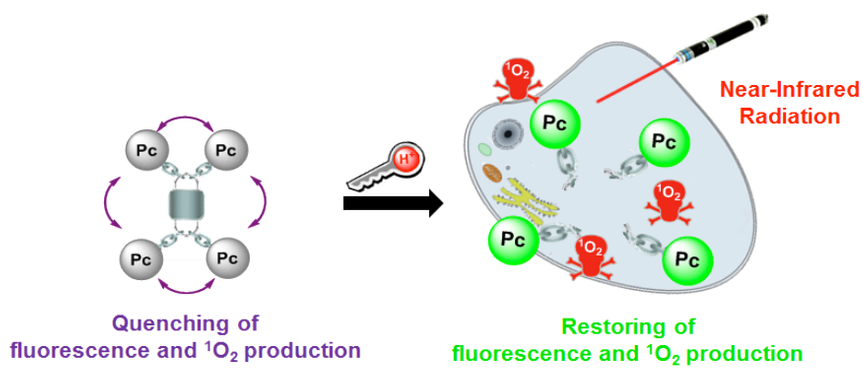
Photodynamic therapy (PDT) is a promising treatment modality for certain localized and superficial cancers.[1] It requires a photosensitive drug, light of specific wavelength, and molecular oxygen to induce a series of photochemical reactions, resulting in the formation of cytotoxic reactive oxygen species (ROS). With a view to improving the therapeutic efficacy, various strategies have been explored to enhance the ROS generation efficiency and tumor selectivity of the photosensitizers.[2] As an alternative approach, "smart" photosensitizing systems that can be activated selectively by tumor-associated stimuli have received considerable attention.[3] As part of our continuing interest in phthalocyanine-based photosensitizers for PDT,[4] we have developed a number of self-quenched dimeric, trimeric, and tetrameric phthalocyanine systems that can be activated by acid and thiols, which can roughly mimic the acidic and reducing environment of tumor, in terms of the fluorescence emission and ROS generation. In this presentation, we will report the molecular design, synthesis, pH- and thiol-responsive behavior, and in vitro and in vivo photodynamic activities of these novel activatable photosensitizers.



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Sacrificial Rotaxane – When Copper Demetallation Fails to Provide Free Base Corrole Porphyrin Conjugates

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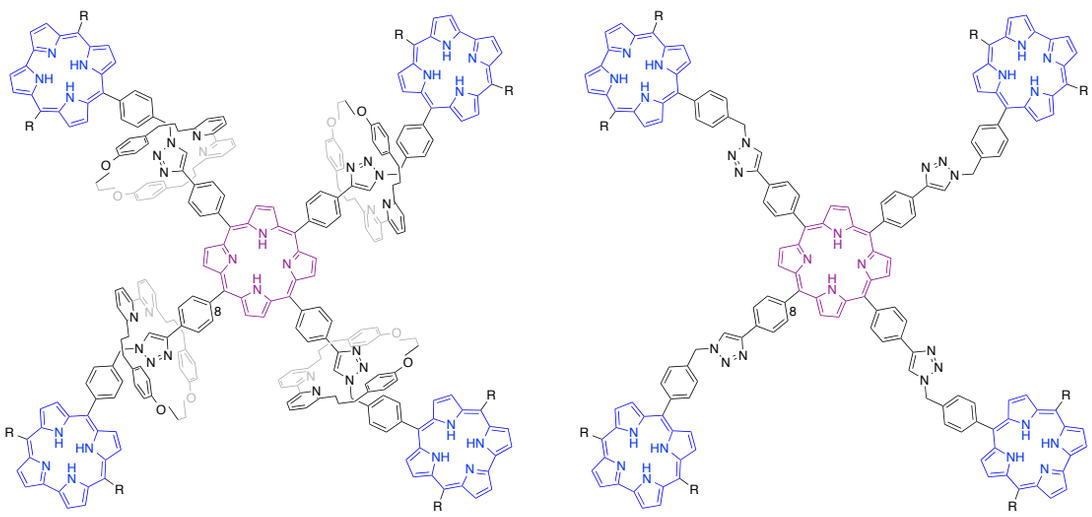
Corrole functionalization has provided a wide range of functional groups to corrole core, allowing the desired properties to be modified for different research fields. Copper center has been used as protecting group during the tedious synthetic procedures. Thanks to various demetallation strategies corrole fluorescence was regained after functionalizations. These procedures tend to fail for conjugates containing multiple copper corrole units. *Via* click and supramolecular chemistry porphyrin core was connected to peripheral corroles by rotaxane linkers. Rotaxane provides a new strategy to use copper catalyzed click reaction to construct non-metallated porphyrin corroles conjugates without demetallation process.



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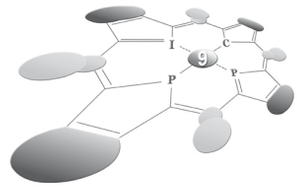

Protein-sensitiser conjugates for theranostic applications

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Fluorescence-guided surgery is emerging as an attractive tool to improve the outcome of tumour resection procedures and therefore the prognosis for the patient. Substitution of fluorescent and photodynamic drugs for fluorescent tags offers the added potential of eliminating any residual cancer cell by exposing the cavity to light of the appropriate wavelength after tumour resection. Antibody-drug conjugates with dual fluorescent and photodynamic activity appear as good candidates for such theranostic applications. We have recently developed a family of chromo- and fluorogenic members of the porphycene family that undergo a colour change when they react with a free amino group of biomolecules.[1] Thus, antibodies labelled with such porphycenes can be used to selectively tag the desired type of cells, image them with near-infrared detectors, and eradicate the cells by the photodynamic effect.

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Conjugates of Phthalocyanines with Nanomaterials for Electrode Modification

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Metallophthalocyanines (MPcs) are employed as electrode modifiers for various applications including the construction of electrochemical sensors for the detection of various analytes such as neurotransmitters and other molecules of biological and environmental importance [1]. The combination of MPcs with nanomaterials such as carbon nanotubes (CNTs), quantum dots (QDs), fullerenes and metal nanoparticles has been shown to improve their catalytic behavior. This work will concentrate on the modification of electrodes with MPc complexes alone or in the presence of QDs, CNTs, graphene, and metal nanoparticles. The MPc may be covalently (amide bonds, or click chemistry) or non-covalently (ππ) linked to nanomaterials. The resulting conjugates and modified electrodes are characterized by several methods including, scanning electrochemical microscopy, X-ray phoroelectron spectroscopy and several voltammetry techniques among others. There are several methods for modifying electrodes using MPc complexes when alone or in the presence of nanomaterials. These include self-assembled monolayer, click chemistry, adsorption and grafting. Fig. 1 shows azide fuctionalized QDs attached to alkyl FePc by click chemistry and used for the modification of electrodes by adsorption.

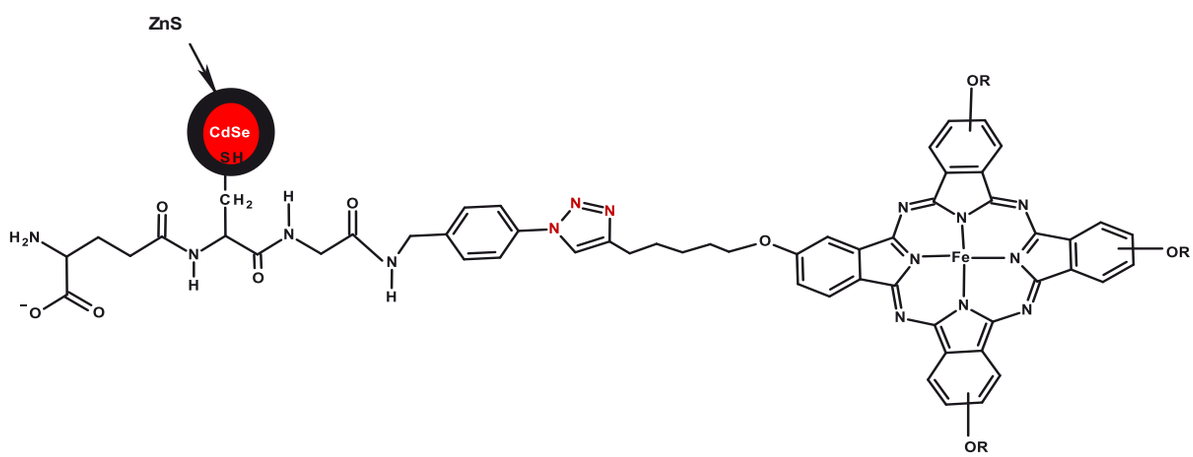

Fig. 1. Structure of a phthalocyanine – QD conjugate formed by click chemistry

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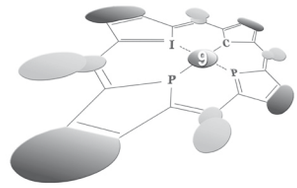

Vitamin B_{12} Catalysis: A Novel Twist on a Classic Compound

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In the vast universe of catalytic reactions, those involving vitamin B_{12} are just a small star in an expansive space. Vitamin B_{12} is a highly functionalized tetrapyrrolic compound bearing a unique central cobalt ion. It has been examined as an oral delivery vehicle for therapeutic agents, as an artificial enzyme and more importantly as a catalyst for various organic reactions.[1] Like most great inspirations, vitamin B_{12} catalysis arose from its natural function, as methylcobalamin and adenosylcobalamin are involved in numerous biocatalytic reactions including isomerization, methylation and dehalogenation.[2] This foundation allowed researchers to build and create a small collection of reactions, including addition to double bonds, halide and alkene coupling, ring expansion, rearrangement, cyclopropanation etc.[3] The advantage of using vitamin B_{12} lays in the complete stability of the central cobalt ion, whereas most catalytic reactions require the addition of toxic metals plus complex ligands into a cocktail of reagents, vitamin B_{12} in itself is a package deal. Furthermore, it has been well documented that the reaction mechanism usually follows a radical pathway, bringing a new dimension to this already interesting field.

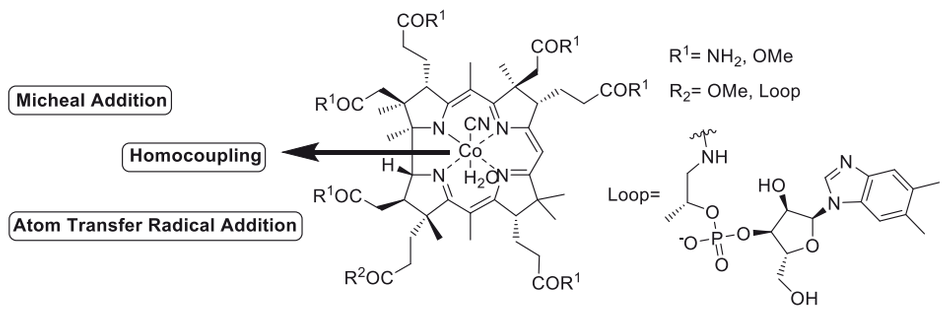

Figure 1. Reactions catalyzed by vitamin B_{12} and its derivatives.

Our work has focused on the unknown. Exploring the vast wilderness that is vitamin B_{12} catalysis. We have found that in a simple reaction of an organic halide and an olefin, using organic soluble vitamin B_{12} deriavaitive heptamethyl cobryinate as the catalyst of choice, numerous selective reactions can occur by only slightly altering the delicate balance of the reaction conditions. These include Michael addition, homocoupling and atom transfer radical addition. Other vitamin B_{12} derivaives examined,[4] such as cobalester, has lead to a treasure trove of new and fascinating discoveries.

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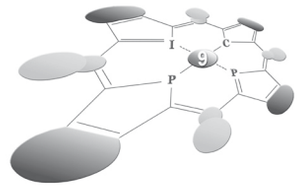

Ultraviolet Resonance Raman Spectroscopic Study on Cytochrome *c* Oxidase P Reaction Intermediate

Takashi Ogura[a, b], **Shoko Watanabe**[a], **Sachiko Yanagisawa**[a], **Satoru Nakashima**[b], **Kyoko Shinzawa-Itoh**[b] **and Shinya Yoshikawa**[b]

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Bovine cytochrome *c* oxidase (CcO) catalyzes four-electron reduction of dioxygen[1)]. This electron transfer reaction is coupled to proton pump across the inner mitochondrial membrane. The proton-motive force thus formed is utilized by F_oF_1-ATPsynthase to generate ATP. Four reaction intermediates in O_2 reduction at heme a_3 are identified and designated as A, P, F and O. The following scheme for O_2 reduction has been established.

$$Fe^{2+} + O_2 \rightarrow Fe^{3+}\text{-}O_2^{-}\ (A) \rightarrow Fe^{5+}{=}O^{2-}\ (P) \rightarrow Fe^{4+}{=}O^{2-}\ (F) \rightarrow Fe^{3+}\text{-}OH^{-}\ (O) \rightarrow Fe^{3+}$$

Here, the oxidation state of Fe^{5+} of the P intermediate is a formal one. Four electron equivalents have been accepted by O_2 to make the P intermediate. Two electrons come from heme a_3 and one from Cu_B; however, the origin of the fourth electron equivalent is still not proved with strong physical evidence. If the origin is Fe, then notation of Fe^{5+} is appropriate. Y244 near heme a_3 has been a candidate of the electron donor to O_2 and if this is the case, presence of a radical at Y244 is expected. An indirect radical detection was reported[2)], however, only very low radical signal intensity was detected relative to that expected in the EPR spectra[3)]. It is interpreted as due to magnetic interaction of the radical site with Cu_B.

In the present study, we applied ultraviolet resonance Raman (UVRR) spectroscopy to the P intermediate to selectively enhance the vibrational modes of aromatic amino acids (Tyr and Trp) to investigate whether tyrosil radical is present or not in the P intermediate.

The P intermediate ($[CuA]^{3+}$, heme a^{3+}, heme a_3^{5+}=O, Cu_B^{2+}) of bovine CcO was prepared by replacing the gas phase of the resting CcO solution at pH 8.0 by O_2/CO mixed gas (1:1 mixture). Mixed-valence and CO-bound form (MV-CcO-CO, $[CuA]^{3+}$, heme a^{3+}, heme a_3^{2+}-CO, Cu_B^{1+}) was prepared by replacing the gas phase of the resting CcO solution at pH 8.0 by pure CO gas. UVRR scattering was excited at 229.0 nm from a frequency-doubled Ar^+ laser (Coherent, 300C FRED) and was dispersed with a polychromator (HORIBA Jobin Yvon, 1000M, f = 1 m) equipped with a 3600 grooves/mm holographic grating blazed at 200 nm. Dispersed light was detected with a liquid nitrogen-cooled CCD detector (Roper Scientific, Spec10: 400B/LN)).

UVRR spectra excited at 229.0 nm contained primarily the contribution from Tyr and Trp residues. The difference of the oxidation states between the P and MV-CcO-CO is in the heme a_3 – Cu_B binuclear center. The UVRR difference spectrum (P minus MV-CcO-CO) showed no evidence for Tyr radical.

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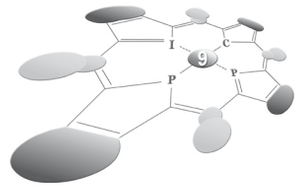

Supramolecular Electron-Transfer Chemistry of $Li^{+}@C_{60}$ with Porphyrinoids

Kei Ohkubo[abc], Shunichi Fukuzumi[abc]

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Extensive efforts have so far been devoted to design and synthesize electron donor-acceptor linked molecules to achieve efficient photoinduced charge separation [1]. We have recently designed and synthesized simple electron donor-acceptor supramolecular complexes composed of lithium ion encapsulated fullerene ($Li^{+}@C_{60}$) with porphyrin and phthalocyanines and chlorin derivatives.[2-6]

Photoinduced electron-transfer dynamics were examined by femto- and nanosecond laser flash photolysis. The charge-separated states were detected as the transient absorption spectra, where $Li^{+}@C_{60}$ radical anion of charge-separated state has a specific absorption at 1035 nm. The lifetimes of charge-separated state were determined from the decay of the absorbance at 1035 nm. The lifetime was 230 μs in the case of a supramolecule between anionic porphyrin and $Li^{+}@C_{60}$ in PhCN. The long-lived charge-separation was also confirmed by EPR spectroscopy [2]. Photoelectrochemical measurements were performed using a standard two-electrode system consisting of a working electrode and a Pt wire gauze electrode in air-saturated MeCN containing LiI and I_2. The maximum IPCE values in the case of OTE/SnO_2/($ZnTPPS^{4-}$/$Li^{+}@C_{60})_n$ attained in these experiments was 77% at 450 nm [3]. The photocurrent generation occurred via photoinduced electron transfer from $ZnTPPS^{4-}$ to $Li^{+}@C_{60}$ in the supramolecular nanoclusters.

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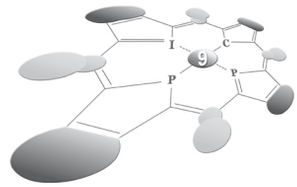

2nd Coordination Sphere Controlled Oxygen Reduction Reaction Catalyzed by a Bio-inspired Iron Porphyrin

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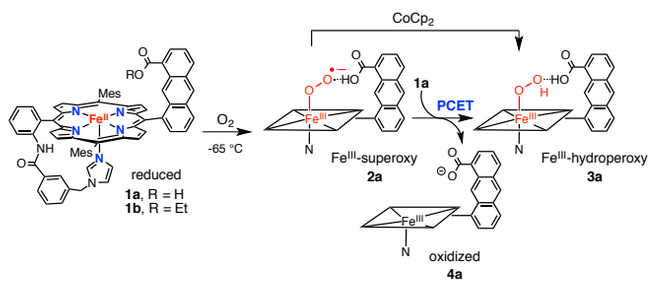
Oxygen reduction reaction (ORR) catalyzed by a bio-inspired iron porphyrin complex was studied. Previously, we reported that a rationally designed iron porphyrin complex that includes a tethered imidazole axial ligand can activate dioxygen to yield a ferric-hydroperoxo intermediate.[1] A highly reactive ferrous-superoxo intermediate was generated by a cryoradiolytic reduction of a ferric-superoxo precursor. The molecular structure of the ferrous-superoxo complex was investigated with cryo spectroscopic methods, providing further insights into the ORR mechanism.[2] Thus, a next generation iron porphyrin complex has been developed by incorporating a H-bond donor at the distal site of heme to harness 2nd sphere interaction with heme-bound O_2.

A new bio-inspired iron porphyrin complex (**1a**) includes an anthoracene substituent attached with a carboxylic acid group positioned over the porphyrin ring. Introduction of dioxygen to a solution of **1a** in 80% $EtCN/CH_2Cl_2$ at –65 °C gave a dioxygen adduct **2a**. Unexpectedly, however, EPR spectrum of this reaction mixture indicated a formation of a small amount of a low-spin end-on ferric hydroperoxide species (**3a**) (g = 2.29, 2.17, 1.95), indicating that an unreacted high-spin ferrous heme (**1a**), donated an electron and a proton to **2a**. Thus, **1a** was examined for its ability to reduce **2a**. After formation of **2a** and a small amount of compound **3a**, excess dioxygen was removed. Then, addition of an equivalent molar of **1a** in THF at –70 °C immediately produced the corresponding high-spin species **4a** (g = 4.5) and a low-spin end-on ferric hydroperoxoide **3a**. In general, a high-spin ferrous porphyrins do not have a potential to reduce the corresponding oxy complexes to the (hydro)peroxy species. This is the first example of a high-spin ferrous heme complex that reduces its ferric-superoxy form, possibly through a proton coupled electron transfer (PCET) mechanism.

Electrochemical ORR study demonstrated that the onset potential of the reaction was shifted to a positive in the presence of 2nd sphere interaction. Resonance Raman and DFT computational analyses of the structural and thermodynamic properties of reaction intermediates give insights into the molecular mechanism by which H-bond interaction enhances the ORR reactivity.



Scheme 1. Oxygen activation by a bioinspired iron porphyrin complex

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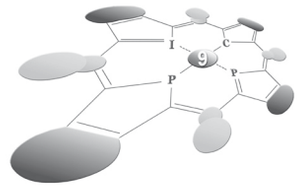

Synthesis of Cyclo[n]pyrroles with Intense NIR Absorptions

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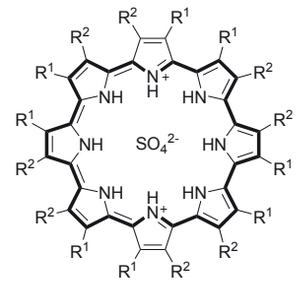
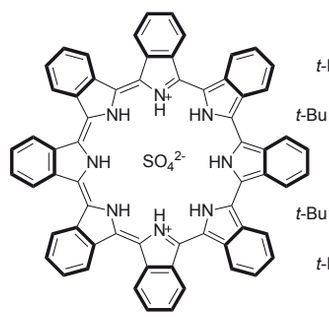
In 2002, Sessler reported the first synthesis of cyclo[8]pyrrole, a ring-expanded porphyrin analogue with no *meso*-bridges.[1] The photophysical, anion–binding and liquid crystal properties of cyclo[n]pyrroles (n = 6–8) have been studied in-depth, along with their electronic structures. However, little is known about π-expanded derivatives while various π-expanded porphyrins have been successfully synthesized. Introduction of fused aromatic-rings resulted in the dramatic shift of the L bands. For example, the longest wavelength absorption of cyclo[4]naphthobipyrrole appeared at 1334 nm with large absorption coefficient.[2]

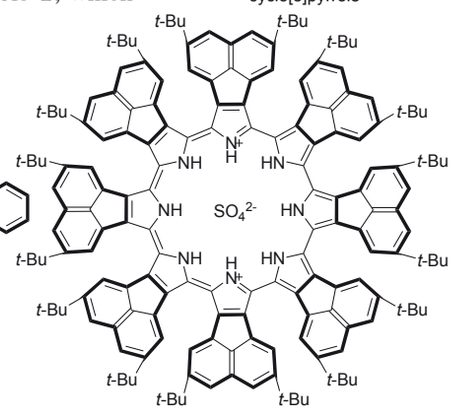


cyclo[8]pyrrole

We have reported the first π-expanded cyclo[8]pyrrole, cyclo[8]isoindole **1**, which have been synthesized based on the retro Diels–Alder strategy from the bicyclo[2.2.2]octadiene(BCOD)-fused precursor.[3a] An acenaphthylene-fused cyclo[8]pyrrole **2** has been synthesized *via* the oxidative coupling of 2,2-bipyrrole, which showed the red-shifted L band at 1515 nm.[3b]

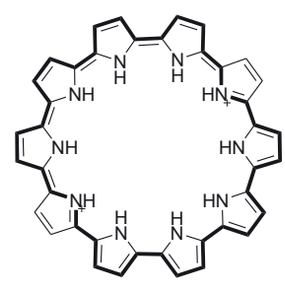


cyclo[8]isoindole **1**
λ_{max} 1078 nm



cyclo[8]acenaphthopyrrole **2**
λ_{max} 1515 nm

On the other hand, the larger structural analogues of cyclo[n]pyrrole (n > 8) was successfuly synthesized and isolated. In the synthesis of **2**, a cyclo[10]acenaphthopyrrole was isolated and purified by repeated column chromatography and GPC after several high-polar fractions had been collected during the purification. The structure was confirmed by X-ray crystallographic analysis. The oxidation conditions of bipyrrole were examined. The use of appropreate dianion template afforded selective synthesis of cyclo[10]pyrrole in high yield more than 50%.



cyclo[10]pyrrole
[38]decaphyrin(0.0.0.0.0.0.0.0.0.0)

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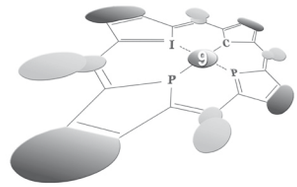

Dibenzoporphycene with Annulated Benzene Rings at Two Ethylene Bridges of the Porphycene Framework

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Porphycene is a constitutional isomer of porphyrin, in which the symmetrically reduced porphyrinoid structure demonstrates notable physicochemical properties such as stronger absorption in the visible region and unique tautomerization of the inner hydrogen atoms. Investigation of porphycene derivatives indicate that they have potential for use as photosensitizers and metal ligands in oxidation catalysts.[1] This has motivated us to prepare new porphycene derivatives.

We designed and prepared *meso*-dibenzoporphycene (**mDBPc**), where two benzene moieties are annulated at ethylene-bridged positions (*meso*-positions) of porphycene in an effort to further delocalize the π-electrons within the porphycene molecule (Figure 1a).[2] The obtained molecule was fully characterized by mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy, and X-ray crystallography. Interestingly, the inner NH signal of **mDBPc** in the ^{1}H NMR spectrum ($CDCl_3$, 25 ºC) appears in the lower field at 8.95 ppm, compared with that of the unsubstituted porphycene (**Pc**) (3.15 ppm). The remarkable lower-field shift suggests the occurrence of stronger intramolecular NH–N hydrogen bonding. The results are correlated with shorter N1–N4 distance compared to that of various porphycenes in the crystal structures. The UV-vis-NIR absorption spectra of **Pc** and **mDBPc** in CH_2Cl_2 are shown in Figure 1b. The longest-wavelength Q-band of **mDBPc** is red-shifted by 418 nm compared to that of **Pc**. Electrochemical measurements suggest that the HOMO is destabilized and the LUMO is stabilized by the annulated-benzene moieties at the *meso*-positions. Furthermore, both X-ray photoelectron spectroscopic and theoretical studies support the presence of a *cis* tautomeric form in the ground state of **mDBPc**, despite the fact that essentially all known porphycene derivatives adopt the *trans* tautomeric form.

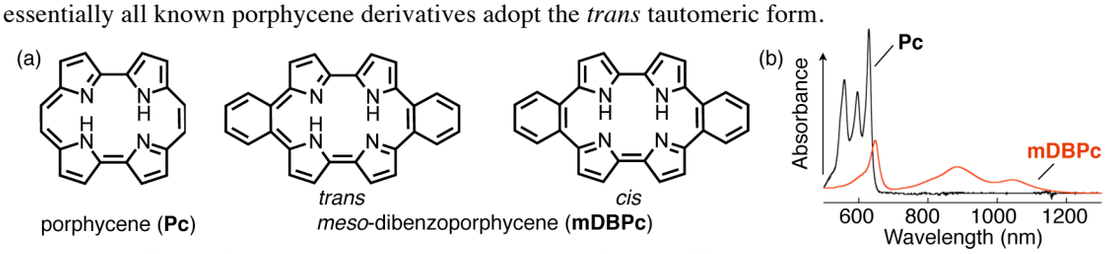

Figure 1. (a) Molecular structures and (b) UV-vis-NIR spectra of porphycenes.

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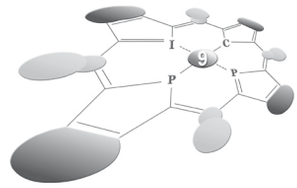

Emergence of Porphycene

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Porphycene is the first constitutional isomer of porphyrin to be reported.[1] Owing to the presence of two bipyrrolic moities in the macrocycle, it is much sensitive to the effect of substituents at its periphery.[2] The synthetic difficulties associated with the preparation of bipyrroles limited the number of porphycenes reported, and hence, lack a detailed studies of the substitution effect. However, in recent times there are several new developments in the pyrrole chemistry, making it possible to design and synthesize new porphycene derivatives. The recent trend shows porphycene exhibits many attributes not noticed in case of the parent porphyrin isomer.[3] This led us to explore the substituent effects in details. Those will be discussed in the context of our recent results.[4]

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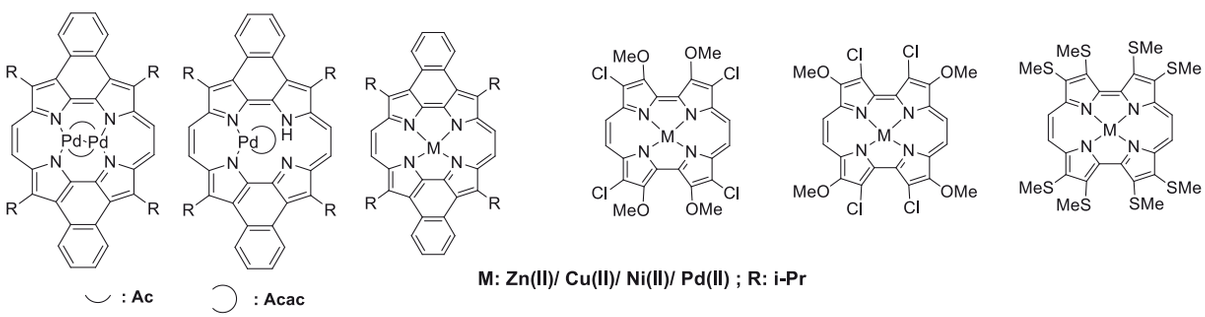

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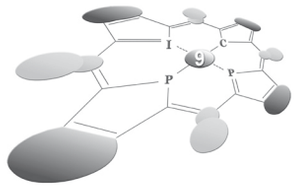

Impact of Delivery Vehicles in Tumor-Target Specificity of Cancer-Imaging and Therapeutic Agents (Theranostics)

Aimee J. Marko, Kevin E. Siters, Farukh Durrani, Ramona Watson, Joseph R. Missert, Joseph Cacaccio and Ravindra K Pandey

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The full potential of drug delivery systems extends beyond treatment. By using advanced imaging technologies with targeted delivery, doctors may someday be able to diagnose and treat diseases in one procedure, a new strategy called Theranostics. Towards this end, various laboratories are building multi-functional agents or nanoparticles than can be introduced into a patient, find the site of disease, diagnose the condition, and deliver the appropriate, personalize therapy. For quite some time, the focus of our laboratory has been to develop multifunctional agents for imaging and phototherapy (PDT), or image-guided surgery with an option of PDT or other treatment modality. This "See and Treat" approach enhances the scope of image guided therapy.

Most of the photosensitizers (PS) investigated and/or being used to date in photodynamic therapy (PDT) are highly fluorescent. This property has been used to guide surgical interventions and PDT. Unfortunately, most of the photosensitizers exhibit small Stokes shift(s) between the long-wavelength absorption and emission and are therefore not desirable candidates for fluorescence imaging of cancer. Conversely, certain highly efficient cyanine dye–based fluorophores (non-porphyrin based compounds) generally do not localize within tumors efficiently, but require an additional moiety or process to provide selectivity, such as an attachment of a peptide or other moieties that bind to a targeted receptor(s) known for high expression in tumors. Promising clinical-PDT results suggest that certain porphyrin-based photosensitizers preferentially accumulate within à wide range of malignancies compared to their normal tissue surroundings. This characteristic has been used in designing bi- and multifunctional agents in which the PS also helps in delivering the desired imaging agent(s) to tumors. For quite some time one of the objectives of our laboratory has been to develop agents that can be used concurrently to detect tumors (via PET, MRI and/or fluorescence) and treat them by PDT.The comparative tumor-imaging and therapeutic potential of these imaging and therapeutic agents in selected delivery vehicles will be presented.

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The organisation of porphyrin and phthalocyanine-functionalised naphthalenediimides into discrete, defined supramolecular architectures

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Aminoacid derived naphthalenediimides form supramolecular nanotubes when dissolves in aprotic solvents with medium polarity such as chloroform or dichloromethane. These supramolecular nanotubes have been shown to interact with fullerenes, ion-pairs and small polyaromatic hydrocarbons. The supramolecular nanotubes are fairly tolerant to modifications on the aminoacid sidechains as long as the derivatives have the required solubility in aprotic solvents. Here we investigate the behaviour of aminoacid derived naphthalenediimides bearing porphyrin appendages (see figure) and polyaromatic moieties. We will discuss an interesting proton-mediated transfer-of-chirality phenomenon as well as similar chirality transfer observed in a series of phthalocyanine derivatives.

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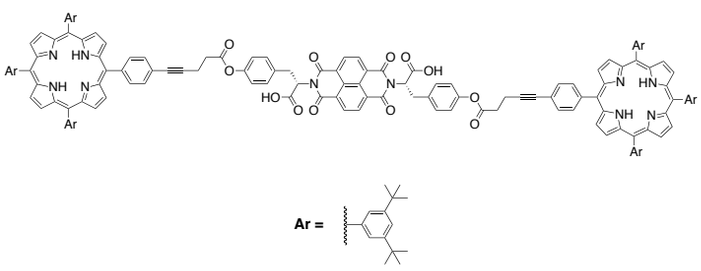

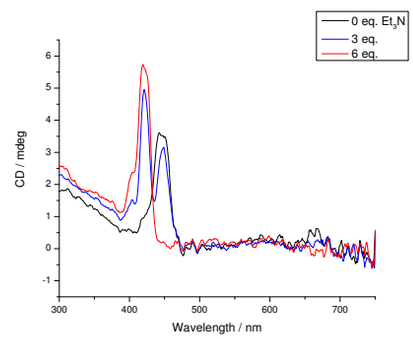

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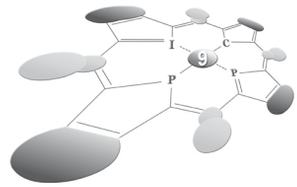

Corroles with annulated aromatic rings

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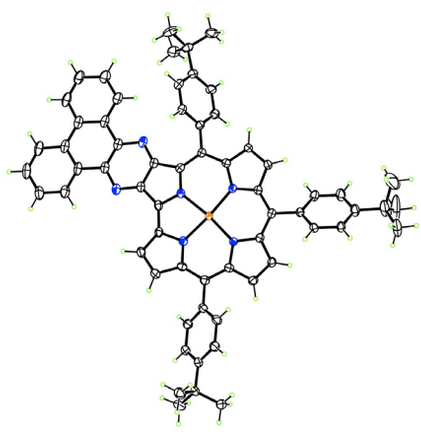
The fine tuning of the corrole properties to match specific applications is an important task that often requires the elaboration of *ad hoc* synthetic procedures and a careful study of the desired molecule features. Among the possible functionalizations, the introduction of fused p-conjugated units demonstrated to be a promising approach, able to significantly modify the electronic characteristics of the macrocycles and leading to the preparation of chromophores with peculiar optical and electrochemical features. Different functional groups have already been inserted in the corrolic peripheral positions that could be used as starting point for the target modification and in particular our attention has been focused on the functionalization of mononitrocorroles, whose preparation and reactivity has been studied in our laboratories.[1] In particular we decided to explore the reactivity of the amino-nitro compounds, obtained by the vicarious nucleophilic reaction of nitrocorroles with triazole,[2] to prepare corroles with annulated aromatic rings.



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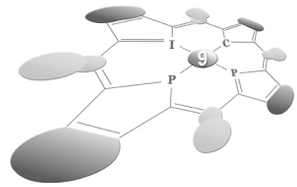

High-resolution imaging of tissue hypoxia with cell-penetrating phosphorescent porphyrin nanosensors

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Cell-penetrating probes based on phosphorescent Pt-porphyrin dyes allow quantitative and real-time imaging of O2 distribution in cell and tissue models with high sensitivity and spatial resolution [1, 2]. The small molecule and nanoparticle structures can be used on standard live cell fluorescent microscopes, however Phosphorescence Lifetime Imaging Microscopy (PLIM) under one or two-photon excitation is a preferred modality for quantitative imaging of tissue O_2. Here we demonstrate the capabilities of this technique with a range of different 3D tissue models, including 2D cell cultures, multi-cellular spheroids and organoids, animal tissue explants, measured on the confocal PLIM-TCSPC imaging platform. Biomedical applications presented include 3D visualisation of tissue hypoxia, studies of stem cell development, monitoring of tissue metabolic responses to physiological and drug treatments, optimisation of culturing conditions for tissue models, multi-parametric metabolic imaging [3].

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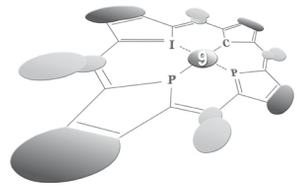

Properties of Oxatriphyrins(n.1.1) Tuned by Coordination

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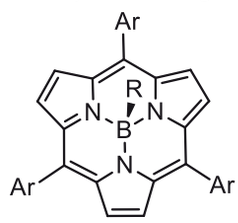
Optical properties of porphyrinoids can be controlled by several factors, i.e. protonation/deprotonation, oxidation/reduction or coordination what drastically influence both – the absorption and the emission behaviour, in some examples shifting these parameters to the near-infrared region. The coordination abilities observed for different macrocycles vary with the space available in their inner. Thus a gradual removal of building blocks from the macrocycle and transformation i.e. a tetraphyrin(1.1.1.1) (*porphyrin*) into a triphyrin(***n***.1.1) (***n*** = 1-3) drastically changes the coordination abilities limiting i.e. the possibility of binding transition metals, but the significantly modified shape of porphyrinoid notably influences observed properties, i.e. redox potentials or absorption and emission behaviour. Boron(III) complex of triphyrin(1.1.1) **1** creates a triangular molecule where the aromatic conjugation is nicely marked as 14π electrons path and the observed properties are derived from this delocalization.[1] The 14π delocalization path has been also reported for triphyrins(2.1.1) **2**. For those macrocycles the optical properties are straightforwardly extracted from the conjugation of 14π electrons as well.[2] The in-plane coordination for this family of macrocycles is observed solely for small cations, i.e. boron what strongly modifies optical properties.



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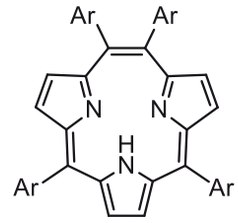

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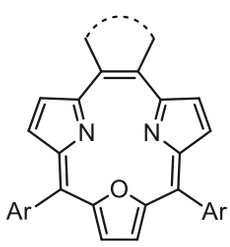
A group of oxatriphyrins - **3** (2.1.1)[3] and **4** (3.1.1)[4a] creates a nice environment for exploring the response of reduced in size porphyriniods on the initiator of coordination or reduction/oxidation. Rationally obtained family of the 2.1.1 structural motif has shown intriguing coordination abilities strongly affecting the aromatic character, and as a consequence also the optical properties. The coordination induced modification of the 3.1.1 structure also significantly changes the conjugation within the macrocycle and the fluorescence properties.[4b] The details of the approach leading to aromaticity control and in the effect changes in the optical properties will be discussed.



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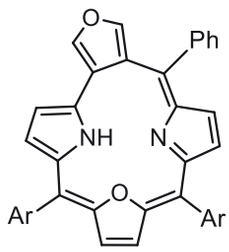

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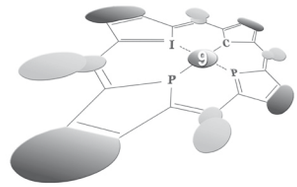

Photodynamic decontamination as tool for increasing food safety

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Introduction: Access to safe food represents a basic right of humans. The use of antibiotics in food production is controversial as it promotes the transmission of resistant microorganisms from animals to humans (1). An outbreak of foodborne illness in the EU in 2011 induced by Escherichia coli O104:H4 emphasised the importance of crop products as shuttle for pathogenic bacteria. Photodynamic Inactivation (PDI) has proven highly efficient against multi-resistant microorganisms and is also applicable to decontamination of foodstuff, in particular if based on natural photosensitizers. **Experimental:** We examined the phototoxicity of Na-chlorophyllin (Na-Chl, approval as food additive E140), a water soluble formulation of curcumin (E100) and novel curcumin derivates (SACURs) against *Staphylococcus aureus*, *Escherichia coli*, *Candida albicans* and *Aspergillus niger* in liquid suspension. The bacterial strains were also inoculated on the surface of cucumber, pepper, salad, chicken meat or porcine skin before PDI. Illumination was performed using LED arrays. **Results:** In liquid suspension, 25 min incubation with 5 µM Na-Chl and subsequent illumination with 17.8 $J.cm^{-2}$ (400 nm) eradicated all *S. aureus* (>7log_{10}). Five micromolar polyvinylpyrrolidone-curcumin (PVP-C, illumination at 435 nm, 33.8 $J.cm^{-2}$) resulted in a >6log_{10} reduction of viable *S. aureus*. For a photoantibacterial effect towards the Gram(-) *E. coli* cell wall permeabilization with $CaCl_2$ prior to addition of 50 μM PVP-C was required (2). Additives could be omitted if SACUR was used against *E. coli* (>7log_{10}, 10 μM). PDI with 50 μM SACUR-II (5 min incubation, 15.8 $J.cm^{-2}$) induced a reduction of *C. albicans* of 5log_{10}. *Aspergillus niger* phototreated with 20 μM natural curcumin lead to a complete stop of fungal growth. More than 99.9% of *S. aureus* on the surface of cucumber and pepper or 98% of these bacteria on chicken were killed by a PDI using 50 μM curcumin formulations (3). Photodecontamination based on 50 μM SACUR against *E. coli* on cucumber or salad induced a photoantibacterial effect (4/6log_{10}). This novel photosensitizer also proved highly phototoxic to *E. coli* on porcine skin (4). The PDI efficiency was independent of the food colour and photodecontamination did not change the optical appearance of the foodstuff. **Discussion:** Photodynamic decontamination based on natural photosensitizers helps to improve food safety. Na-Chl and PVP-C represent excellent photosensitizers for this application due their approval as food colorant. For an photoantibacterial effect against *E. coli* on various substrates including porcine skin SACUR is effective. Both, natural curcumin and SACUR-II may be applicable as photofungizides in human medicine and on surfaces.

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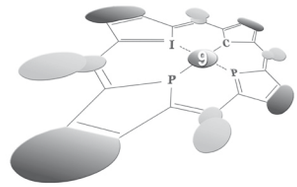

One molecule and two chelating systems for more binding opportunities

Federica Mandoj[a], Giuseppe Pomarico[a], Frank R. Fronczek[b], Kevin M. Smith[b], Roberto Paolesse[a]

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The modification of porphyrin macrocycle by introducing particular functional groups (dyes [1] or electron-active [2] moieties) allows the achievement of new materials, usually endowed or enriched of the main characteristic of any component. At this regard, we focused our interest toward a new class of compound: a porphyrin unit bearing a pincer group (Figure 1, left), such as the bis(2-pyridylimino)isoindole (BPI), a very versatile catalyst for many reactions [3]. Some reasons attracted our interest toward this unprecedented porphyrin-BPI: both the molecules have a characteristic UV-vis spectrum, and the resulting hybrid material can display the complementary absorption of individual chromophores (Figure 1, right), also affected by the solvents system. Much more, either porphyrin and BPI are able to bind many metal ions, allowing the formation of a bimetalated substrate. The porphyrin-BPI dyad was prepared by a multistep procedure and the features of this compound investigated by spectroscopical techniques. Finally we studied the catalytic properties of this compound by insertion of a suitable metal ion in the peripheral pincer.

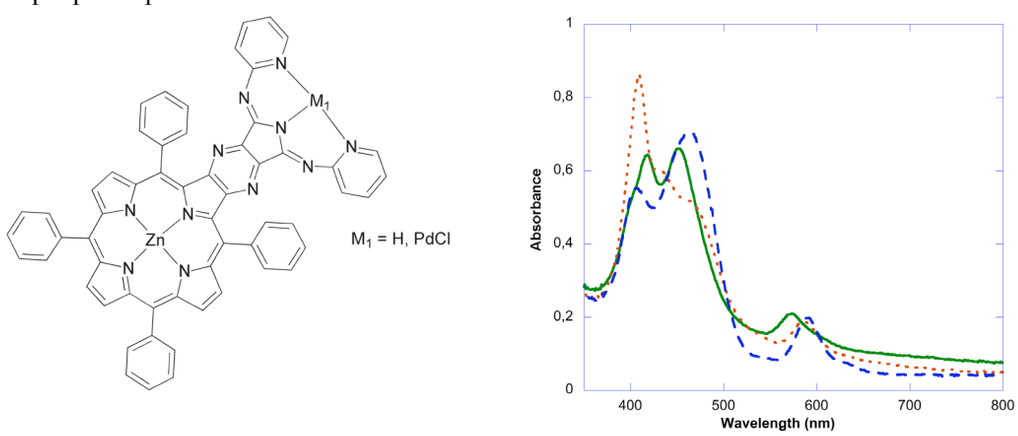

Figure 1. Left: structure of the porphyrin-BPI investigated. Right: UV-vis spectrum in CH_2Cl_2 (full line), CH_2Cl_2/CH_3OH (dotted line) and CH_2Cl_2/Pyridine (dashed line).

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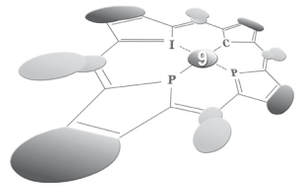

Kinetic, Structural, and Computational Approaches to Peroxidase Catalysis

Anton P. Arce[c], Georges Chreifi[a], Matthias Heyden[b], James B. Fields[b], Hugo I. Magaña-Garcia[a], Scott A. Hollingsworth[a], Thomas L. Poulos,[a,b,c] and Douglas J. Tobias[c]

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The *Leishmania major* peroxidase (LmP)-cytc complex crystal structure has been solved and is quite similar to the more well known yeast CCP-cytc system. However, for detailed studies the LmP system offers some advantages owing to the relatively straightforward kinetic behaviour and the requirement for specific ion pairs at the interface which are lacking in yeast CCP. A combination of Brownian and molecular dynamics (BD/MD) has been used to probe the initial association reaction and validated by mutagenesis and kinetics. Cytc rapidly forms a nonspecific complex at a site far removed from the ET site but then moves toward the active ET site in a "bind and crawl" mechanism.

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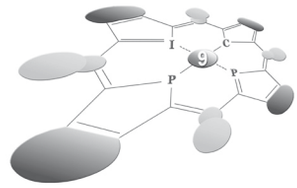

Oxygenic ligands in the catalysis by highly oxidized species of heme and non-heme iron enzymes

Denis A. Proshlyakov[a], **Christopher John**[a], **Yegor D. Proshlyakov**[a], **Dawei Chen**,[a] **Zipin Zhang**[a], **John L. McCracken**[a], **Greg M. Swain**[a], **Robert P. Hausinger**[b]

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Highly oxidized species of heme and non-heme enzymes catalyze some of the most difficult and intriguing chemical transformations. Tight kinetic control over electron transfer in P450s greatly hinders direct studies on the substrate oxidation upon conversion of between Compounds **I** and **II**. Compounds **P** and **F** in heme-copper oxidases drive proton pump, but details of structural difference between the two ferryl-oxo species and their relationship to proton pumping remain unclear. Both reactions represent key transformation of oxygenic ligands, whose structures and thermodynamic properties determine catalytic abilities of corresponding enzymes. We aim to circumvent existing limitation of spectroscopic techniques and gain insight into structural dynamics and the mechanisms of these and related iron enzymes.

Direct resolution of the hydrogen atom abstraction by taurine/a-ketoglutorate dioxygenase, TauD, a non-heme analog of P-450, unexpectedly revealed that TauD species corresponding to Compound **II** in P-450 reaction shows no evidence of protonation at pH 8,[1] implying significantly higher acidity than expected based on modeling studies. Ensuing investigation of alkaline horseradish peroxidase (HRP) lead to detection of a new Raman species assigned to the high-spin, 6-coordinate species with significant deuteration sensitivity, and distinguished from the previously reported dominant low-spin, 6-coordinate species.[2] Careful re-examination of the 6C-LS state showed that the $\nu_{Fe=O}$ is insensitive to deuteration. Previously reported up-shift is attributed to vibrational mixing in the active site. Furthermore, comparative HYSCORE study on 6C-LS hemes in alkaline HRP and alkaline myoglobin strongly argued against the presence of proton on the oxygenic heme ligand in LS HRP. Raman studies on pH-dependence of HS/LS equilibrium showed that the pK_a of this transition falls below pH 10 and lead to formulation of indirect ligand stabilization mechanism. This finding has fundamental implications for redox and proton chemistry of heme and non-heme enzymes.

These results are complemented by the development of thin- and novel thick-layer spectro-electrochemical approaches for direct studies on iron ligands and associated conformational changes in proteins. Potentiometric titrations have been used to achieve reversible conversion between Compounds **I** and **II** in HRP with the detection in FTIR and optical domains. $IrCl_6$ is an effective mediator for oxidation of HRP, but not for other enzymes (cytochrome c oxidase, TauD), where it likely undergoes coordination state change with the formation of reducing catalytic site. More robust mediators, such as Fe and Ru bipyridine complexes, are stable against coordination state change and can be used for studies on Fe^{III}/Fe^{IV} states. Electrochemical re-generation of these oxidants *in situ* allows to overcome their rapid reduction by water and to generate Compound **I/II**-type ferryl-oxo species quantitatively and reversibly from bulk water without the use of O_2. We will report on the current efforts to generate heme and non-heme Fe^{IV}=O species, as well as an unusual redox-coupled conformational changes in the Fe^{III}-TauD, which may be responsible for pK_a of its ligand at 15 units below the expected range.

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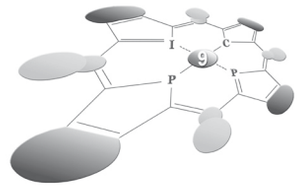

Novel application(s) of Hydrophobic PDT Molecules for onsite Cargo Release from Lipid-based Drug Delivery Platforms

Mathias Viard[a,b], Henry Reichard[a], Jules Chabot[a], Farkuh Durrani[c], Aimee Marko[c], Ramona Watson[c], Ravindra Pandey[c] & Anu Puri[a]

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Cancer nanomedicine is a promising area for improved delivery of drugs & bioactive agents (1). Among these, lipid-based nanoparticles (LNPs), especially liposomes, have made discernible strides. The avenues that require further developments have also been recognized. Nanoparticles with desirable biodistribution characteristics with improved plasma stability *in vivo* as well as viable technologies for on-demand spatial and temporal release of loaded cargo from the LNPs (Figure 1) are important arenas that are likely to enhance the clinical suitability of nanomedicine (2, 3). I will present our recent data on the design and development of (i) light-activatable nanoparticles for multiple drug release by photoactivation of the hydrophobic PDT drug, HPPH (4) in a human breast cancer model (5& Fig. 1B), and (ii) a novel lipid-based formulation with a substantial increase in loading of HPPH and enhanced accumulation in tumor xenografts in mice. Since HPPH in our formulations is activated by light, these platforms have built-in engineered triggering mechanism for nanoparticle disruption as targeted sites.

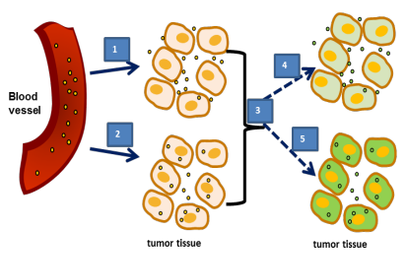

Figure 1A

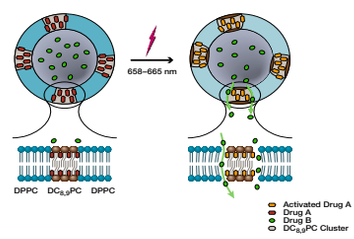

Figure 1B

Figure 1A: Steps involved in liposomal cargo delivery **:** Passive targeting (EPR effect) (1); Active targeting (2); Triggering (3); Free drug diffusion into cells (4); Intracellular release of drug (5). (From Reference 2),
Figure 1B: Design Principle of Photoactivable liposomes (From Reference 5).

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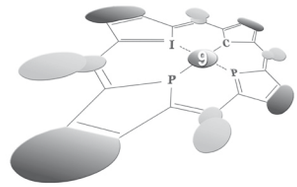

Corroles-Polynucleotides interactions.

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Synthetic porphyrins have been a useful tool to fully understand the complex reactions performed by these macrocycles in biological systems.[1] Furthermore, the attempt to mimic the peculiar chemistry operated by natural porphyrins opened the way to their possible exploitation in a wide range of practical applications. [2]
However, a similar possibility is rarely found with regards to porphyrin analogues, macrocycles having some modification in the molecular skeleton with respect to that of the parent porphyrin.[2] Distinguishable from the core structure of porphyrin by the absence of one of the four meso-positions, corroles contain three "pyrrole-type" hydrogens and a direct pyrrole–pyrrole link.
The synthesis of pyridyl-substituted corrole has been rarely reported.[3] There are only a few reports about a corrole with positively charged substituents.[4] The corrole with three remote positive charges displayed significantly better efficacy in inhibiting tumour progression and metastasis in animal models than analogous porphyrins.
CD, UV-visible absorption, Fluorescence and RLS studies with tricationic water-soluble corrole, (TMPC), show that this species can serve as probes to discriminate between single and double strand conformations of polynucleotides poly A and poly C.[5] Furthermore the Germanium (GeTMPC) derivate is able to discriminate between single strand of polyadenilic acid and polycytosine acid, forming extended assemblies in presence of polyA single strand.

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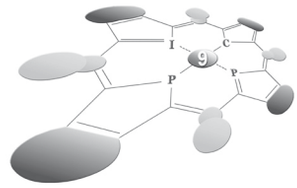

The Octupolarization Hidden in Porphyrin/Phthalocyanine Skeletons: Theoretical Comprehension to the Second-order Nonlinear Optical (NLO) Properties

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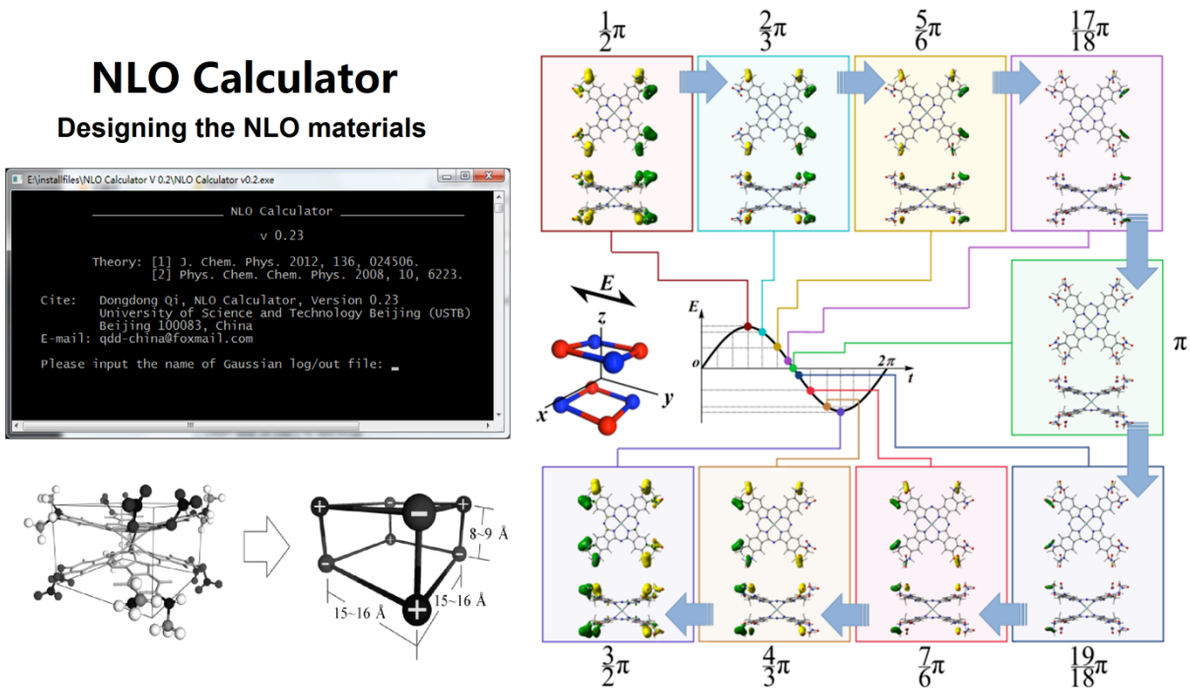

Employing *NLO Calculator* program, an NLO material designing software created by ourselves, the excellent second-order NLO properties, the anisotropic $P^{(2)}$-E response sensitivity, especially the unique octupolar periodical vibrational modes of intrinsic electric field driven by the external electromagnetic field, are clarified on the basis of coupled perturbed density functional theory.
Software download : http://pubs.acs.org/doi/suppl/10.1021/jp3079293/suppl_file/jp3079293_si_002.zip

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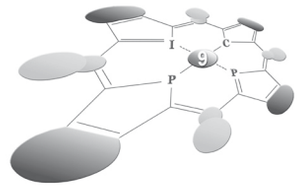

Heme-dependent regulation of circadian rhythm

Emma Raven

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The circadian clock is the internal timekeeping system that generates a daily rhythm in physiology, biochemistry and behaviour of almost all higher organisms and some prokaryotes. In mammals, the transcription factors CLOCK and BMAL1 activate transcription of period (per) and cryptochrome (cry) genes, whose products feed back and negatively regulate their own transcription. There is an accumulating body of evidence that indicates that heme iron affects circadian control, through binding to various circadian proteins, but the mechanisms of regulation are largely unknown. Numerous circadian proteins – including REV-ERB, mPER2, NPAS2 and CLOCK – have all been convincingly shown to bind heme (reviewed in (1)).
Our preliminary work has identified human CLOCK as target for heme binding. This talk will examine the interaction of heme and heme ligands with human CLOCK, and the effect of heme on formation of the CLOCK/BMAL1 dimer and DNA binding.

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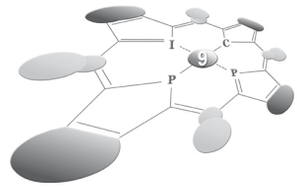

High Valent Metal Oxo Cores in Chemistry and Biology

Kallol Ray

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Although terminal Co^{IV}-O, Ni^{III}-O and Cu^{III}-O intermediates have been implicated as active intermediates in a number of important chemical transformations, no spectroscopic evidences for the species are available, leaving the pathway uncertain.[1],[2] Evidences of the presence of terminal M-O units (M = Cu(III), Ni(III) or Co(IV)) are to date limited to mass spectrometric studies in the gas phase.[2] Theory suggests that they should be powerful oxidants,[2] perhaps even more reactive than the related $[Fe^{IV}=O]^{2+}$ units that have been extensively studied.[3] In this presentation, we will summarize some of our recent efforts to stabilize the elusive metal-oxo and isoelectronic metal-imido units of Cu(III), Co(IV)[4] and Ni(III)[5]) in solution phase at low temperatures. The high-valent metal-oxo or metal-imido assignments are made on the basis of a variety of spectrscopic methods. The reactivity of the intermediates in hydrogen atom abstraction and oxo transfer reactions are also discussed.

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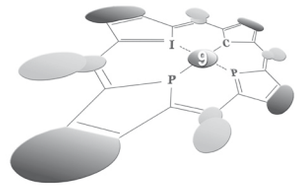

Porphyrin-Functional Material Systems as Efficient Recyclable Biomimetic Catalysts for H_2O_2 Oxidation

Qizhi Ren, Kaifang Sun, Cheng Cai and Lintong Guo

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Porphyrin-containing Cytochrome P450 and peroxidase enzymes are ubiquitous in nature, and found in a variety of biological oxidation catalysts. Laboratory synthesized metalloporphyrins have been extensively used as model compounds to mimic the wide range of oxidation reactions of these enzymes [1,2]. Here, we report a series of novel and stable film catalysts which can be easily assembled at water-chloroform interface by noncovalent interaction between meso-tetrakis (4-sulfonatophenyl) porphyrins (H_2TPPS, FeTPPS and ZnTPPS) and polypeptide-containing hyperbranched polymers with different molecular weights. These films showed high retention for the photooxidation of 1, 5- dihydroxynaphthalene (Fig. 1). They were much higher than the corresponding porphyrin systems without polymers. These films can be utilized over 10 times catalytic runs with a slight decrease in both TONs and yields. We also report here the preparation and characterization of porphyrin-nanotube multifunctional nanomaterials which have been used as photocatalysts for H_2O_2 oxidation (Fig. 2).

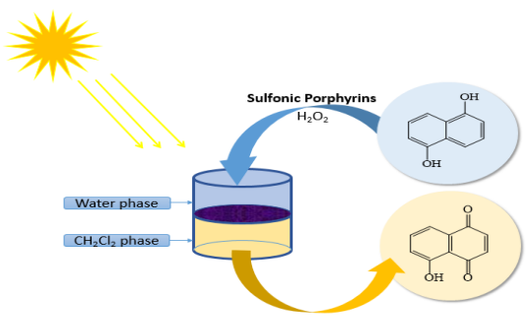

Fig. 1 Photocatalytic sketch for degradation of 1,5-dihydroxynaphthalene by porphyrin-dendritic copolymer systems

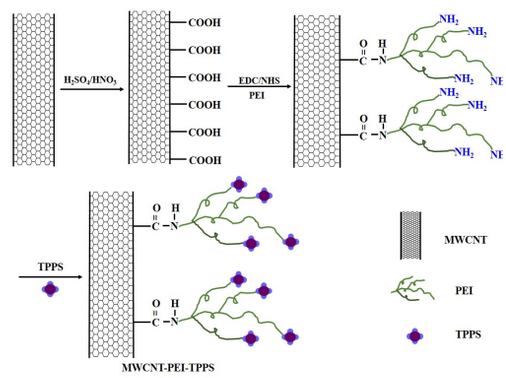

Fig. 2 Schematic Representation of MWCN-PEI-TPPS

Acknowledgment
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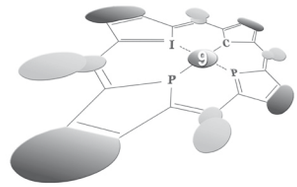

Synthesis and Properties of Porphyrins Conjugated with Peripheral *N*-Heterocyclic Carbene Gold(I) Complexes

Sébastien Richeter[a], **Jean-François Longevial**[a], **Magali Gary-Bobo**[b], **Charles H. Devillers**[c], **Sébastien Clément**[a], **Pierre D. Harvey**[d]

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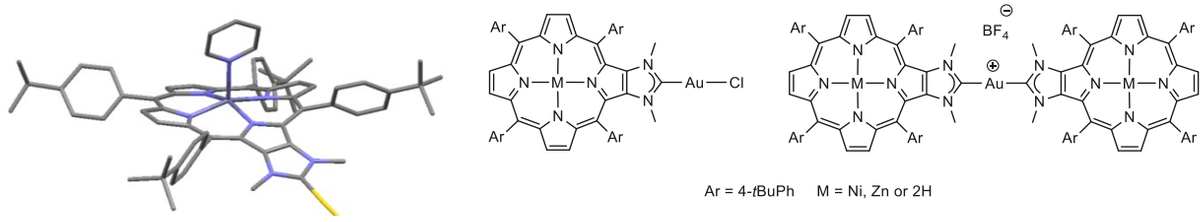
N-Heterocyclic carbene (NHC) ligands are extensively used in organometallic and inorganic coordination chemistry, because they are able to bind almost any transition metal, whether in low or high oxidation states. One of the main fields of applications of NHC-metal complexes is catalysis,[1] but they have also emerged as a new class of metallodrugs displaying anticancer properties.[2]
In the course of our studies, we have shown that porphyrins fused to imidazolium rings can be used as precursors of NHC to anchor various metal complexes at their periphery, such as palladium(II)[3] and rhodium(I)[4] complexes. Here, the synthesis and characterization of several mono- and bis-NHC gold(I) complexes, including homo- and heteroleptic complexes, will be presented. Knowing that these compounds combine metallodrugs (*i.e.* NHC-Au(I) complexes) and photosensitizers (*i.e.* porphyrins), their use for chemo-photodynamic dual therapy is clearly appealing. Some preliminary results will highlight how it is possible to dramatically increase the (photo)cytotoxic effect of these compounds according to the nature of the ligands coordinated to the peripheral gold(I) complexes.



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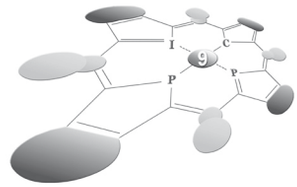

Hydride Attack at the Coordinated Nitrosyl in a Ferric Porphyrin Generates the Fe-HNO Derivative

Erwin Abucayon,[a] Rahul L. Khade,[b] Yong Zhang,[b] and George B. Richter-Addo[a]

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Nitrosyl hydride (HNO; "nitroxyl") is an important small molecule that is biologically active. HNO has been found to elicit several biological responses that complement those attributable to its relative nitric oxide (NO). For example, HNO elicits responses such as vasodilation and muscle constriction, but its actions are distinct from those elicited by NO. It is thus not surprising that significant efforts have been placed in the last decade on the design of HNO donors for use in physiology. Importantly, HNO is also an intermediate in various processes catalyzed by heme proteins. Such heme-HNO intermediates have been proposed to form during the enzymatic detoxification of NO by fungal cytochrome P450 nitric oxide reductases (P450nor), and during nitrite reduction by cytochrome *c* nitrite reductase. We have prepared a heme model compound containing the Fe-HNO moiety from hydride attack on the ferric heme model nitrosyl precursor. The (OEP)Fe(HNO)(5-MeIm) (OEP = octaethylporphyrinato dianion) product has been characterized by infrared and ^{1}H NMR spectroscopy. This product is, however, prone to decompose to the known five-coordinate ferrous (OEP)Fe(NO) and dihydrogen. We have utilized DFT methods to probe the hydride attack on the cationic $[(\text{porphine})\text{Fe(NO)(5-MeIm)}]^{+}$ precursor (porphine = unsubstituted porphyrinato dianion). We show that the N-pathway, namely direct attack of the hydride at the nitrosyl N atom, is the preferred pathway for the formation of the Fe-HNO derivative.
Importantly, this (OEP)Fe(HNO)(5-MeIm) compound represents the first report of hydride attack at the a ferric heme-model nitrosyl group to generate a Fe-HNO product, and the first spectroscopic characterization of the HNO ligand in a heme model Fe-HNO derivative (*J. Am. Chem. Soc.,* DOI: 10.1021/jacs.5b12008). The preparation, spectroscopic characterization, reactivity, and DFT investigation of the (OEP)Fe(HNO)(5-MeIm) derivative will be presented and discussed.

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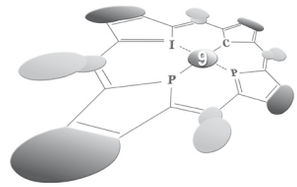

New Photosensitizers Based on Porphyrazines

M. Salomé Rodríguez-Morgade, Javier Fernández Ariza, Diana Paola Medina, Esmeralda Caballero, Maxence Urbani and Tomás Torres

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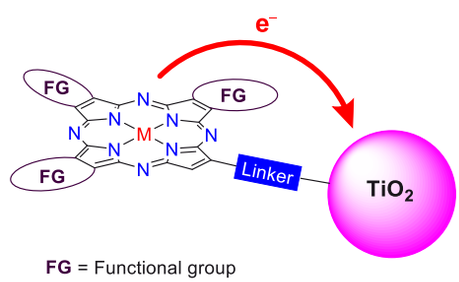
Solar energy is deemed to be one of the most reliable energy sources for the future. But so far, harvesting solar light and converting it into electricity or chemical fuels at low cost remains a huge challenge. One of the most promising areas is that of organic photovoltaic cells (OPV). In this context, dye-sensitized solar cells (DSCs)[1,2] and related electrochemical systems are emerging as a promising technology for producing electricity from solar light. Chemical tactics to carry out the design of these systems use a modular approach, with individual components for light absorption, energy transfer, electron transfer, etc. investigated separately, optimized in performance, and assembled into a single device.[3] This opens the possibility of adapting the device to every particular application by tuning the photophysical behaviour of the organic dye.

Thus, one of the key components in DSCs is a suitable photosensitizer with strong spectral response in the red and near-IR regions. As an alternative to ruthenium complexes, porphyrins and phthalocyanines (Pcs) are being tested as the organic components of photovoltaic and artificial photosynthetic devices. One of the main appeals of phthalocyanines relies in their high extinction coefficients in a wavelength range that extends to around 700 nm, where the maximum of the solar photon flux occurs.[4]

Porphyrazines (Pzs) also display strong absorptions in the red region.[5] However, in contrast to the numerous studies involving porphyrins and phthalocyanines, the application of porphyrazines to solar energy conversion is still unexplored. We have designed a new series of photosensitizers based in porphyrazines. The synthesis of these chromophores, as well as their performance as components of DSCs will be discussed.



FG = Functional group

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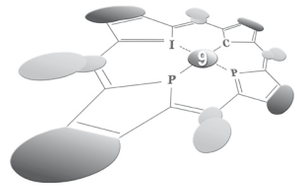

2D singlet oxygen luminescence observation of photodynamic inactivation of microorganisms on surfaces

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The most common form of microorganism existence is in biofilms. Biofilms are the symbiosis of different microorganisms like bacteria, fungi, green algae, cyanobacteria, and lichen. They consist of the microorganism cells and the matrix of so-called extracellular polymeric substance (EPS). Growing on buildings, monuments, or technical installations biofilm forming microorganisms cause aesthetic, ecological, and economical damage. Additionally, spore forming microorganisms like mold fungi can provoke problems to human health. Therefore, significant amounts of biocides are used to combat biofilm growth on solid surfaces worldwide. The release of biocides into the environment provokes new risks to human health and environmental problems. Moreover, the adaptability of microorganisms, caused by their fast reproduction rate, generates a fast increase of resistances to the biocides. To break this vicious circle new strategies to combat biofilm-forming microorganisms are necessary. One possible approach is using photodynamic inactivation (PDI). It is well investigated that the photodynamic effect can be used for inactivation of bacteria. The asexual life cycle of mold fungi, especially their development of highly resistant spores, makes mold fungi very difficult to combat by biochemical strategies. The high potential of PDI to combat mold fungi and their spores has been shown by several groups. A proof of concept of the sufficient PDI of green algae and cyanobacteria as phototrophic primary settler in subaerial biofilms has been done already.

Here we will report about the observation of singlet oxygen luminescence kinetics being a very effective approach towards understanding the mechanism of PDI on a cellular level in biofilms. In this study, the first ever measurement of singlet oxygen kinetics in phototrophic microorganisms on surfaces during photodynamic inactivation is presented.

We established a system of reproducible algae samples on surfaces, incubated with two different cationic, antimicrobial potent photosensitizers. Fluorescence microscopy images indicate that one photosensitizer localizes inside the green algae while the other accumulates along the outer algae cell wall. A newly developed setup allows for the measurement of singlet oxygen luminescence on the green algae sample surfaces over several days. The kinetics of the singlet oxygen luminescence of both photosensitizers show different developments and a distinct change over time, corresponding with the differences in their localization as well as their photosensitization potential.

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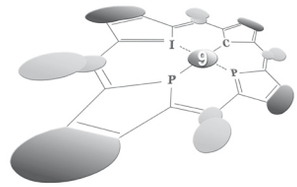

Platinum(II) Insertion in Meso Tetraaryl Porphyrins: Mechanistic Insights from Density Functional Theory Calculations

Angela Rosa[a], **Giampaolo Ricciardi**[b], **Giovanna De Luca**[c], **Andrea Romeo**[c], **Maria Rosaria Plutino**[d], **Luigi Monsù Scolaro**[c]

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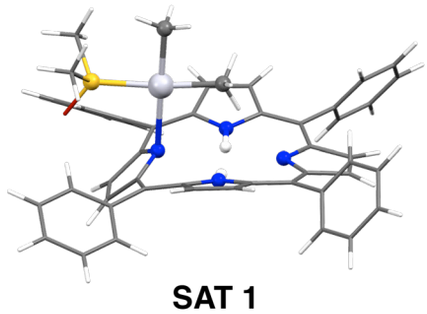
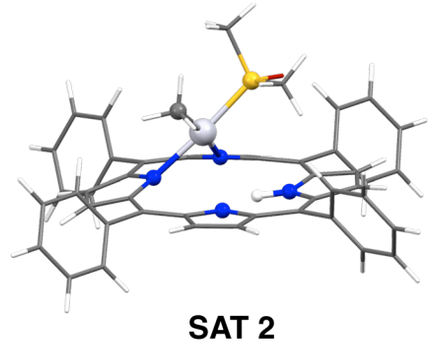
The interaction of a series of meso tetraaryl porphyrins with the platinum(II) complexes *cis*-[$PtCl_2(Me_2SO)_2$], *trans*-[$PtMeCl(Me_2SO)_2$], and *cis*-[$PtMe_2(Me_2SO)_2$] has been kinetically investigated in different experimental conditions through UV-visible and ^{1}H NMR spectroscopy. For the latter, the reaction results in the quantitative insertion of the metal into the porphyrin cavity, thus providing an efficient and substantially inexpensive approach to obtain platinum(II) porphyrin derivatives in quantitative yield and under mild conditions.
Mechanistic insights into the metal insertion reaction have been obtained by detailed density functional theory (DFT) studies of the interaction of the *cis*-[$PtMe_2(Me_2SO)_2$] complex with the tetraphenyl porphyrin, H_2TPP.
It is found that the reaction initiates with the formation of a *sitting atop* (SAT) complex,[1] **SAT 1**. This complex is generated by interaction of the coordinatively unsatured platinum(II) species, $PtMe_2(Me_2SO)$, with a pyrrolenine nitrogen atom of H_2TPP. The attack of a pyrrolic proton to one of the Pt–C bonds leads to release of a methane molecule and formation of the **SAT 2** intermediate. The subsequent attack of the remaining pyrrolic proton to the residual Pt–C bond leads to formation of PtTPP and release of a second methane molecule.
The electronic structure analysis and the energetics of the Pt(II) insertion reaction will be illustrated in this presentation.



SAT 1



SAT 2

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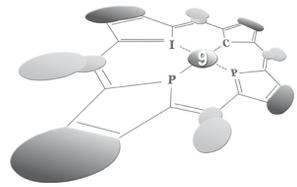

Physicochemical approach for the assessment of targeting efficiency of glycoconjugated tetraphenylporphyrins usable in one- and two-photon PDT

Véronique Rosilio[a], Ali Makky[a], Jean-Philippe Michel[a], Donia Essaid[a,c], Katia Daghildjian[a], Su Chen[b], Athena Kasselouri[c], Philippe Maillard[b]

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Retinoblastoma is a cancer that usually develops in childhood. It could be treated by photodynamic therapy, a methodology based on the intravenous injection of a photosensitizer and subsequent illumination of the tumor by a laser. Tetraphenylporphyrins (TPPs) activated by light in the presence of oxygen induce the formation of singlet oxygen that eventually leads to cell death. In order to be efficient, TPPs must penetrate into cancer cells. However these molecules are poorly soluble in aqueous media, aggregate and bind to serum proteins. They also lack specificity.

Glycoconjugation may improve TPPs solubility and amphipathy. Moreover, it may allow their targeting towards sugar receptors overexpressed at the surface of retinoblastoma cells. Various series of glycoconjugated TPPs with different chemical structures (monomeric with flexible structure, dendrimeric or dimeric) have been synthesized.[1] Phototoxicity experiments and flow cytometry did not allow full characterization of the specific/non-specific mechanism of internalization of the new compounds into Y79 cells. Therefore, a physicochemical approach was considered for the analysis of TPPs uptake.

Dendrimeric and dimeric TPPs were embedded into liposomes, exposing their saccharide moieties towards the aqueous medium, so that they could be specifically recognized by membrane receptors. In order to identify the physicochemical parameters involved in the mechanism of interaction of free TPPs and TPP-bearing nanocarriers with retinoblastoma cells, we used various biomimetic models of a cell membrane. These models were monolayers, vesicles and planar bilayers with a lipid composition based on the retinoblastoma lipidomic analysis, and the presence (or absence) of a lectin. Surface pressure, fluorescence spectroscopy, dynamic light scattering and quartz crystal microbalance measurements showed that generally, the specific interactions contributed more than the non-specific ones to the overall interaction of a glycoconjugated TPP with a membrane[2]. The length of the spacer separating a sugar from the tetrapyrrolic ring appeared to be crucial for controlling the surface properties of the tetraphenylporphyrin derivatives, the extent of their interaction with the sugar receptor and their incorporation into membranes.

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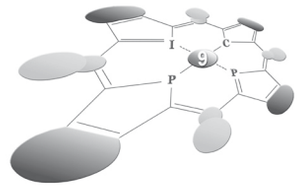

Serial Femtosecond X-Ray Crystallography of Oxidized Bovine Cytochrome c Oxidase

Denis L. Rousseau[a], Masahide Hikita[a], Izumi Ishigami[a], Shibom Basu[b], Chelsie Conrad[b], Garret Nelson[b], Chufeng Li[b], Meng Liang[c], Mark S. Hunter[c], Petra Fromme[b], Raimund Fromme[b] and Syun-Ru Yeh[a]

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Many high resolution structures of bovine cytochrome *c* oxidase (bC*c*O) and other heme-copper oxidases have been obtained at cryogenic temperatures with high intensity synchrotron radiation. These structures have significantly advanced our understanding of this wide class of enzymes. However, it is well established that radiation damage and photoreduction have occurred in many of these studies, especially in the oxidized forms of C*c*O in which radiation effects have caused ambiguity in the structure of a putative peroxide moiety bound in the heme a_3-Cu_B binuclear center. To eliminate the deleterious effects of the high X-ray flux, diffraction of micro-crystals in a flowing jet obtained with pulses from an X-ray free electron laser (XFEL) yield structures at room temperature without radiation damage and without the presence of any cryoprotectants. Diffraction is obtained from the 44 fs pulses prior to the onset of damage and destruction of the small crystals. We have used this technique, called Serial Femtosecond X-Ray Crystallography (SFX), to obtain the structure of bC*c*O at room temperature without damage and refined it to a resolution of 2.8 Å. The data confirm the presence of peroxide bridging the iron atom of heme a_3 and the Cu_B moiety.

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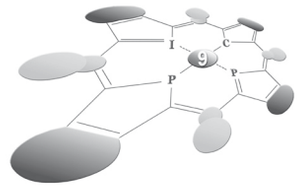

Electronic and Magnetic Interactions between Porphyrins

Romain RUPPERT

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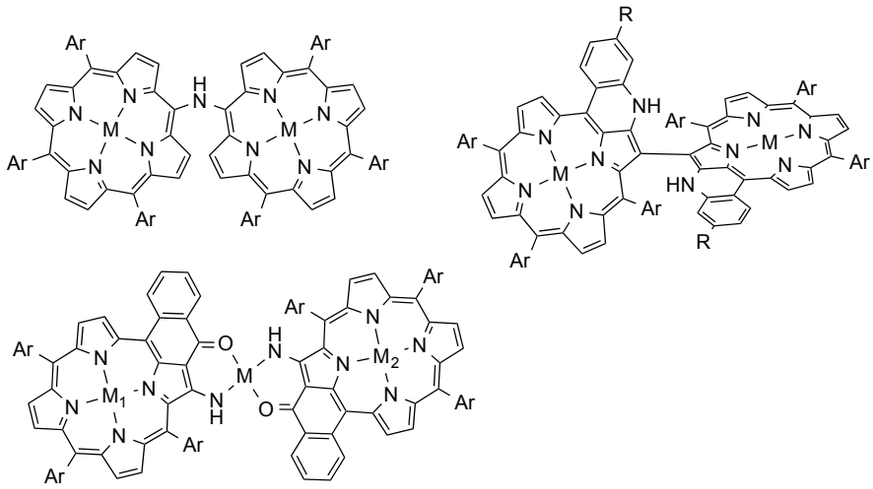
The peripheral functionalization of porphyrins has been one way to access extended porphyrins. Intramolecular cyclizations or the fusing of aromatic groups are the two main reactions used to prepare these conjugated molecules.[1] Starting from these already extended porphyrins, we prepared a few series of porphyrin dimers or oligomers linked covalently or held together with coordination bonds (see Scheme).[2] The electronic and magnetic interactions between the individual chromophores were studied by different spectroscopic techniques. In particular, ultrafast energy transfer was observed in palladium or platinum linked dyads.[3] Oxidation reactions also gave access to new chiral porphyrin dimers in a very simple reaction sequence.[4]



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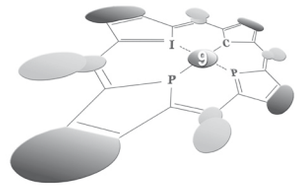

Bright Long-wavelength Pyrrolic Dyes – Prospects for Applications in Fluorescence Sensing

Knut Rurack

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Since more than 20 years, optical spectroscopic techniques, in particular fluorescence-based methods, are on the rise in many different areas of chemical and biochemical analysis, with no end being in sight.[1,2] Advances in miniaturization and remote applications on one hand and ground-breaking developments in microscopy and laser-based high-throughput instrumentation on the other hand have fuelled these developments substantially.[3,4] At the core of utmost of these applications however is not only the instrument, but a small entity that is able to absorb and emit photons and thus to report on the actual (bio)chemistry that is going on in a particular sample of interest.[5,6] Besides intense research on various types of luminescent particles (e.g., quantum dots and carbon dots) and proteins, dye chemistry has thus seen its revival and the number of publications dealing with the design, synthesis and application of new fluorescent dyes as probes, stains, labels or indicators is still continuing to grow. Among the various classes of dyes available as bright fluorophores for a wavelength range that is compatible with many (bio)analytical applications and the respective instrumentation, in particular pyrrolic dyes that do not belong to the classical porphyrins or phthalocyanines have received strong attention recently. Starting perhaps with the revival of the traditional boron-dipyrromethene laser dye ca. 15 years ago,[7] these so-called BODIPYs have developed into a colourful spectrum of different derivatives.[8] However, the interest in expanding the range of pyrrole-containing π-systems beyond BODIPYs has also constantly increased and has brought about several other pyrrole-based ring systems such as diketopyrrolopyrroles[9] or dipyrrolonaphthyridinediones which possess a favourable brightness and other interesting properties. The present contribution will give a critical overview of the field, pinpointing advantages and prospects as well as discussing potential aspects of improvement with an emphasis on the chemical sensing and the longer wavelength range.

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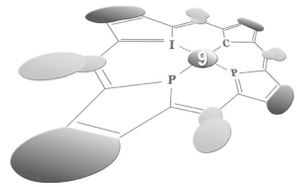

Electrochemical and Spectroscopic Studies of the Reaction of Iron Porphyrin Nitroxyl Ions with Weak Acids

Michael D. Ryan and Md. Hafiz Rahman

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The pulse polarographic reduction of Fe(P)(NO) (P = porphyrin) in THF and substituted phenols has been previously studied on our laboratory [1]. The voltammetric behaviour of the wave followed Nernstian behaviour, indicating that the electron transfer process and protonation steps were reversible. Kinetic data supported the following mechanism:

$$Fe(P)(NO) + e^- \rightarrow Fe(P)(NO)^- \quad (1)$$

$$Fe(P)(NO)^- + PhOH \rightarrow Fe(P)(HNO) + PhO^- \quad (2)$$

$$Fe(P)(HNO) + PhOH \rightarrow Fe(P)(H_2NO)^+ + PhO^- \quad (3)$$

where PhOH and PhO^- are substituted phenols and phenolates, respectively. In this work, the mechanism above were studied in more detail using rotating ring-disk electrode (RRDE) voltammetry. As was seen with the pulse polarographic results, the disk limiting current (due to Reaction 1) was independent of the concentration of the phenol. This indicated that the hydrogen evolution reaction seen by us [2] and others [3] was slow on the voltammetric time scale. The ring electrode was set at a potential where $Fe(P)(NO)^-$ could be oxidized in order to measure the collection efficiency (N_k = -ring current/disk current), which is a measure of the chemical reversibility of the protonation reactions. It was found that the N_k value increased as the rotating rate decreased. This result was consistent with Reactions (2) and (3) being slow and reversible. Addition of phenolate increased the rate of the reverse steps of Reactions (2) and (3), indicating that the second order reaction of the phenolate with the protonated nitroxyl was the rate limiting step.

In addition to RRDE experiments, ^1H and ^2H NMR were used to identify the HNO species formed. By the use of deuterated substituted phenols and d_4-meso octaethylporphyrin, it was possible to identify the resonances due to the various species formed. The $^1H/^2H$ resonances of HNO were very temperature dependent, probably due to hydrogen bonding with the phenolate. At room temperature, the δ value was consistent with other reports [4]. Visible spectroscopy showed reversible behaviour between the nitroxyl and HNO complex, similar to the features observed by Goodrich et al. [3]. Further evidence on the structure of the HNO complex was obtained from FTIR spectroelectrochemistry, and the results were compared to a recent report by Abucayon et al. [4].

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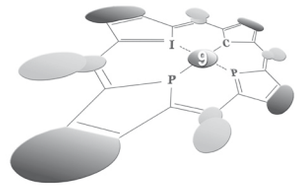

Multichromophoric Assemblies from Directly-linked Corrole-Porphyrin Units

Jeyaraman Sankar[a] **and Muthuchamy Murugavel**

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Covalently-linked multichromophoric molecular systems are highly interesting due to their applications in artificial photosynthetic light harvesting and organic photovoltaic devices. Embedding these molecules with an array of different metals in their wide range of oxidation states can help us to identify new materials with hitherto unknown novel properties. In this direction, we envisage that a molecular marriage between porphyrins and corroles can result in molecular assemblies with intriguing electronic properties. Recently we have started our journey on the development and understanding of these novel molecular assemblies. We have reported the first examples of porphyrin-corrole-porphyrin triads connected through the *meso-meso-* fashion.[1] Prior to this, we have also developed a symmetric corrole-porphyrin-corrole triad. The stability and solubility of the trimers are carefully balanced by planting electron withdrawing substituents on the corrole ring and sterically bulky groups on the porphyrins. The new hybrids are capable of stabilizing more than one metal ion in a single molecular scaffold. The versatility of the triads has been demonstrated by successfully stabilizing homotrinuclear and heterotrinuclear coordination motifs onto it. It is especially noteworthy that the Por-Cor-Por hybrid can further be manipulated due to the presence of substituent-free *meso-* positions on both the terminals. In this current talk, recent results on these molecular systems and a few selected larger assemblies will be highlighted.

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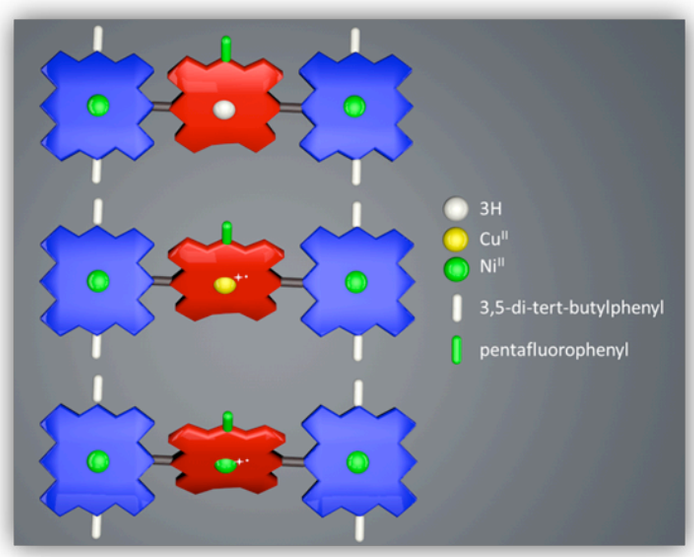

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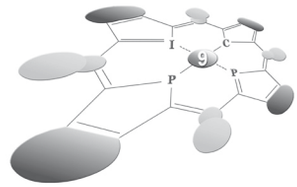

'Naked-eye' Detection of Toxic Anions using Porphyriniod Chemosensors and Their Reusability Studies

Mandeep K. Chahal, Nivedita Chaudhri, Kamal Prakash, Ravi Kumar, Nitika Grover, Pinky Yadav and Muniappan Sankar

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The design of anion receptors with high selectivity and sensitivity has been subject of intensive research due to their potential applications in environmental and health sectors.[1] Most systems developed use complimentary binding sites through ion pairing, hydrogen-bonding, anion-π interactions, metal-to-ligand binding, etc. A variety of instrumental techniques have been developed for the determination of anions which require time-consuming procedures and sophisticated instrumentation. Now-a-days, the most attractive approach focuses on highly selective colorimetric anion sensors, which allows "naked eye" detection of toxic anions by means of colour change. Porphyrin derivatives are ideally suited for colorimetric sensor design due to their rich spectroscopic and electrochemical redox properties.[1] A wide range of porphyrin-based receptors for anions has been constructed through the derivatization of *meso*-positions[1d,1e] having appropriate binding pockets whereas only a few reports on *β*-functionalized porphyrins[1f] due to their synthetic difficulties. Herein, we present the facile synthesis of *β*-substituted porphyrins and some *meso*-functionalised corroles/N-confused porphyrins (Chart 1) and their utilisation for the detection of toxic anions in aqueous/non-aqueous media and their reusability studies in detail.[2]

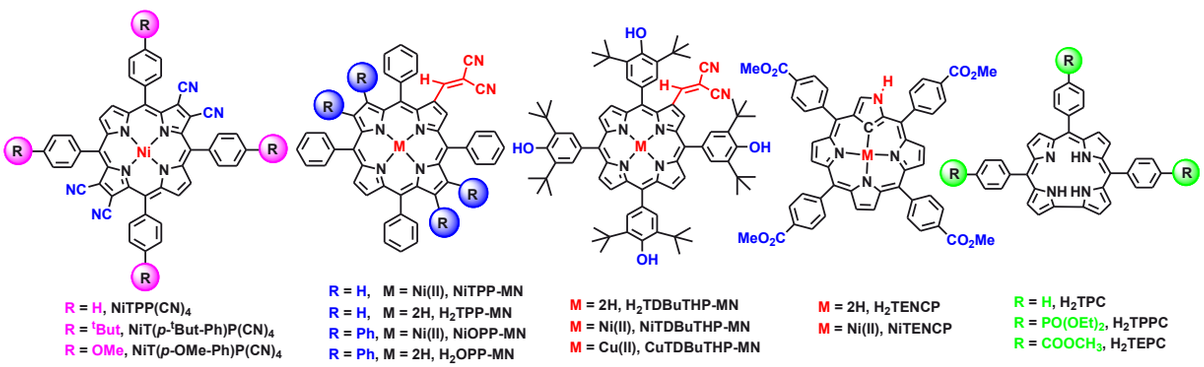

Chart 1. Molecular structures of porphyrinoids utilised for the selective detection of toxic anions.

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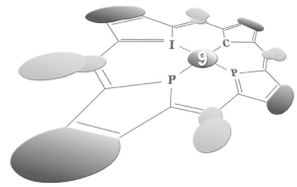

Fully Conjugated Phthalocyanine-Electroactive Systems in Dye Sensitized Solar Cells

Ángela Sastre-Santos,[a] Jorge Follana-Berná,[a] Desiré Molina,[a] Luis Martín-Gomis,[a] Martín M. León[a] and Fernando Fernández-Lázaro[a]

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Phthalocyanines (Pcs) are outstanding dye candidates in for dye sensitized solar cells (DSSCs) due to their high extinction coefficient in the visible and near-infrared spectral region and to their high thermal and chemical stabilities[1]. Pcs incorporated in DSSCs have achieved PCEs as high as 6.4 %[2], still far away from the 12.75% PCE obtained by porphyrins, their closest relatives. An elegant strategy to improve the light-harvesting ability of the Pcs is the extension of the aromatic structure by generation aromatic-fused analogues of Pc having a red-shifted absorption.

Herein, we will report our more recent results related with the synthesis of different unsymmetrically substituted phthalocyanines fully conjugated with electroactive systems[3] and the improvement in efficiency of DSSCs[4].

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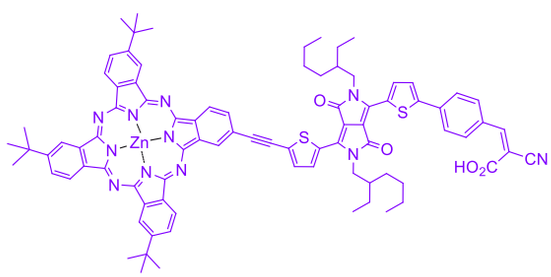

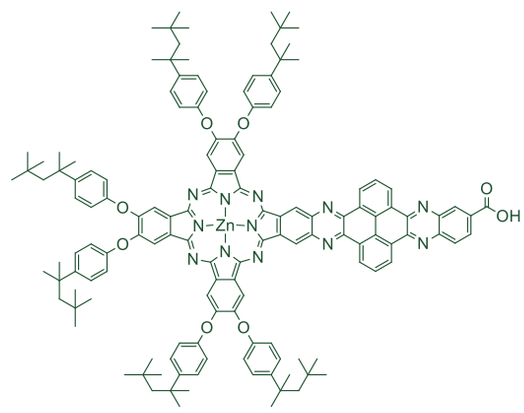

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Vibrational Spectroscopy of Synthetic Malarial Pigment

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Malarial pigment or hemozoin is a microcystalline "side-product" of a heme aggregate resulting from hemoglobin digestion by the malarial parasite infecting red blood cells. While its extreme insolubility prevents the formation of reactive oxygen species that would be toxic to the parasite, it also makes characterization challenging. Hemozoin has been considered a drug target since disruption of its formation is indeed fatal to the parasite. We have applied nuclear resonance spectroscopy (NRVS), which probes the vibrational dynamics of iron.(1) We have probed the stable form of the hematin model as well as a metastable kinetic intermediate trapped during the formation of the stable form. This metastable form displays vibrational properties distinct from the stable product. Computational models are consistent with the idea that variations in the geometry of the iron carboxylate linkage strongly influence the vibration dynamics of iron. Vibrational studies of possible interactions of anti-malarial drugs are currently being pursued.

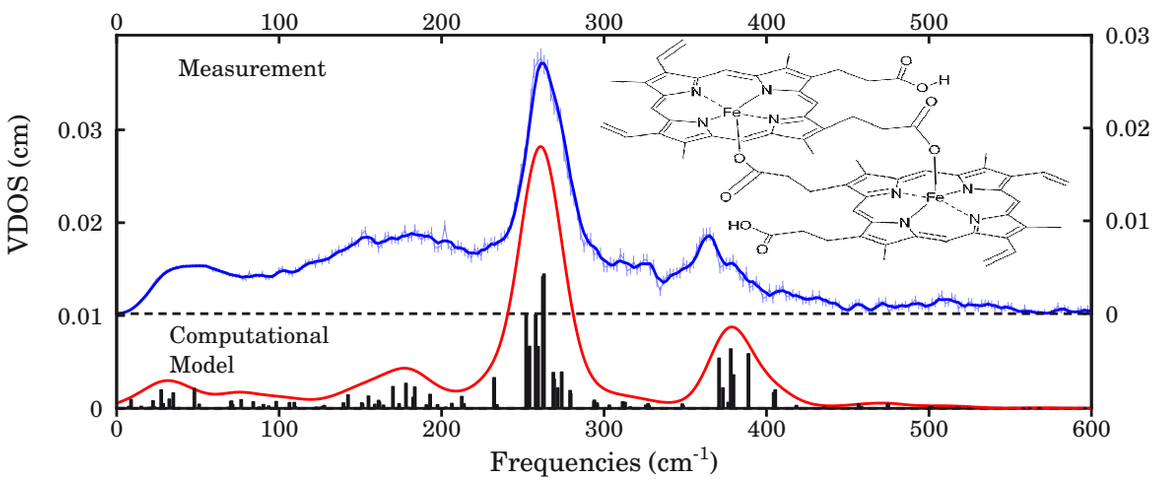

Figure: Calculation for the dimeric β-hematin structure (derived from X-ray powder diffraction(2)) reproduces the measured vibration properties of the stable microcrystalline product.

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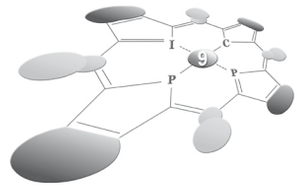

Photochemical CO_2 Reduction Catalyzed by Mono- and Dinuclear Phenanthroline-Extended Tetramesityl Porphyrin Complexes

Matthias Schwalbe[a], **Corinna Matlachowski**[a]

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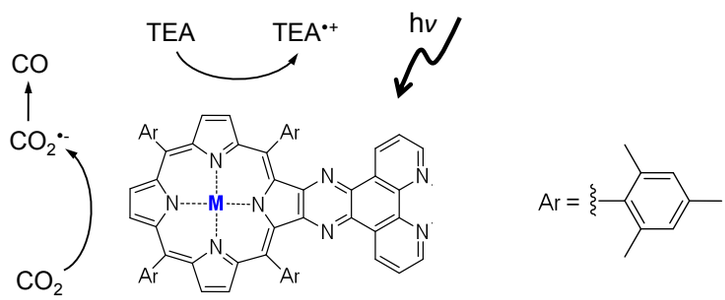
The catalytic reduction of CO_2 to CO or into liquid fuels represents a crucial challenge due to the global warming problem and the fossil fuel scarceness. This energy demanding process is favorably driven using sunlight as energy source.[1,2]
Fujita and Neta could show that iron and cobalt porphyrins are suitable for photochemical CO_2 reduction.[3] We like to develop their system further and use mono- and dinuclear complexes with a phenanthroline-extended tetramesityl porphyrin ligand (**H_2-1**).[4] This ligand can selectively coordinate a second metal fragment in the phenanthroline coordination sphere while any other metal can reside in the porphyrin cavity. This allowed the construction of multiple heterodinuclear compounds and the influence of any metal center on the lightdriven CO_2 reduction activity could be tested.
Thorough catalytic investigations on **M-1** compounds (**M** = 2H, Cu, Pd, Co, FeCl) with or without a second metal fragment attached (i.e. a $Ru(tbbpy)_2$ or $Re(CO)_3Cl$ fragment) were done in DMF saturated with CO_2 and in the presence of triethylamine (TEA) as sacrificial electron donor.



M-1
M = Cu, Pd, Co, FeCl

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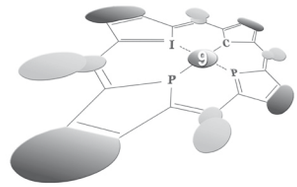
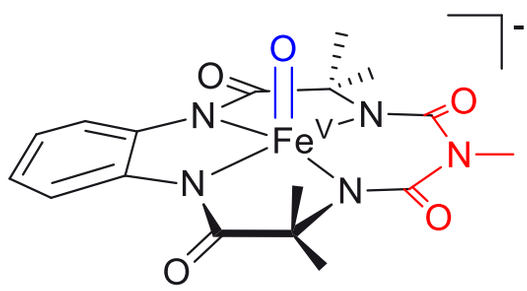


The Reactivity Landscape of the Elusive $Fe^{V}(O)$- submitted to the International Conference on Porphyrins and Phthalocyanines

Sayam Sen Gupta, Santanu Pattanayak, Kundan Singh, Munmun Ghosh

CSIR-National Chemical laboratory-Pune

High valent iron-oxo intermediates play key roles in enzymatic oxidations. For example, in the cytochrome P450 enzymes, the high valent $Fe^{IV}(O)$(porphyrin radical-cation), isoelectronic with $Fe^{V}(O)$, has been shown to be the reactive intermediate in the selective hydroxylation of camphor. In the Rieske dioxygenase enzyme family an $Fe^{V}(O)$ active intermediate has been proposed. $Fe^{V}(O)$ has also been proposed as the reactive intermediate for several oxidation reactions catalysed by Fe-based non-heme complexes. We have successfully synthesized an $Fe^{V}(O)$ complex of a biuret-containing Fe-complex at room temperature. This complex displays remarkably higher stability at room temperature. This higher stability has allowed us to study oxidation reactions with C-H, C=C and O-H bonds at room temperature. I will discuss the mechanism of oxidation by $Fe^{V}(O)$ and also compare the reactivity with the corresponding $Fe^{IV}(O)$. Finally the reaction of $Fe^{V}(O)$ with H_2O leading to the formation of O-O bond during water oxidation will also be discussed.



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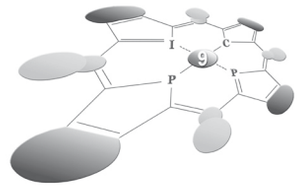

Spatial Organization and Molecular Modulation of Photosynthetic Chromophores and Biomimetic Multi-porphyrin Arrays

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Porphyrins are a unique class of ubiquitous natural compounds that function in a wide variety of roles ranging from oxygen transport, electron transfer and oxidation reactions to photosynthesis. They are important natural cofactors and are crucial regulatory effectors in many biochemical processes and diseases. Their natural function is controlled by their spatial arrangement and a subtle interplay between the cofactor conformation and the apoprotein.[1,2] Using conformational control as a common design principle tetrapyrroles with optimal photophysical and materials properties are now within reach in biomimetic chemistry.[3] The underlying chemistry allowed us to elucidate how cofactor properties are controlled in nature and has significant application potential.[4] Using the tetrapyrrole pigments of the photosynthetic reaction center as an example, statistically reliable evidence has been obtained for the existence of functional classes of specific conserved porphyrin conformations.[5] Thus, the conformation of the porphyrin macrocycle is a key factor in determining its functional behavior and (photo)biological function.

Biomimetic approaches for multi-chromophoric light-harvesting systems require construction principles that will allow for spatial design using scaffold and framework molecules and linker units. Here, rigid scaffold molecules which impart a spatially defined orientation are of special interest. One example is triptycene, which has a rigid, symmetric and shape persistent framework allowing the projection of functional groups in a three-fold 120° orientation. In order to allow for the presentation of multiple units rational building strategies and appropriate synthons have been developed for the use of triptycene as a rigid hexafunctional presenting scaffold. Palladium catalyzed cross-coupling reactions, such as Sonogashira and Suzuki style couplings were used to install a variety of different synthetic handles around the triptycene periphery in a high yielding and controlled manner using one-pot, hexasubstitution reactions.[6] Current applications focus on the use as antenna and multi-drug delivery systems. In the same context cubane is explored as a linear, nonconjugating linker unit. Initial results on the transition metal catalyzed functionalization of cubane[7] and its use as a molecular isolator indicate that cubane can also be used as an attractive synthon for the construction of complex systems. Additionally, 2D-surface aggregation can be used to preposition functional molecules for covalent bond formation to yield electronically conducting porphyrin-graphene nanoribbons.

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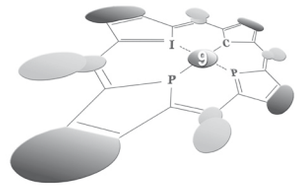

Synthesis of bay substituted PDI derivatives for PVs

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A great deal of interest in the field of solar photochemistry and solar energy conversion has stimulated many researchers to design electron donors and acceptors ensembles based on nature-inspired porphyrin-quinone arrays. Among the donors, phthalocyanines (Pcs) have been extensively used due to their outstanding optoelectronic properties and structural flexibility required for the practical organic solar cells. On the other hand, perylene diimides (PDI) have also been successfully proven to be the most significant electron acceptors due to their stability, intense light absorption, rich redox chemistry and high charge-carrier mobility. In regards, covalent systems based on PDI covalently linked to one or two Pc units have been successfully designed and synthesized [1]. Thus, D-A hybrids, dyads, triads and polyads were built up by connecting Pc units to PDI through the imido positions. Both energy and charge transfer dynamics have been observed in these planar systems upon photo-excitation of the Pc units.

Previously, we have presented ZnPc-PDI supermolecule in which two photo-active moieties were covalently linked together with four dioxybenzene units. Due to increasing of the distance between the D and A units and also the non-planarity of the conjugate system, the observed photovoltaic conversion efficiency was found to be 3.55% under AM 1.5G illumination [2], that was higher than the those of planar CuPc and non-planar metal Pc, but lower than the expected value. In order to increase the device performance, we have design more compact structure that has no linkage, thus providing more electronic interaction due to closer distance between the two units in face-to-face position with less distortion and a very small HOMO-LUMO gab.

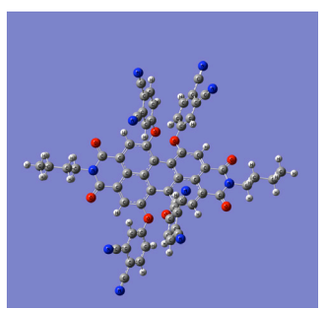

Figure 1. Gas phase optimized geometry of the bay substituted PDI.

Reaction of tetrachloro-PDI with *p*-methoxyphenol takes place readily, however, reaction with 4-hydroxyphthalonitrile is troublesome. The alternative methods for the preparation of the target compounds will be discussed.

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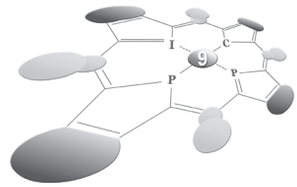

Unraveling the mechanism of CYP3A4 catalysis and inhibition: challenges and advances

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[b]*Departments of Chemistry and Pharmaceutical Sciences, University of California, Irvine, California 92697-3900, USA*

Human cytochrome P450 3A4 (CYP3A4) is the most abundant and clinically relevant xenobiotic-metabolizing P450 in humans and is well known for its extreme promiscuity in substrate specificity and allosteric behavior. In addition to the metabolism of drugs and endogenous compounds, CYP3A4 is implicated in the oxidation and bioactivation of carcinogens and environmental pollutants. CYP3A4 can also be inhibited and activated by xenobiotics, which may lead to undesired drug-drug interactions, toxicity and human death. Despite the central role of CYP3A4 in drug metabolism, its mechanism of inhibition and activation are still poorly understood. Our studies address key issues in both areas of the CYP3A4 research. In particular, investigations on the CYP3A4 interaction with analogs of ritonavir, the most potent pharmacoenhancer marketed to date, allowed us to build and test the pharmacophore model for a CYP3A4-specific inhibitor through rational inhibitor design.[1,2] To investigate the underlying mechanism for the allosteric behavior of CYP3A4, thought to arise from the multiple substrate binding, we utilize an integrated structural, biochemical and biophysical approach. Our recent findings which provide novel insights into the mechanism of CYP3A4 activation, substrate cooperativity and drug-drug interactions will be presented.

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Artificial Porphyrinoids Embedded with Functional Building Blocks

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Porphyrins are aromatic macrocycles that exhibit distinguished photophysical and chemical properties, such as strong absorption in the UV-visible region, redox interconversion and metal coordination. To meet the requirements for applications in material science, various synthetic strategies have been employed to construct novel artificial porphyrin homologues, such as meso- and β-substitution, ring-contraction and ring-expansion, isomerization and core-modification, with the main purpose of regulating their structural and electronic properties.[1]

Herein we report our recent efforts on the synthesis, structural and electronic properties of artificial porphyrinoids in which one or more pyrrole subunits are replaced by other heterocycles or small conjugated moieties (Figure 1).[2-4] These artificial porphyrinoids are excellent candidates not only for the basic study on the aromaticity of macrocycles, but also for many potential applications such as near-infrared (NIR) dyes, magnetic materials, molecular switches and nonlinear optical materials.

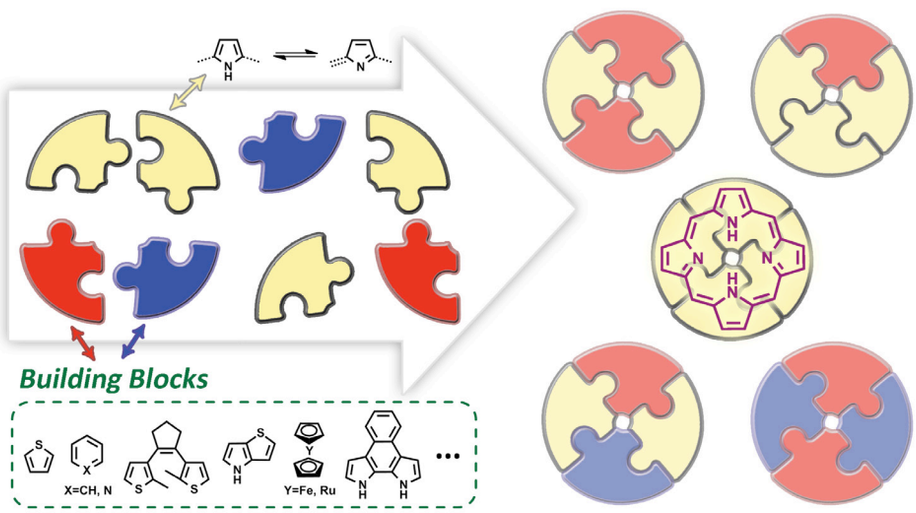

Figure 1. Artificial porphyrinoids embedded with various functional moieties.

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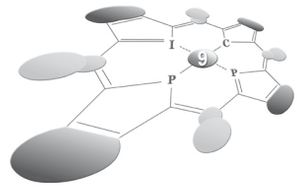

Assembly and Functionalization of Block Polymers/Porphyrins

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Block polymers as a kind of synthetic building blocks have been widely used in in the researching field of assembly. Amphiphilic block polymers in selective solvent can form aggregates with different shapes and sizes, such as micelles and vesicles. Porphyrins have received much attention because of their important role as catalysts and sensitizers in a wide variety of in chemistry, material science, life science, and nanotechnology.

The aggregation of porphyrins has a deep impact on many physicochemical properties of these molecules. We have reported that block polymers poly(ethylene glycol)-block-poly(4-vinylpyridine (PEG-b-P4VP), possessing aromatic units, resulted in the monomeric form and aggregates of TPPS. Inspired by natural photosynthesis, we employed polymeric micelles to encapsulate hydrophobic metallo-tetraphenylporphyrin by complexation with PEG-*b*-P4VP via axial coordination. The hydrophilic PEG shells guarantee colloidal stability of the complex micelles in aqueous media, and these micelles can effectively improve the water solubility of metallo-TPP and protect them against demetallization, aggregation and photodegradation.

The bioactive aggregates such as enzymes, and hemoglobin etc. possessing unique physiological property have been attracting lots of scientific efforts to mimic these adaptive structures and marvelous functions. Following an inspiration from peroxidase, an artificial peroxidase was constructed through the assembly of diblock copolymers and hemin, which formed a functional micelle with peroxidase-like activity. Hemoglobin is contained in red blood cells as efficient carriers of oxygen and carbon dioxide. However, due to the complexity of structures and variety of functions, successful examples of hemoglobin models have been rarely reported. Therefore, we anticipate combining the chemical synthesis and technology of assembly of small molecules and macromolecules is possible strategy to construct the model hemoglobin. Herein, a complex micelle as a hemoglobin functional model with biaoactive function of reversible oxygen transfer was constructed through the hierarchical assembly of diblock copolymer poly(ethylene glycol)-block-poly(4-vinylpyridine-co-N-heptyl-4-vinylpyridine) (PEG-b-P(4VP-co-4VPHep)), Tetrakis(4-sulfonatophenyl)porphinato iron(II) (Fe(II)TPPS) and β-cyclodextrin (β-CD). The μ-oxo dimer of Fe(II)TPPS was successfully inhibited through host-guest interaction with β-CD. The Fe(II)TPPS coordinating with pyridine groups functions as the active site to reversibly bind dioxygen. In addition, the host-guest inclusion was encapsulated in the hydrophobic core of the complex micelle and tightly fixed by P4VP chains, which formed double hydrophobic barriers. The hydrophilic PEG blocks stretched in the aqueous solution constitute the shells which stabilize the structure of the complex micelle as well as impart the complex micelle sufficient blood circulation time. The quaternary amine N-heptyl-4-vinylpyridine can coerce abundant $S_2O_4^{2-}$ into the core of the complex micelle to endow the self-reduction process. Dioxygen can be bound to the Fe(II)TPPS located in confined space and excellent reversibility of the bind-release process of dioxygen can be achieved. As a continuation, a biocompatible complex micelle with core-shell structure as an oxygen nanocarrier was constructed through the hierarchical assembly of diblock copolymer poly(ethylene glycol)-block-poly(L-lysine), Co(II)TPPS, Heptapeptide and heptakis(2,3,6-tri-O-methyl)-β-cyclodextrin (TM-β-CD). Therefore, the rationally designed amphiphilic structure can work as promising artificial O_2 carriers. Potentially, the complex micelle can be expected to improve the curative effect of diseases linked with hypoxia.

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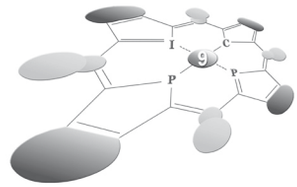

Functionalization of An Antiaromatic Porphyrinoid Norcorrole Ni(II) Complex

Hiroshi Shinokubo

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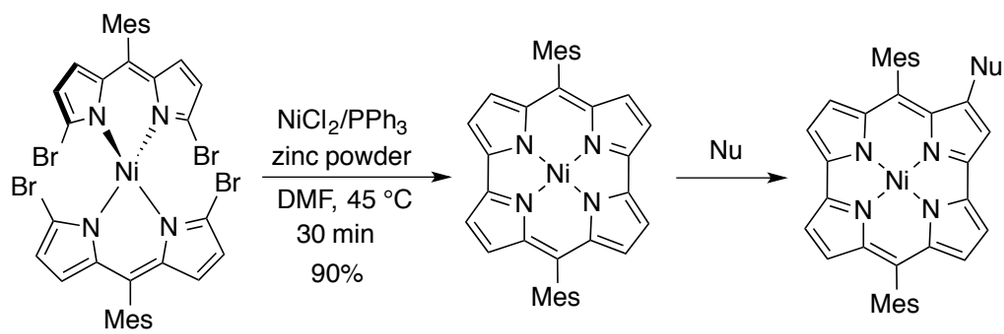
Norcorrole is a ring-contracted porphyrin, which lacks two *meso*-carbons from regular porphyrins, of which synthesis has been quite challenging.[1] Recently, we have succeeded to synthesize *meso*-mesityl-substituted norcorrole Ni(II) complex in good yield in a gram scale from dibromodipyrrin Ni(II) complex.[2] The planar structure and 16π-conjugation of the norcorrole Ni(II) complex lead to distinct antiaromatic nature. However, *meso*-dimesitylnorcorrole Ni(II) was quite stable under air at room temperature, although most of antiaromatic porphyrinoids with 16π-conjugation are generally unstable.

Because of the stability of *meso*-dimesitylnorcorrole Ni(II), we expected that this compound could be a probe to investigate the chemistry of antiaromatic porphyrinoids. Consequently, we have been exploring the reactivity of *meso*-dimesitylnorcorrole Ni(II).[3,4] Recently, we have found that the reaction of several nucleophiles with *meso*-dimesitylnorcorrole Ni(II) selectively afforded functionalized norcorroles through a formal direct substitution reaction.[5] The introduced substituents had significant influence on the optical and electrochemical properties of norcorrole Ni(II) complexes.



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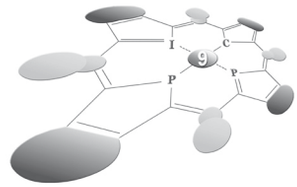

Molecular Mechanism of NO Reduction by Bacterial Nitric Oxide Reductases

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Bacterial nitric oxide reductase (NOR) is involved in denitrifiation, which is a kind of anaerobic respiration. In the denitrification, highly cytotoxic NO is generated as a intermediate compound from nitrite NO_2^- catalyzed by heme-ezyme nitrite reductase (NiR). To detoxify NO, NOR catalyzes the NO reduction reaction ($2NO + 2H^+ + 2e^- \rightarrow N_2O + H_2O$) at its active site, which is a binuclear center comprised by heme (heme b_3) and non-heme iron (Fe_B). One simple question is how the NO generated by NiR is transferred to NOR without diffusing into the cell. Another question is how the NO is reduced by the nibuclear center of NOR. In the enzymatic reaction by NOR, three short-lived intermediates have been proposed for the coordination of two molecules of NO to the binuclear center; i.e., *trans*-, *cis*-heme b_3- and *cis*-Fe_B-coordinations. To establish the molecular mechanism of the NO reduction by NOR, we have been studying the time-resolved spectroscopies to characterize the coordination and electronic structures of the intermediates, which are appeared in the micro- to milli-second time region after the reaction of the ferrous enzyme with the NO molecule(s). On the basis of the time-resolved optical, ESR and IR spectral changes, we have proposed that the *trans*-mechanism seem favorable for the NO reduction mechanism by bacterial NOR. We will discuss the NOR reaction with referring their crystallographic structural data which we reported.

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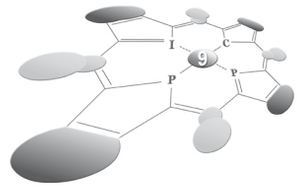

Metal-Porphyrin Asymmetric Catalysis in Water

Gerard Simonneaux, Paul Le Maux, Daniel Carrie and Soizic Chevance

UMR 6226 Institut Sciences Chimiques de Rennes, Campus de Beaulieu, Université de Rennes 1, 35042 Rennes, France

The development of environmentally benign reactions is an important goal in synthetic organic chemistry and chemical engineering. However, catalytic enantioselective reactions using transition-metal complexes in protic or aqueous solvents are within limited ranges. Our current applications of asymmetric catalysis using metalloporphyrins will be reported (1). Distinct methodologies have been developed for carbene transfer and oxidation reactions such as the use of water-soluble catalysts. As applications asymmetric sulfoxidation, epoxidation of alkenes and hydroxylation catalyzed by iron and manganese porphyrins will be described in water solutions (2-4).

We will also report NH insertion of amino esters using various diazo esters as reagents and the site selective modification of terminal NH_2 group of insulin using water-soluble 5,10,15,20-tetrakis-(4-sulfonato-phenyl)-porphyrin-iron(III) chloride (FeTSPPCl) as catalyst (5). In the context of possible bioconjugation to proteins, synthesis and reactivity of new diazoporphyrin esters will also be described.

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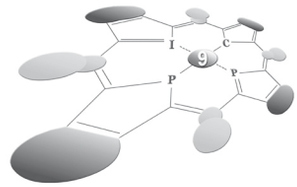

PDT Sensitizers Derived from Chlorin-e_6

Kevin M. Smith, R. G. Waruna Jinadasa, Hui Chen, Lijuan Jiao, Zehua Zhou, Alex L. Nguyen, Frank R. Fronczek and M. Graça H. Vicente

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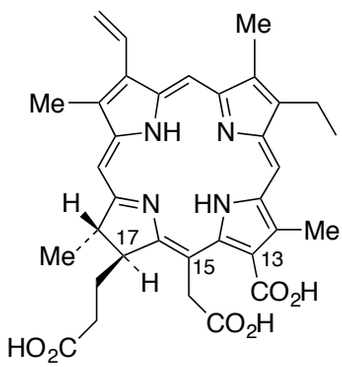
Chlorin-e_6 (**1**) is a degradation product of chlorophyll-a that possesses three chemically distinct carboxylic acid groups that can be conjugated with biomolecules. Because of the long-wavelength light-absorption properties of chlorophyll derivatives, they have been used extensively as photosensitizers in photodynamic therapy (PDT) studies. In PDT, tumor cells are destroyed by intracellular production of toxic activated oxygen species upon exposure of a photosensitizer to both oxygen and light.



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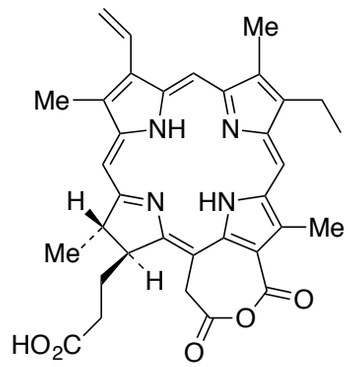

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The presentation will focus on various regioselective synthetic methodologies devised to prepare 17^3-, 15^2- and 13^1-mono- and bis-amino acid conjugates of chlorin-e_6 (**1**),[1,2] and will report details of toxicity, cell uptake and subcellular localization of these new sensitizers. The cyclic anhydride (**2**)[3,4] is shown to be a pivotal intermediate in some of the conjugation reactions.

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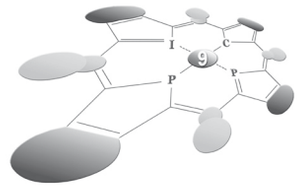

Photoelectronic properties of DNA-porphyrin complexes

Walter F. Smith[a], **Peco Myint**[a], **Emma R. Oxford**[a], **Collence Nyazenga**[a], **Stefanos G. Logothetis**[a], **Zhengqing John Qi**[b], **A. T. Johnson**[b]

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Self-assembled molecular circuits hold the promise of dramatic reductions in manufacturing and energy costs compared to conventional lithographic techniques, as well as the possibility of completely new functionalities. Many applications require only simple geometries. However, the creation of truly complex self-assembled circuits requires an easily programmable and sophisticated recognition capability. The only apparent way to achieve this capability while preserving chemical robustness is by using DNA. Because its mechanical properties are relatively predictable, it has been used to form a remarkable array of nanostructures and mechanical devices. It has now been shown clearly that DNA itself is electrically conductive over short lengths.[1-4] However, for distances longer than 50 nm, the conductivity of DNA is poor, especially in the dry state.

When meso-tetrakis(N-methyl-4-pyridiniumyl)porphyrin (TMPyP) forms complexes with DNA, it intercalates into the base stack of the DNA (for appropriate solution conditions).[5-8] There is significant red shift and hypochromism of the Soret absorption peak. This suggests strong coupling of the electron states in the DNA with those in the porphyrin.

We have measured the photoconductivity and dark conductivity of these complexes in an N_2 environment, as a function of relative humidity (RH), for length scales up to 400 nm. Beginning at low humidity, we observe no dark conductivity or photoconductivity. As the humidity is increased, we first observe photoconductivity at 30% RH. The photoconductivity and dark conductivity continue to increase as the humidity is increased. Then, as the humidity is decreased both dark and photoconductivity decrease, but to levels much higher than observed in the first part of the experiment.

We hypothesize that the humidity affects the DNA-porphyrin hybrids by altering the structure of the DNA[9], and/or by the effect of water molecules on the electron distribution in the DNA.[10]

Surprisingly, the dark current does not vary in the same way with humidity as does the photocurrent (defined as the increase in current caused by shining light on the sample). This shows that the conduction path or mechanism for photoconductivity is different from that for dark conductivity.

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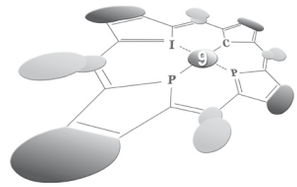

Cytochrome c-Cardiolipin interaction at the molecular level

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Cytochrome c (cyt c) has two important functions, that of electron transfer (1) and that involving its interaction with the mitochondrial membrane phospholipid cardiolipin (CL), which determines its peroxidase activity and the initiation of apoptosis (2). The peroxidase activity of cytochrome *c* is ascribed to partial unfolding and rupture of the bond between the heme Fe and its axial ligand, Met80 (3); however, the mechanism of the cyt *c*- CL interaction is uncertain. While it has become clear that the structure of cyt c changes upon interaction with CL, the extent and sequence of conformational rearrangements associated with this ligand replacement remain a subject of debate since many, not always consistent, results in vitro has been reported. The comparison of the results obtained for the horse heart cyt c-CL complex at room and low temperature using resonance Raman and EPR spectroscopy, together with the effects induced on the complexation process by mutation of key protein residues (His26, His33, Lys72, Lys73 and Lys79) generally considered to play some role in the interaction, has allowed us to clarify which particular residues are involved as distal axial ligands in the ferric cyt c -CL complex and to gain insight into the mechanism of the interaction at a molecular level. Upon titration of cyt c with CL, we found that the interaction is complete at a protein-lipid molar ratio (R) of 1:30. Wild type (WT) cyt c, characterized by His-Fe(III)-Met80 coordination, is observed to undergo spin and coordination changes upon interaction with CL. The first conformer which appears at a 1:5 molar ratio, following a partial detachment of the Met80 ligand, is a bis-His conformer. This species grows in and represents the major form at the end of the titration. Single mutation of His33 or His26, the only two His residues able to bind the heme Fe in the CL complex, did not allow us to identify which histidine binds the heme, since as previously observed for the interaction between cyt c and CL liposomes, in the absence of His26, His33 binds the heme iron and vice versa (4). However, the formation of a bis-His species indicates that a global protein rearrangement occurs, as His26 and His33 are not located in close proximity of the heme iron. Interestingly, the mutant lacking both His residues is still capable to bind CL, but displays a very different spectroscopic signature. Upon increasing the cyt c:CL ratio, Met80 becomes fully detached leading to the formation of a minor 6cHS and a 6cLS species, corresponding to the replacement of the native Met80 residue by H_2O and OH^- ligands, respectively. A Lys-ligated species has also been suggested to form upon cyt c interaction with cardiolipin (CL) membranes (5), but neither EPR nor RR gave any evidence of a Lys ligated signature. In addition, the variant lacking the Lys residues gave a complex with CL spectroscopically very similar to that of the WT. The results will be discussed in terms of the structural rearrangements of cyt c following CL complexation.

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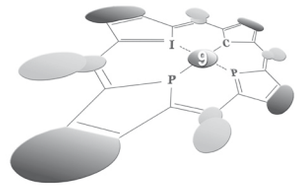

The Synthesis of Carbohydrate Porphyrin, Bacteriochlorin and Phthalocyanine Conjugates for Photodynamic Therapy

Nicole L. Snyder[a], Joshua V. Ruppel[b], Taylor P. Adams[c], Dennis J. Akrobetu[a], Rachel G. Barkley[a], Morgan A. Burch[a], Gabriel E. Cambronero[a], Shamus L. A. Cooper[a], David Dennis[b], Ryan D. Dolewski[b], Peter F. Garrett[c], Kevin W. Graepel[c], Hilary Langat[c], George T. Mukosera[a], Rachel F. Rothbarth[c], Raymond Q. Wiggins[d], W. Erin Xu[a]

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Porphyrins, bacteriochlorins, phthalocyanines and related compounds have proven useful as phototherapeutics in the treatment of bacterial infections and cancer. However, the development of new phototherapeutics is often hindered by the hydrophobicity of the core macrocycles, which limits the solubility of these compounds in biological fluids, and a general lack of specificity. In our efforts to address these challenges, we are synthesizing carbohydrate porphyrin (CPCs), carbohydrate bacteriochlorin (CBcCs) and carbohydrate phthalocyanine (CPcCs) conjugates. The carbohydrate component, which naturally imparts water solubility, can also be selected target specific cellular proteins (e.g. Ag85 of *Mycobacterium tuberculosis*). In this paper, we present our most recent efforts for synthesizing mono- and multivalent CPCs, CBcCs and CPcCs, including C-O and C-N coupling and click chemistries. We also demonstrate how this work is being applied to the synthesis of a new class of trehalose-based phototherapeutics for the treatment of *M. tuberculosis.*

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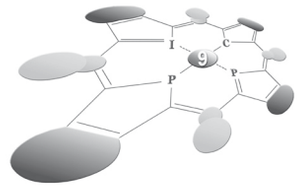

Photosensitizers as efficient agents for photo-antibacterial surfaces

Vincent SOL

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Microbial contamination is of great concern in a variety of areas such as medical devices, healthcare products, water purification systems, hospitals, dental office equipment, food packaging, food storage, household sanitation, etc. In the last years, major interest has grown in the preparation of materials endowed with antibacterial properties for use in a wide range of fields such as food packaging and transportation, housekeeping, handling of medical and military items. The need for a control of potentially pathogenic microorganisms in exposed environments has led to the development of antibacterial products. Antimicrobial surfaces have been obtained by incorporating active agents, currently under study or commercially available, among which can be mentioned quaternary ammonium salts, N-Halamines, guanidine polymers, antibiotics or Ag/TiO_2 nanoparticles. However these agents are not entirely satisfactory because material can be loss antibacterial properties in noncovalent systems, release of environmentally hazardous agents, obligation on direct contact between antimicrobial molecules and microorganism, emergence of antimicrobial resistance.

Our strategy was to develop a new polymer (biopolymers,...) material bearing a covalent linker between polymeric surface and new antimicrobial molecules. Indeed, biopolymers are an excellent starting material for developing a more sustainable material from renewable resources and porphyrins are molecules of considerable interest due to their ability to act as photosensitizers when irradiated with visible light and recent studies have shown that porphyrins could be used in PDI.

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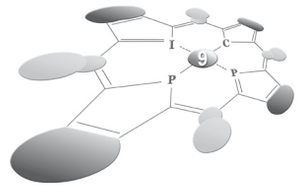
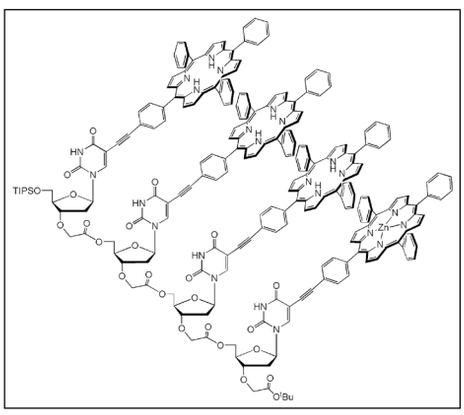


Nucleotidic and Peptidic Multi-Porphyrinic Devices: when the Desired Conformation is Determined by Chiral Flexible Linkers.

Nathalie Solladié*

Groupe de Synthèse de Systèmes Porphyriniques, Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse cedex 4, France, Fax: 33-(0)5-61-55-30-03, e-mail:nathalie. solladie@lcc-toulouse.fr.

In natural photosynthetic systems, the solar energy is collected by pigment molecules attached to the light harvesting complexes, where the chlorophylls are held in a favored spacing and orientation by fairly short α-helical polypeptides. When a photon hits one of the chlorophylls, the absorbed energy spreads extremely rapidly to the others until the reaction center is reached within the cell membrane, where the solar energy is converted into chemical energy used by the cell to grow. Beyond the control of the structure of multi-chromophoric arrays, monitoring the spatial orientation of the chromophores in artificial light harvesting devices is a challenge of growing interest. Indeed, multi-porphyrinic arrays attract more and more attention for the elaboration of photonic and electronic wires.



Polypeptides bearing pendant porphyrins have thus been prepared in our group.[1] Beyond a certain degree of oligomerisation, a secondary structure such as a 3_{10} helix is observed, which forces the porphyrins to arrange in a defined spatial arrangement. Due to the overlap of the porphyrins in such a conformation, the chromophores undergo a sufficient electronic coupling to favor a good exciton migration.[2] This pre-organization creates cavities within the peptides, enabling them to accomodate guests through ligand coordination pattern.[3]

We also prepared oligonucleotides with pendant porphyrins to investigate the ability of nucleotidic backbones to orientate chromophores in space and organize multi-porphyrinic hosts in order to enable them to complex multiple bidentate guests.

Acknowledgements
This work was supported by the CNRS and the French Ministry of Research.

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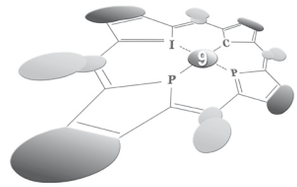

Construction of multi-Porphyrin Arrays

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In the recent decades much attention has been paid to study on the construction of multi-porphyrin arrays, whih has potential applications in optoelectronic devices, sensors, photovoltaic devices, non-linear optical(NLO) materials, photodynamic therapy (PDT) pigments, light-harvesting models, and host-guest chemistry. The manipulation of interporphyrinic interaction is often essential to achieve desirable electronic and photophysical properties. In order to prepare multi-porphyrin arrays, many strategies have been used. Recently, the Osuka group developed a transition metal-catalyzed coupling reaction that has been proven to be very useful to construct multiporphyrinic systems. Till now we have adopted this strategy and prepared many heterocycles bridged β-to-β porphyrin arrays, including porphyrin barrel[1], newly directly-bridged β-to-β porphyrin nanorings[2], azobenzene bridged porphyrin nanorings[3]. The experiment results indicated that the building blocks will remarkably affect the target molecules. As the bridge is thienylene, the main products is cyclic dimer, trimer, when the bridge is pyridylene, there are trace cyclic products are obtained. when the bridge is free base or Zn(II) porphyrin, bigger loop are formed, while Ni(II)porphyrin is used, the products is much simple. As to synthesis of porphyrin nanobarrel, if the porphyrin monomer is free base or Zn(II) porphyrin, no porphyrin barrel is obtained, this means that only ruffled porphyrin monomers can be used to synthesis porphyrin barrels. Synthesis of directly linked porphyrin nanorings is affected by the meso-substituent on porphyrin, when the substituent is aryl, only trimer and twinned pentamer can be prepared, when the substituent is alkyl, tetramer and twinned heptamer can be obtained.The photophysical study revealed that these porphyrin arrays exhibit either longer fluorescent lifetime, larger two photon absorption values or strong electronic interaction. Motivated by their fascinating structure and properties, some new porphyrin arrays recently have been constructed through Pd-catalyzed cross-coupling reactions (Figure 1), further study on their properties is underway in our lab.

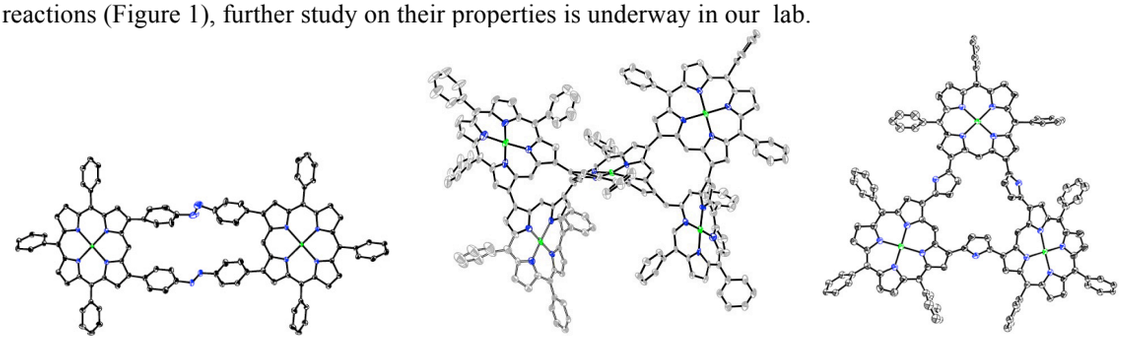

Figure 1. Crystals of multi-porphyrin arrays

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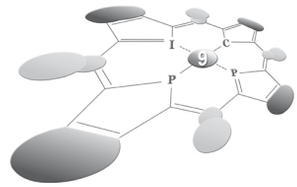

Carbonization of Self-assembled Porphyrin as Highly Efficient Electrocatalysts toward Oxygen Reduction Reaction

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High performance non-noble metal electrocatalysts (NNMEs) are required to replace costly Pt-based electrocatalysts for widespread commercialization of fuel cells and metal-air batteries.[1-2] Study of unique synthetic routes is of particular significance for the creation of highly efficient NNMEs yet remains a bottleneck issue. Herein, we report an unprecedented synthetic approach that combines self-assembly of iron (III) porphyrins (FePs) with traditional pyrolysis to prepare interesting NNMEs with controlled morphology. Remarkably, the initial shape of nanostructures of self-assembled FePs was nearly reserved after carbonization, enabling highly desired manipulation over the size and shape closely related to the performance of NNMEs. Molecular Dynamics (MD) simulations turned out that pi-pi interaction of neighbouring FePs primarily contributes to the morphology maintenance after pyrolysis. The as-prepared NNMEs exhibited superb oxygen reduction reaction (ORR) activities, excellent durability and methanol tolerance in both alkaline and acidic solution. This study opens up an innovative avenue to produce high performance NNMEs with controllable structural features that are difficult to be achieved prior to this study.

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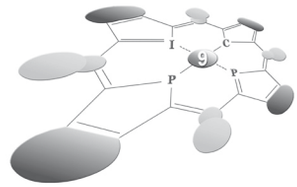

Single-Atom Bridged Diiron Macrocyclic Complexes: Influence of the structure on catalytic properties

Alexander B. Sorokin

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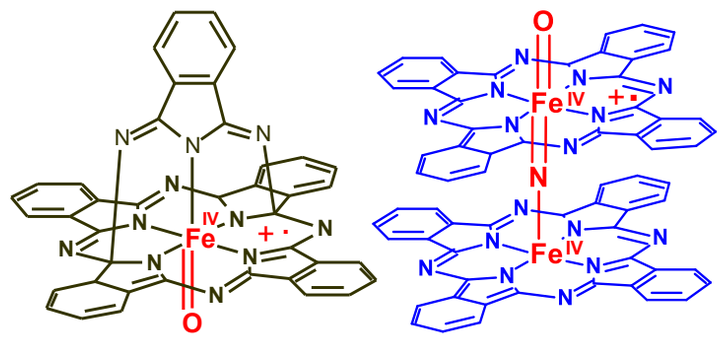
Metal phthalocyanine[1] and porphyrin[2] complexes are widely used in many catalytic applications and their catalytic chemistry is well-documented. These macrocycles can be assembled in more elaborated structures, e.g. μ-oxo, μ-nitrido and μ-carbido diiron complexes which haven't been considered as catalysts until recently. Quite unexpectedly, some single-atom bridged diiron complexes are capable of reacting with oxidants retaining their dimeric structure to form ultra high-valent diiron species.[3] These short-living species were detected and characterized by UV-vis, EPR, ESI-MS, Fe K edge EXAFS, XANES and Mössbauer techniques.

Of particular interest are the unusual catalytic properties[3,4] of these highly electrophilic species which are able to oxidize methane and to perform oxidative transformation of the aromatic C-F bonds under very mild conditions.

Another example of promising catalytic properties of "exotic porphyrinoid systems" is the iron helmet phthalocyanine complex which performs a very efficient and selective large-scope epoxidation of olefins.[5]



Mechanistic issues of this unusual reactivity and influence of the structure on the catalytic properties are discussed.

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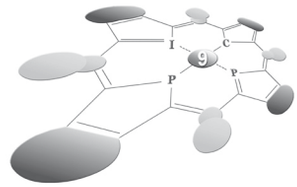

Structures of modified B_{12} molecules

Bernhard Spingler[a], **Felix Zelder**[a]

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The structure of vitamin B_{12} has fascinated chemists for over 50 years.[1] We have studied cyanocobalamin structures that were modified at the CN unit [2], the carboxylic acid positions [3], the sugar [4] and around the b-ring [5].
In our presentation, we will discuss our most recent efforts in the crystallisation [6,7] and structure determination of various interesting B_{12} derivatives.[8]

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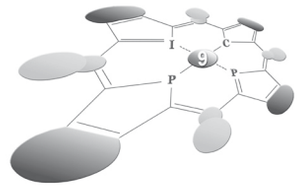
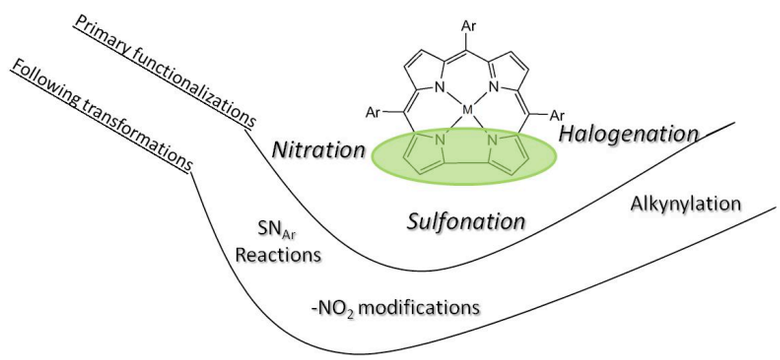


New Synthetic Methodologies Leading to β-Substituted Corrole Derivatives

Manuela Stefanelli[a], Federica Mandoj, Mario Luigi Naitana, Sara Nardis, Giuseppe Pomarico and Roberto Paolesse

Università di Roma Tor Vergata, Dipartimento di Scienze e Tecnologie Chimiche, via della Ricerca Scientifica 1, 00134 Roma, Italy (e-mail:manuela.stefanelli@uniroma2.it)

The peripheral elaboration of corrole macrocycle has experienced impressive advancements in the last decade, as witnessed by the numerous synthetic approaches reported, addressing both the meso-aryl and β-pyrrolic positions.[1] The possible preparation of a wide range of meso-triarylcorroles with tunable properties has allowed a more deepened knowledge of the properties of these macrocycles, triggering their promising use in several applicative fields, catalysis and medicine above all. Within this framework, the need to comply with the requirements of a specific application has prompted the development of synthetic procedures to synthesize corroles possessing peripheral functionalities, which can be the entry point for subsequent modifications. In this contribution, we report the most recent results obtained in our laboratories regarding the regioselective introduction of functional groups of primary importance, evidencing in many cases the key role of the metal coordinated on the reaction oucome. Furthermore, we present the following exploitation of the chemical reactivity of the inserted functionalities to achieve novel β-substituted corrole derivatives of particular interest.[2,3]



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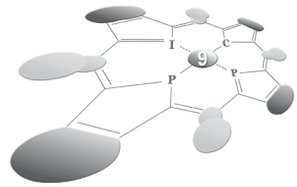

Trends in the Absorption Spectra of Peripherally-substituted Porphyrins and Phthalocyanines as a Function of the Energies of the Top Two Occupied and the Lowest Two Unoccupied Orbitals

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The intricacies of the electronic structures of the porphyrins control an electronic absorption spectrum that supports all life on this planet. Understanding the specific effects and then quantifying changes in the electronic properties that leverage major changes in the absorption spectrum provides information for use in designing novel compounds with tuned spectro-optic properties (1-3). We report on the trends in spectral properties for a wide range of peripherally-substituted porphyrins and phthalocyanines using DFT and TDDFT calculations to quantify the connection between electronic structure and experimental data. Magnetic circular dichroism (MCD) spectra provide essential assignment criteria necessary to identify the remnants of the original set of transitions to the degenerate S1 and S2 states. Emission spectra act to define the energy of the S1 state. The combination of experimental data and TDDFT calculations allows for predictions of optical properties prior to synthesis.

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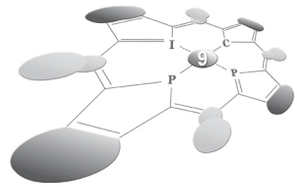


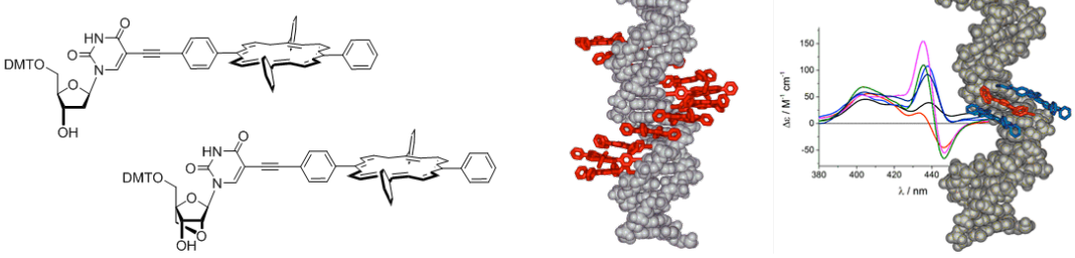
Chrial porphyrin assemblies using DNA as scaffold

Eugen Stulz, Iwona Mames

University of Southampton, School of Chemistry, Highfield, Southampton SO17 1BJ, UK

DNA has become very attractive as scaffold for functional molecules on the nanometre scale.[1] The sequence specific insertion of modified nucleotides using automated DNA synthesis allows for the creation of new designer molecules with a wide range of potential applications. We have established a general synthetic route to porphyrin-nucleosides and their subsequent site specific incorporation into oligonucleotides to create multiporphyrin arrays. Up to eleven consecutive porphyrins could be incorporated into DNA giving access to a multiporphyrin array of approximately 10 nm in length, which corresponds to the highest amount of DNA modification with a large hydrophobic metal complex.[2] The spectroscopic data and structure calculations indicate the formation of a stable helical array in the single strand porphyrin-DNA. The π-stack of the porphyrins leads to strong electronic interaction between the chromophores. A zipper array with induced stability and energy transfer properties has recently been realised, providing access to the first reversible photonic wire based on a DNA scaffold.[3]

We will present our latest results in terms of structure analysis of porphyrin modified DNA, which includes the stepwise built up of a porphyrin-DNA system and its detailed analysis using CD spectroscopy, molecular modelling and thermal analysis with absorption and fluorescence spectroscopy. In addition, a novel LNA derived porphyrin building block will be discussed which show large differences in excitonic coupling depending on the DNA sequence.[4]



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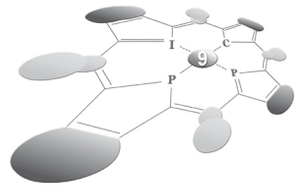
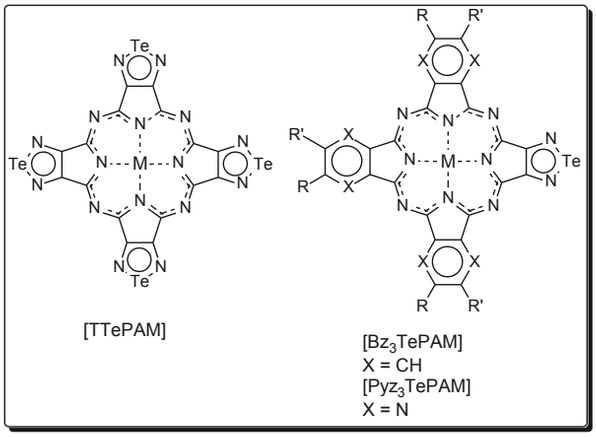


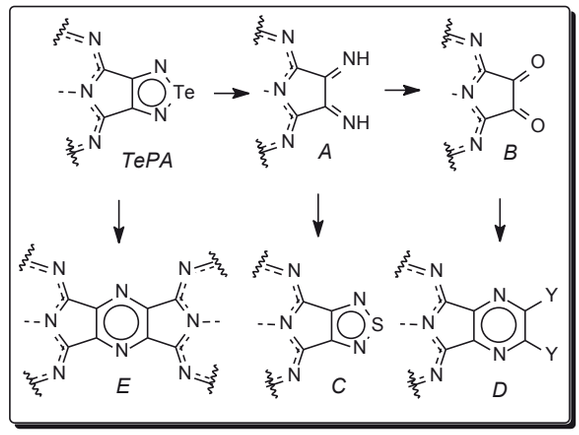
1,2,5-Telluradiazoloporphyrazines and Their Peripheral Modification

Pavel A. Stuzhin[a], **Oskar I. Koifman**[a], **Maksim S. Mikhailov**[a]

[a]*Research Institute of Macroheterocycles, Ivanovo State University of Chemical Technology, RF-153000 Ivanovo, Russia; e-mail: stuzhin@isuct.ru*

First Te-containing phthalocyanine analogues - porphyrazines with fused 1,2,5-telluradiazole rings have being obtained and characterized both as symmetrical species [TTePAM][1] and low-symmetry porphyrazines containing 1,2,5-telluradiazole fragment in combination with three fused benzene rings [Bz_3TePAM][1] or pyrazine fragments [Pyz_3TePAM].[2] The influence the Te-atom has on the electronic structure, spectral and electrochemical properties of porphyrazine macrocycle is analyzed on the basis of experimental and theoretical study of the series of 1,2,5-chalocogenadiazoloporphyrazines.





The easy detelluration of 1,2,5-telluradiazoloporphyrazines (*TePA*) occurring in acidic conditions allows to consider them as synthetic precursors for 2,3-diimino- (*A*) and 2,3-dioxoporphyrazines (*B*) which can be used for direct transformation of 1,2,5-telluradiazole fragment affording, e.g. the 1,2,5-thiadiazole (*C*) or pyrazine (*D*) fused porphyrazines.[3] It is also demonstrated that detelluration can be used for design of two-dimentional porphyrazines (*E*), e.g. binuclear bisphthalocyanine having bridging pyrazine ring.

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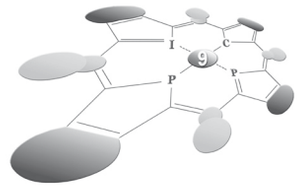
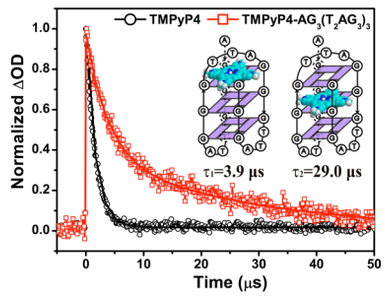


DNA G-Quadruplex / Porphyrin Interactions Studied by Transient Absorption Spectroscopy

Hongmei Su[a,b]

[a]*College of Chemistry, Beijing Normal University, Beijing 100875, China*
[b] *Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China*
Email : hongmei@iccas.ac.cn



Due to their chemical, biological, and medicinal importance, substantial efforts have been made to investigate G-quadruplex/ligand interactions, which, however, are difficult to monitor, because of complex structures and versatile topologies of G-quadruplexes. We report a new transient spectral method utilizing triplet excited state as sensitive reporters to monitor and differentiate the multiplex G-quadruplex/ligand interactions in a single assay, which is a difficult task and usually requires a combination of several techniques. From a systematic study on the interactions of porphyrin (TMPyP4) with each telomeric G-quadruplexes: $AG_3(T_2AG_3)_3$, $G_2T_2G_2TGTG_2T_2G_2$, $(G_4T_4G_4)2$, and $(TG_4T)4$, it is convincingly shown that the ligand triplet decay lifetimes are sensitive to the local bound microenvironment within G-quadruplexes, from which the coexisted binding modes of end-stacking, intercalation, and sandwich are distinguished and their respective contribution are determined. The complete scenario of mixed interaction modes is thus revealed, shedding light on the past controversial issues. Additional control experiments demonstrate the sensitivity of this triplet reporter method, which can even capture the binding behavior change as the G-quadruplex structures are adjusted by Na^+ or K^+.

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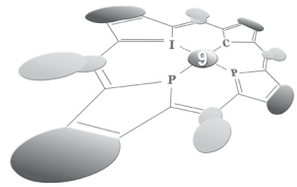

Rapid Stabilization of Atherosclerotic Plaque with 5-Aminolevulinic Acid Mediated Sonodynamic Therapy

Xin Sun[a], Zhitao Li[b], Shuyuan Guo[a], Ye Tian[a,b]

[a]*Division of Cardiology, the First Affiliated Hospital, Cardiovascular Institute, Harbin Medical University, Harbin 150001, China.*
[b]*Division of Pathophysiology, the State-Province Key Laboratories of Biomedicine-Pharmaceutics of China, Key Laboratory of Cardiovascular Research, Ministry of Education, Harbin 150086, China.*

Object: 5-Aminolevulinic acid mediated sonodynamic therapy (ALA-SDT) has been found effective in promoting apoptosis of atherogenic macrophages. This study aims to evaluate the therapeutic effect of ALA-SDT on plaque stabilization in rabbits.
Methods: Atherosclerotic plaque was induced in the right femoral artery of rabbits by a combination of silastic tube placement and atherogenic diet. Sixty rabbits were randomly divided into control (n = 12) and SDT (n = 48) groups. In the SDT group, under the previously optimized dosage of 60 mg/kg ALA, ultrasound intensities of 0.75, 1.00, 1.50 and 2.00 W/cm2 (n = 12 each) were used. Seven days after the treatment, pharmacological triggering was performed to induce plaque disruption in rabbits and the subjects were processed for contrast-enhanced ultrasound imaging and histological examinations.
Results: The best plaque-stabilizing effects of ALA-SDT were observed at an ultrasound intensity of 1.5 W/cm2, which decreased the frequency of plaque disruption by 88% (1 of 12 versus 8 of 12 in control, $P < 0.01$), positive area of macrophages by 94% ($P < 0.001$) and percentage content of lipids by 60% ($P < 0.001$), while percentage content of collagens was increased by 127% ($P < 0.001$). ALA-SDT was associated with increased macrophage apoptosis in plaques. Moreover, ALA-SDT decreased the percentage contents of matrix metalloproteinase-2, 9 and increased the percentage contents of tissue inhibitors of matrix metalloproteinase-1, 2 in plaques.
Conclusion: ALA-SDT promotes atherosclerotic plaque stabilization by inducing macrophage elimination and inhibiting matrix degradation, thus reduces the frequency of plaque disruption.

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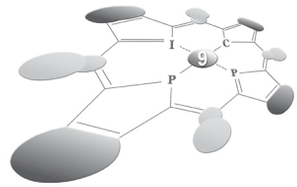

Quaterpyrrole and Sexipyrrole: Extended Bipyrroles for Expanded Porphyrins?

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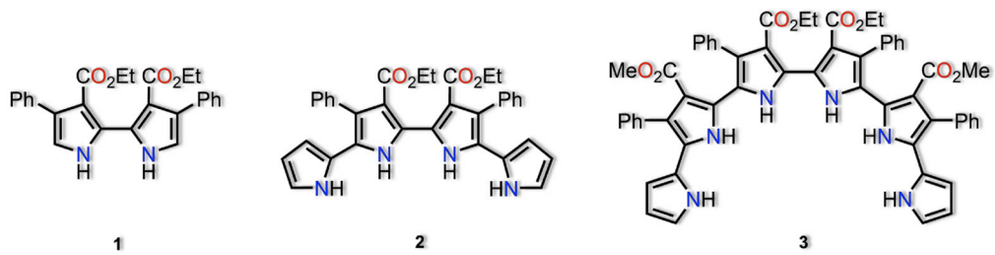
α,α-linked oligopyrroles play a crucial role in the synthesis of expanded porphyrins [1]. The preparation of macrocycles such as porphycenes, amethyrins or cyclopyrroles are based on the coupling or condensation of the proper functionalized bipyrrole or terpyrrole [2]. Although longer α,α-linked oligopyrroles have been reported [3], their chemical instability has hampered their use as synthetic building blocks.
Our group have developed a new family of 2,2'-bipyrroles **1** which possesses a remarkable chemical stability ascribed to the presence of two electron withdrawing groups [4]. Bipyrroles **1** can be easily brominated at the α positions allowing their homologation with pyrrole units by means of palladium catalyzed reactions [5]. This strategy has allowed the concise preparation of quaterpyrrole **2** and sexipyrrole **3**. In this presentation, the preparation of these oligomers and their use to obtain new expanded porphyrins will be discussed.



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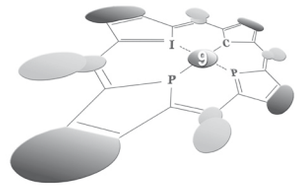

Semisynthesis of chlorophyll-*c* analogs by oxidative modification of naturally occurring chlorophyll-*a*

Hitoshi Tamiaki, Meiyun Xu, Shogo Matsubara and Yusuke Kinoshita

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Chlorophyll-*a* (Chl-*a*) was extracted from cells of cyanobacterial *Spirulina* species and modified to methyl pyropheophorbide-*a*. The resulting 3-vinyl-chlorin was transformed to zinc complex of the corresponding 3-acetyl-porphyrin. The zinc porphyrin was oxidized to give *cis*-7,8- and 17,18-dihydroxy-chlorins as well *cis*-7,8-*cis*-17,18-tetrahydroxybacteriochlorin [1,2]. After zinc-demetallation, the isolated *cis*-7,8- and 17,18-diols were reduced at the 3-acetyl group and triply dehydrated under acidic conditions to afford two regioisomeric 3-vinyl-porphyrins, methyl divinyl-pyroprotopheophorbide-*a* (**2**) possessing the 8-vinyl group and 17-propionate residue (one of the DV-PChl-a_H derivatives) and methyl pyropheophorbide-c_1 (**3**) possessing the 8-ethyl group and 17-acrylate residue (one of the Chl-c_1 derivatives), respectively (see Fig. 1) [2]. The other product 7,8,17,18-tetrol was reduced and then acidically treated, giving five-fold dehydrated free base porphyrin, methyl pyropheophorbide-c_2 (**4**) possessing the 3,8-divinyl groups and 17-acrylate residue (one of the Chl-c_2 derivatives) [2].

The visible absorption and fluorescence emission spectra of the three semisynthetic 3-vinyl-porphyrins **2**–**4** in dichloromethane were compared with those of the corresponding 8-ethyl-porphyrin **1** bearing the 17-propionate residue (one of the PChl-a_H derivatives). The Soret and Qy absorption maxima were shifted to longer wavelengths with an increase of π-conjugation in a molecule: **1** < **2** < **3** < **4**. The 17^1,17^2-dehydrogenation broadened the absorption bands. The emission maxima were bathochromically shifted in the same order. The reaction mechanism of the present dehydration indicates that the biosynthetic pathway of Chls-*c* would include the hydroxylation of the 17-propionate reside at the 17^1-position and successive dehydration to the 17-acrylate residue [3].

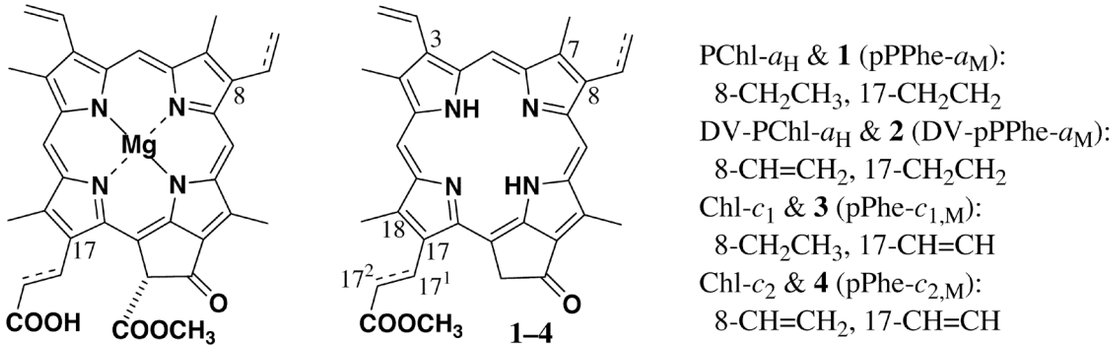

Fig. 1. Molecular structures of natural chlorophyll(ide)s (left) and their synthetic analogs **1**–**4** (right)

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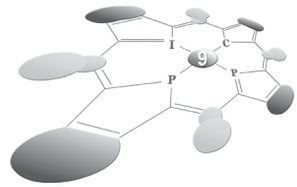

Redox-Interconversions in Fused Corrole Dimers

Takayuki Tanaka,[a] Shota Ooi,[a] Kento Ueta,[a] Atsuhiro Osuka[a]

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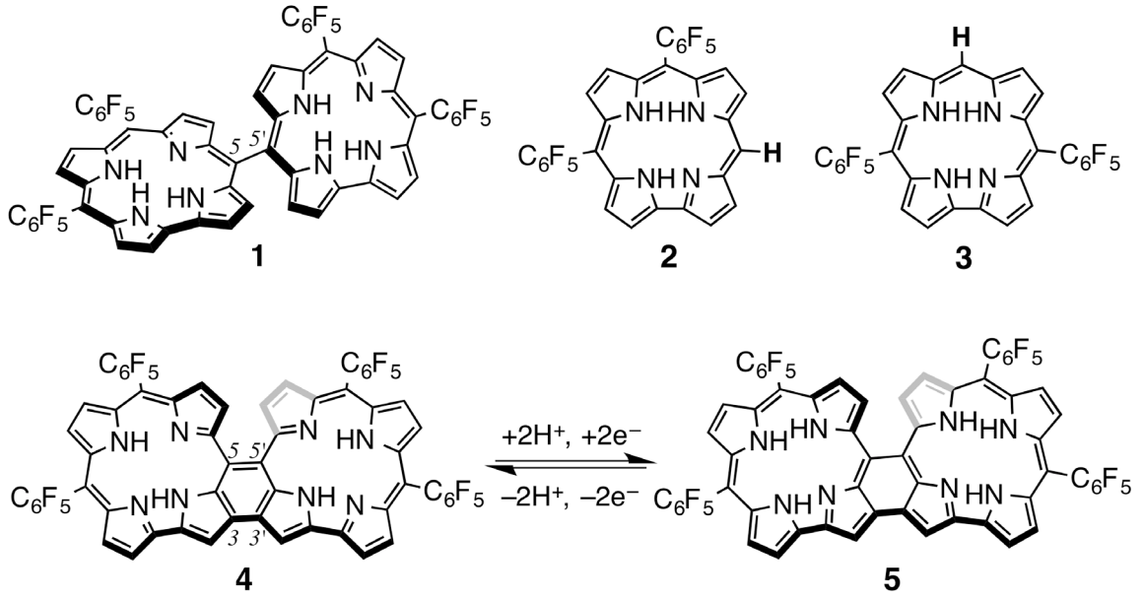
Conjugated porphyrin arrays have been extensively studied for the last two decades in light of their attractive electronic, optical, and electrochemical properties.[1] Various porphyrinoids have been employed in numerous studies to demonstrate their potential. Corrole is a ring-contracted porphyrin bearing a direct pyrrole–pyrrole linkage. The synthesis of *meso*-aryl-substituted corroles has been dramatically developed since seminal works were reported independently by Gross, Paolesse, and Gryko in early 2000s. Despite these contributions, only a limited number of directly linked corrole dimers have been reported so far.

Recently, we devised a formal [2+2]-type protocol for the synthesis of *meso*-triarylcorroles, which facilitates preparations of otherwise difficult-to-access *cis*-A_2B-type corroles.[2] On the basis of this novel synthetic protocol, we have successfully obtained 5,5'-linked corrole dimer **1** and *meso*-free corrole **2**.[3] Another *meso*-free corrole **3** was prepared more efficiently by a stepwise route.[4] 3,3'-5,5'-Doubly linked corrole dimer **4** (fused corrole dimer) was accomplished by DDQ-mediated oxidation of 5,5'-dimer **1**. Fused corrole dimer **4** was revealed to exhibit inner two pyrrolic protons with disrupted 18π aromatic conjugation, while its reduced form **5** displayed recovered aromaticity as seen in their ^{1}H NMR spectra. This redox-interconvertible character will be discussed in detail in this presentation, with analogous examples we recently developed.



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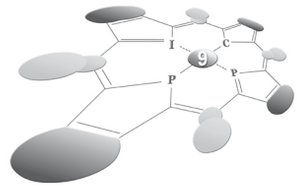

Ligand Rotational Motions of Metal Bisporphyrinate Double-Decker Complexes Revisited with C_{60}

Kentaro Tashiro[a]

[a]*International Center for Materials Nanoarchitectonics, National Institute for Materials Science*

Metal bisporphyrinate double-decker (DD) complexes are a type of metal complexes composed of two porphyrin ligands, orienting in a face-to-face fashion, with a metal center sandwiched by them. As these compounds possess π-electron rich concave surfaces, it would be interesting to investigate their supramolecular interactions with fullerenes. Through our studies on this topic we found an unexpected effect of the ligand rotational motions of DD complexes on the interaction with C_{60}.

Long years ago we revealed that the ligand rotation activity of DD complexes is very dependent on the metal center, where the corresponding cerium complexes have much larger activity than the zirconium analogues [1]. Since this rotational dynamics can be tuned by the redox reactions on DD complexes [2], more recently we started a new investigation by using STM, and succeeded in manipulating the ligand at the single molecular level [3]. Separately, we also obtained co-crystals of C_{60} with either of a cerium or zirconium DD complex [4], whose structures also inspired us to study the hybridization of C_{60} with a monolayer of DD complexes prepared on a substrate [5]. Although the molecular structures of the cerium and zirconium DD complexes used here are quite similar, we found that the compatibility of their monolayers with C_{60} is much different, where more fluxional cerium DD provides the monolayer with higher affinity with C_{60}. More detail studies suggest the contribution of the ligand rotational activity in DD complexes to make a C_{60}-compatible surface.

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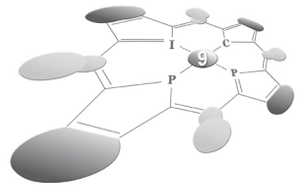

Rapid stabilisation of atherosclerotic plaque with 5-aminolevulinicacid-mediated sonodynamic therapy

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5-Aminolevulinic acid-mediated sonodynamic therapy (ALA-SDT) effectively induces the apoptosis of atherogenic macrophages, but whether it can stabilise atherosclerotic plaque in vivo is unclear. Here, we used an animal model to evaluate the effects of ALA-SDT on plaque stabilisation. Sixty rabbits were induced atherosclerotic plaques in the femoral artery with a combination of silastic tube placement with atherogenic diet, and randomly assigned into control (n = 12) and SDT (n = 48) groups. In the SDT group, after intravenous injected with ALA (60 mg/kg) animals underwent the treatment of ultrasound with intensities of 0.75, 1.00, 1.50 and 2.00 W/cm2 (n = 12 for each intensity). Seven days after the treatment, the plaque disruption assay was performed to test plaque stability. We found that ALA-SDT with ultrasound intensity of 1.5 W/cm2 showed the strongest efficacy to stabilise plaques. Under this condition, the frequency of plaque disruption decreased by 88 % ($p < 0.01$), positive area of macrophages reduced by 94 % ($p < 0.001$) and percentage content of lipids dropped by 60 % ($p < 0.001$), while percentage content of collagens increased by 127 % ($p < 0.001$). We also found that the plaque stabilisation by ALA-SDT was associated with increased macrophage apoptosis and apoptotic cell clearance. Moreover, ALA-SDT decreased the contents and activities of matrix metalloproteinase-2,9 and increased the levels of tissue inhibitors of matrix metalloproteinase-1,2 in plaques. Our studies demonstrate that ALA-SDT promotes plaque stabilisation by inducing macrophage elimination and inhibiting matrix degradation. This method might be a promising regimen for atherosclerosis therapy.

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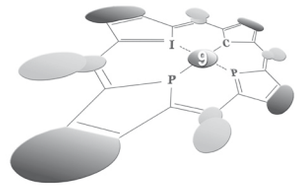

Photoinduced Charge Transfer Across Organic Monolayer on Semiconductor Surface

Nikolai V. Tkachenko, Hanna Hakola, Kati Stranius, Lijo George, Alexander Efimov

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Photoinduced electron transfer at and across semiconductor-organic interface play an important role in many today applications, e.g. in organic and hybrid solar cells [1]. The range of applications depends strongly on our ability to control the electron transfer and to engineer semiconductor-organic interfaces with predefined photoresponse. Two widely used approaches to this problem are selection of organic compounds with different redox properties and modification of linker connecting the organic molecule to the semiconductor. Another alternative chosen in this study is to add second molecular layer on top semiconducor-organic interface to produce semiconductor-organic-organic structure. The second layer is aimed to interact with the primary organic layer and modify the overall electronic response of the system in a desired manner. With the goal of photoinduced vectorial charge transfer across the structure, this approach has two aims. Firstly, the primary electron transfer can occur at organic-organic interface and can be tuned independently of the semiconductor substrate. Secondly, another organic layer can act as a secondary donor/acceptor, which picks up the photo-generated charge from the primary organic layer. This sort of functionality is particularly important for solar cell applications, in which case the secondary organic layer is hole (or electron) transporting layer connected to an electrode.

As an example of the first type of behaviour a TiO_2-fullerene-porphyrin architecture was designed and studied [2]. A self-assembled monolayer (SAM) of fullerene C_{60} derivative with carboxylic linker was deposited on a TiO_2 nanoparticle film. The bulky C_{60} moiety leaves possibility to form the second layer of molecules with long enough alkane-carboxylic linker, which was the SAM of a porphyrin derivative. Time resolved spectroscopy study has shown that selective excitation of the porphyrin chromophore results in primary charge separation between porphyrin and C_{60} layers in <5 ps. In a hundred picosecond time domain the fullerene anion donated electron to TiO_2 resulting in long-lived (>20 ms) charge separation with electron in TiO_2 and hole in porphyrin layer.

A system with secondary electron donating layer was prepared using ZnO nanorod film covered by a SAM [3] of zinc phthalocyanine (ZnPc) derivatives and depositing a hole transporting layer of poly(3-hexylthiophene) (P3HT) or spiro-MeO TAD by spin coating method. With selective excitation of ZnPc the primary charge separation reaction is an electron transfer from the the excited ZnPc to ZnO nanorod in a subpicosecond time domain. This charge separated state recombines in 0.1-1 ns time domain. However, addition of P3HT or spiro-MeOTAD resultes in a fast (tens of picoseconds) hole donation from ZnPc layer to the hole transporting material and formation of a long-lived charge separated state with ZnPc relaxed to the ground state.

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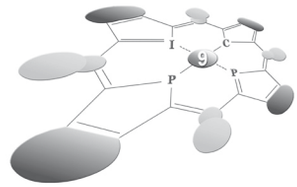

Amphiphilic Phthalocyanines for Photomedicine

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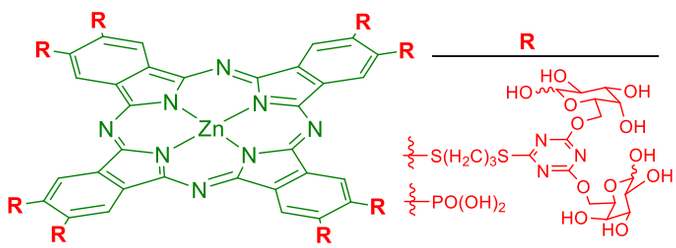
Phthalocyanines (Pcs) have unique photophysical and photochemical properties, which make them very valuable for scientific and technological applications. Towards the design of novel Pcs, many different synthetic strategies were explored, namely the decoration of the macrocycle periphery with different motifs and varying the central metal to fine-tune their properties for different applications. The strong red shifted Q-bands in the near infrared region and high reactive oxygen species (ROS) generation, when irradiated with light with the appropriate wavelength in the presence of molecular oxygen, make Pc derivatives extremely interesting for photobiological applications, such as: cancer photodynamic therapy (PDT)[2] and pathogenic microorganisms photodynamic inactivation (PDI).[3] However, for these biomedical applications the novel photosensitizers (PSs) should be highly specific to the target cells and water soluble or, at least, amphiphilic molecules with ability to partition from the cytoplasm into cancer cell membranes. In this talk, some of our recent works on Pc derivatives will be highlighted. The synthetic strategies used and some of the obtained results in PDT will be presented.[2,4]



Acknowledgements: Thanks are due to FCT/MEC for the financial support to QOPNA and IBILI research units (FCT UID/QUI/00062/2013 and FCT UID/NEU/04539/2013) through national founds and where applicable co-financed by FEDER, within the PT2020 Partnership Agreement, and to the European Union for the Marie Curie Initial Training Networks (grant agreement n° 316975). PMRP and NVR acknowledge FCT for their doctoral and post-doctoral grants SFRH/BD/85941/2012 and SFRH/BPD/79000/2011, respectively.

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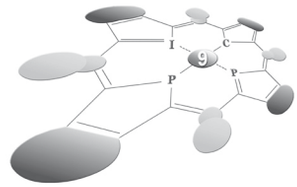

Tetradiazepinoporphyrazine-based sandwich-type rare earth complexes

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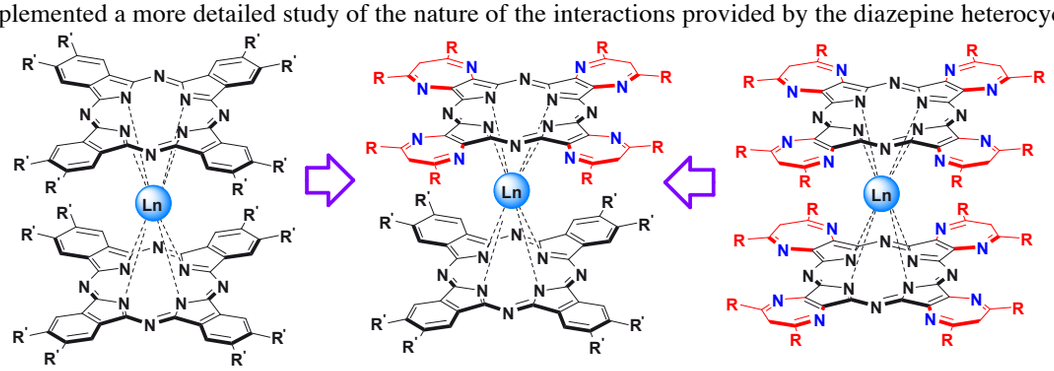
As known, sandwich tetrapyrrole complexes of rare earth elements (REE) are promising materials for advanced applications. In turn, diazepinoporphyrazines, owing to specific intramolecular interactions provided by the diazepine heterocycles [1], represent promising ligands for the synthesis of REE complexes.
Previously we have reported the synthesis of a series of homoleptic REE bis(tetradiazepinoporphyrazinates) [2,3]. It has been found that specific interligand interactions involving diazepine heterocycles result in formation of the double-decker complexes under comparatively mild conditions and allow obtaining stable early REE double-deckers [3].
In continuation of this study, we obtained new tetradiazepinoporphyrazine-based sandwich-type REE complexes and implemented a more detailed study of the nature of the interactions provided by the diazepine heterocycles.



Thus, tetradiazepinoporphyrazine-based homoleptic cerium(IV) double-decker was first synthesized [4], whose specific spectral features indicated the presence of additional sterically determined interligand interactions.
Synthetic approaches to heteroleptic REE double-deckers were also developed, which allowed us to obtain the first heteroleptic (tetradiazepinoporphyrazinato)(phthalocyaninato) lutetium and europium complexes.
The financial support was provided by RFBR (Grant Nos. 16-33-00097, 15-03-05890, 15-33-21012).

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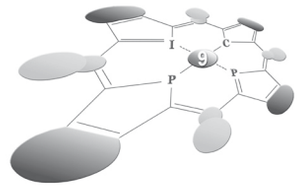

Discrete Ladders and Macroporous Film from Zipper-like Dimerization of meso-meso Linked Zinc Porphyrin Arrays

Kohei Kose and Akihiko Tsuda

Department of Chemistry, Graduate School of Science, Kobe University

Stimulated by supramolecular functional assemblies such as photosynthetic antennas LH1 and LH2, extensive studies have been conducted on exploration of three-dimensional assemblies by complexation of metal porphyrins with multi-dentate coordinating ligands. In these assembling processes, structural motifs of metal porphyrins and coordinating ligands are translated into tertiary structures of resulting supramolecular assemblies. Reversible and thermodynamic features of these assembling processes have been used for molecular machines, cyclic antenna complexes, and self-sorting assemblies. However, applications of these assembling processes of metal porphyrins for exploration of polymeric materials with attractive properties are rare, to the best of our knowledge.

Fabrication of a multi-stranded polymer having a strong rigid linear structure compared with a single-stranded one has been one of challenging subjects in polymer and supramolecular chemistry. Polymeric double-strands with helical and non-helical conformations can assemble through attractive noncovalent interactions. Although supramolecular helical double-strands have been extensively studied as inspired by DNA, ladder-shaped polymers have attracted little attention. However, we expected that such ladder-shaped polymers may have higher stiffness, linearity, and lower elasticity owing to their rigid structures. As a building block of ladder-shaped polymers, meso-meso linked Zn^{II} porphyrin arrays are promising because of their linear shapes and high solubilities in common organic solvents.[1]

In this study we found that meso-meso linked Zn^{II} porphyrin arrays underwent zipper-like dimerization upon complexation with di(pyrid-3-yl)acetylene (DPA) in chloroform to form discrete double strand porphyrin ladders.[2] Similar assembly of poly(Zn^{II}-porphyrinylene) with DPA gave a thermo-responsive gel, whose three-dimensional network structure was so strong to give a macroporous xerogel film.

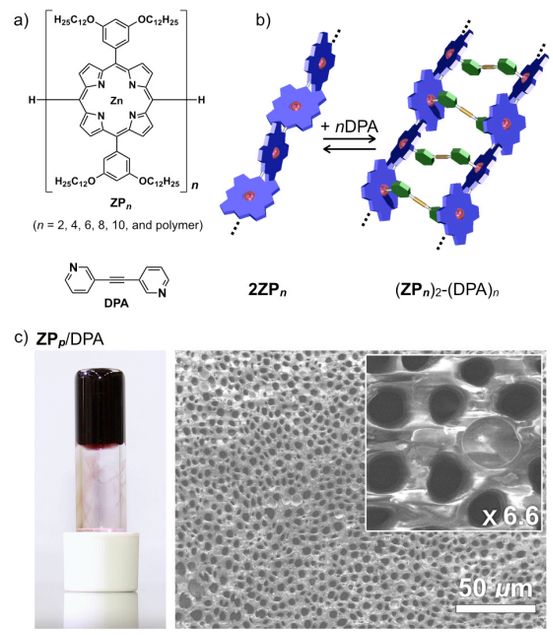

Figure 1. a) Directly meso-meso linked multiporphyrin arrays (ZP_n) and bidendate ligand. b) Schematic illustration for formation of a supramolecular ladder complex of ZP_n and DPA through Zn–N coordination bonds. c) Organogel and xerogel film prepared from a mixture of ZP_p and DPA in $CHCl_3$.

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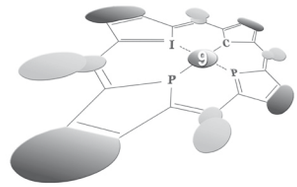

Subporphyrinatoboron(III) Hydrides and Peroxides

Eiji Tsurumaki[a], **and Atsuhiro Osuka**[a]

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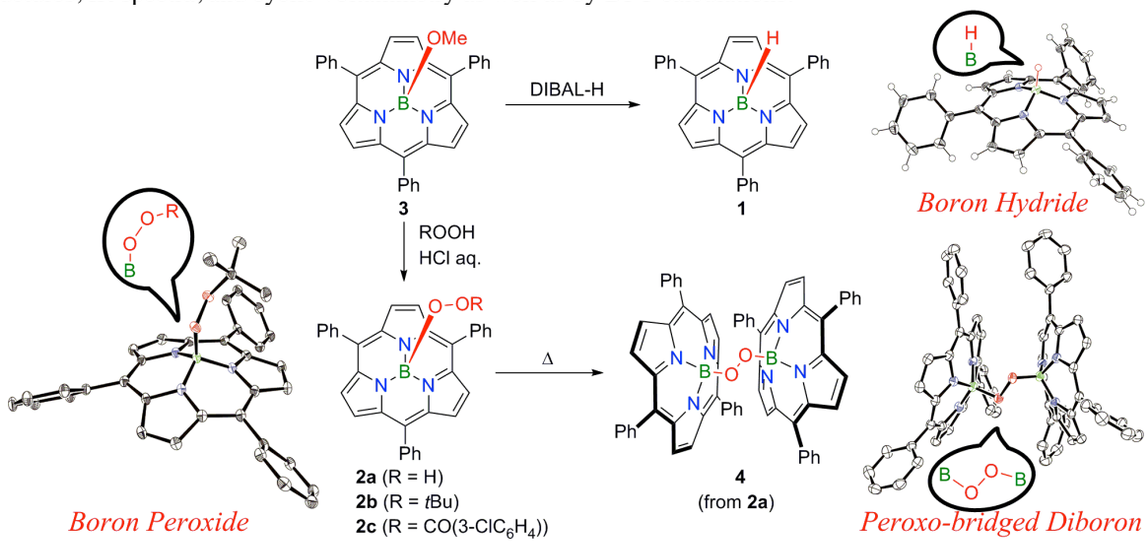
In recent years, subporphyrinatoboron complexes (hereafter referred to as subporphyrins) have emerged as a new class of functional molecules,[1] most of which are chemically and thermally stable, because the boron atom is tightly embedded in a small cavity of divalent and tridentate subporphyrinato ligand. While subporphyrins and porphyrins share many common attributes such as strong absorption, fluorescence, and aromaticity, the former bears an axial *B*-substituent that can be easily exchanged by acid catalyzed S_N1 reactions[2] and used for fine-tuning of the electronic properties. Taking advantage of these characteristics, we attempted to synthesize novel boron complexes with a subporphyrinato ligand. In this talk, we present the synthesis and full characterizations of subporphyrin *B*-hydrides and *B*-peroxides.

Subporphyrin *B*-hydride **1** has been prepared by reduction of subporphyrin *B*-methoxide **3** with diisobutylaluminium hydride in good yield. The authenticity of the B—H bond has been confirmed by ^{1}H and ^{11}B NMR signals, B—H infrared stretching frequencies, and single crystal X-ray diffraction analysis. The hydridic character of **1** has been demonstrated by the controlled reductions of aromatic aldehydes and imines in the presence of a catalytic amount of $Ph_3C[B(C_6F_5)_4]$.

A series of subporphyrin *B*-peroxides **2** was prepared effectively by acid catalyzed substitutions of **3** with corresponding hydroperoxides. In addition, thermal dimerization of subporphyrin *B*-hydroperoxide **2a** provided peroxo-bridged dimer **4** quantitatively. These peroxides **2** and **4** are fairly stable under the ambient conditions, allowing for their isolation and fully characterization as the first examples of structurally authenticated acyclic and neutral boron peroxides. The boron peroxides thus prepared were comparatively investigated by their crystal structures, IR spectra, and cyclic voltammetry as well as by DFT calculations.



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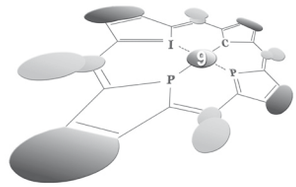

Heme proteins interactome: an NMR view

Paola Turano

CERM, University of Florence, Italy

NMR spectroscopy has the ability to detect weak/ultraweak interactions among proteins and offer structural informaiton, thus leading to the identification of the interaction area and providing experimental restraints for the modeling of protein-protein complexes. On the other hand, NMR suffers from size limitations, which become even more detrimental for paramagnetic signals due to Curie relaxation phenomena, and from the need of isotopically enriched samples. Here, a few show-cases will help defining troubles and possible remedies in the context of heme-mediate protein-protein interactions and protein-protein assemblies involving heme proteins.

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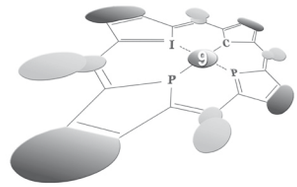

Synthesis of pyrrolic compounds as a promising candidate for NIR-selective dyes

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Linearly conjugated pyrroles are commonly unstable toward oxidation due to their high HOMO energy levels. For an example, tetrapyrroles were easily oxidised to dipyrrolyldiazafulvalene, which dimerized to form cyclo[8]pyrroles.[1] When a methylene unit exists between the pyrrole moieties, the methylene pyrrole units becomes an azafulvene sleleton by oxidation. We planned to prepare linear pyrrolic near-infrared (NIR) dyes such as boron dyppylomethenes (BODIPYs), pyrrolic squaraines and pyrrolic croconaines, which consist of both pyrrole and azafulvene skeletons. BODIPYs and squaraines are well known to show single strong absorption bands in the visible region, and extensive application studies as a fluorescence probe *etc*. have been reported.[2] When the π system of pyrrole is enlarged at the α,β- and β,β-positions, the electronic transition bands are bathochromically shifted. In the case of the BODIPY chromophores, the transition along to the long axis is allowed, and effective bathochromic shifts are expected when aromatic units are fused at the ends of the long axis. We succeeded in the preparation of BODIPYs fused with fluoranthobenzene[3] and BODIPY dimers fused at the β,β-positions with benzene, namely benzene-fused bisBODIPYs, which were proven to have sharp and strong absorption and emission bands in the red to NIR region and to keep good transparency in the other visible region.[4] The dyes are a promising candidate for selective NIR dyes. In this session, I would like to discuss about the synthesis and properties of bisBODIPYs as well as pyrrolic squaraines and croconaines in detail.

Pyrrolic dyes **1**, **2**, and **3** shown in Figure will be discussed in this session. They showed strong absorption bands in red (*ca*. 600 nm) to NIR (*ca*. 900 nm) region. The absorption maxima of *anti*-bisBODIPY *anti*-**1** with the lowest energy were longer than those of the corresponding *syn*-**1**. The bisBODIPYs were stable under ambient conditions, when R^1 was the electron-withdrawing sbstituents such as cyano and ester groups. In ^{1}H NMR, squaraines **2** and croconaines **3** existed as mixtutes of isomers (*syn :anti* = 2 :3 to 3:4), rotational barriers of which were low and recrystalization gave the pure *syn* or *anti* isomer determined by X-ray crystallography.

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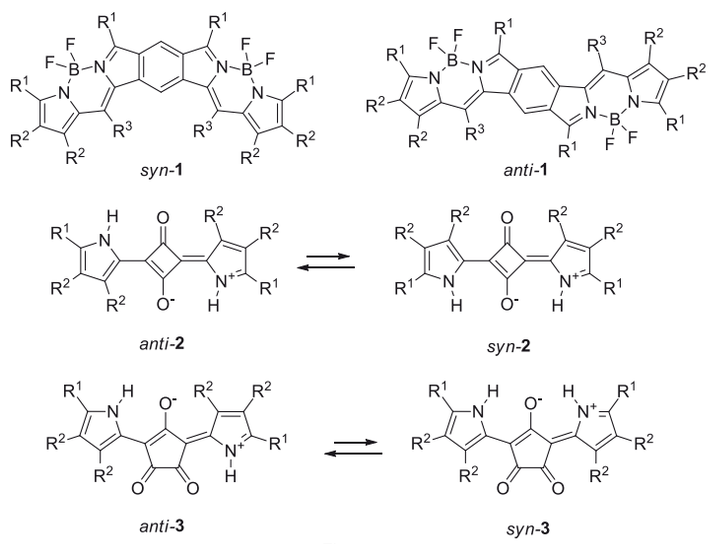

Figure

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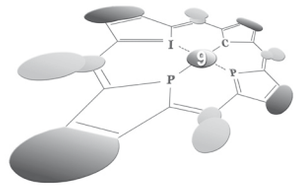

Polymeric Micelles' Application in Photodynamic Therapy

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Many efficient photosensitizers to be applied in photodynamic therapy are hydrophobic and require a delivery system to enable preferential uptake in the diseased tissues.[1] As an example, we present the in vitro photocytotoxicity and cellular uptake, including the effect of lipase-catalyzed micelle degradation, of polymeric micelles composed of biodegradable mPEG-b-poly(ε-caprolactone) with the photosensitizer mTHPC (meta-tetra(hydroxyphenyl)chlorine or temoporfin).[2] Micelles based on polymers with a benzoyl (Bz) or naphthoyl (Np) end group were formed and loaded with mTHPC by the film hydration method. The cellular uptake of the mTHPC-loaded micelles, and their photocytotoxicity are investigated. The micelles had a loading capacity up to 30% (w/w), which may be ascribed to π-π interactions between the aromatic end group and the photosensitizer. MTHPC-loaded micelles did not display photocytotoxicity up to an mTHPC concentration of 2 μM, nor any mTHPC-uptake by UM-SCC-14C cells at 10 μM mTHPC, in contrast to free mTHPC and liposomal mTHPC. Interestingly, after dilution of the loaded micelles below the critical aggregation concentration (CAC), or after incubation with lipase causing micelle degradation, photocytotoxicity and cellular uptake of mTHPC were restored. The high loading capacity of micelles, the high stability of mTHPC-loaded micelles above the CAC, and the lipase-induced release of the photosensitizer makes these micelles very promising carriers for photodynamic therapy in vivo. Latest results and other examples will be presented in this contribution.

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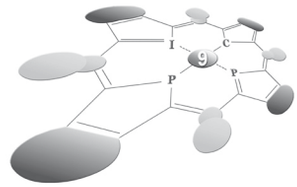

Encapsulation of Porphyrinic Photosensitizers into Polymers monitored by NMR Spectroscopy

Martina Vermathen, Ilche Gjuroski and Julien Furrer

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Owing to several favorable properties such as phototoxicity combined with tumor accumulation and low dark toxicity, porphyrinic compounds have been playing an important role as photosensitizers in photodynamic therapy (PDT) for a long time. However, most porphyrinic photosensitizers exhibit low solubility in biological media due to their intrinsic tendency to aggregate in aqueous solutions thereby decreasing PDT efficiency. Formation of porphyrin-nanoparticles or porphyrin-polymer systems represents an elegant way to cope with this problem. Some porphyrin-carrier systems such as Photolon®, which is a polyvinylpyrrolidone (PVP) complex with chlorin e6 (Ce6), have already gained approval for medical application in PDT. [1, 2] Recently, we have characterized a series of naturally derived porphyrin and chlorin e6 derivatives by NMR spectroscopy with respect to their propensity to form aggregates, their aggregate structures, as well as their interactions with membrane models. [3] The results showed that the porphyrin and Ce6 compounds formed different aggregate structures due to their specific substitution patterns. Moreover, small structural modifications can have a large impact on the aggregation behavior and thus solubility of the compound. Therefore, the suitability of a carrier system needs to be adopted and optimized according to the specific properties of its guest compounds. To this respect, NMR spectroscopy has proved a powerful method for monitoring the disaggregation process and the interactions between host and guest compounds on a submolecular level as we have recently shown for Ce6-derivatives. [4]

The aim of the present study was to characterize and compare the disaggregation capability and loading capacity of different polymers, such as PVP and the triblock copolymer Kolliphor P188 (KP188) for selected porphyrin compounds and chlorin amino acid conjugates in biological media using NMR spectroscopy as the main technique. The analysis of the ^{1}H-NMR chemical shift and line width changes allowed us to monitor and characterize in detail the disaggregation process in the presence of both PVP and KP188 polymers. Furthermore, intermolecular interactions between the polymers and the porphyrin compounds could be identified and characterized using 2D ^{1}H-NOESY, T_1 and T_2 relaxation time measurements and 2D ^{1}H-diffusion ordered spectroscopy (DOSY) experiments. The preferential binding sites of the polymers to the different porphyrins indicate that the formation of the complexes is mainly governed by hydrophobic interactions between the porphyrin and the polymers. In addition, the results suggest that PVP forms rather stable complexes with the porphyrins, while a dynamic equilibrium between free and bound porphyrins exists using KP188. This may have a considerable impact on the pharmacokinetic properties of the corresponding delivery systems. Further studies are currently in progress to investigate the cell metabolic response to the different delivery systems applying HR-MAS NMR spectroscopy.

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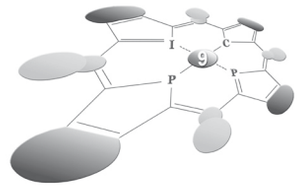
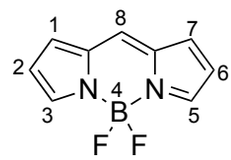


Functionalization of the BODIPY platform

M. Graça H. Vicente, Ning Zhao, Alex L. Nguyen, Sunting Xuan, Qianli Meng, Tyrslai Williams, and Kevin M. Smith

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA

BODIPY dyes are finding numerous applications in various imaging, sensing and analytical applications, due to their excellent properties that include high molar absorption coefficients, sharp fluorescence emissions generally with high quantum yields, good solubility and high thermal and photochemical stabilities. Moreover, their photophysical and chemical properties can be fine-tuned by functionalization at the various positions on the BODIPY core (**1**). Various methods can be used for the functionalization of BODIPYs, for example electrophilic and nucleophilic substitutions, palladium-catalyzed cross-couplings, aromatic ring fusion, and Knoevenagel condensations. I will present our recent methodologies for the regioselective halogenation of BODIPYs, and their multi-functionalization using palladium(0)-catalyzed cross coupling reactions, nucleophilic aromatic substitutions and nucleophilic addition/eliminations.[1,2] I will also present methodologies for boron functionalization via nucleophilic substitution of the fluorides, or by reactions of dipyrromethenes with functionalized boron compounds.[3,4]



BODIPY
(BOron DIPYrromethene)

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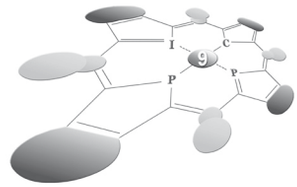

Two-Photon Microscopy of Oxygen with Porphyrin-Based Phosphorescent Probes

Sergei A. Vinogradov, and Tatiana V. Esipova

[a] *University of Pennsylvania, Department of Biochemistry and Biophysics.*

The ability to quantify oxygen *in vivo* in 3D with high spatial and temporal resolution is much needed in many areas of biological research. Our laboratory has been developing the *phosphorescence quenching* method for biological oximetry - an optical technique that possesses intrinsic microscopic capability. Several years ago we expanded our design on special two-photon enhanced phosphorescent probes. These molecules brought about first demonstrations of the two-photon phosphorescence lifetime microscopy (2PLM) of oxygen *in vivo*, providing new information for neouroscience and stem cell biology. However, current two-photon oxygen probes suffer from a number of limitations, such as sub-optimal brightness and high cost of synthesis, which dramatically reduce imaging performance and limit usability of the method. Here we present new approach to two-photon oxygen probes based on porphyrins with internally enhanced two-photon absorption cross-sections. So far our best performing molecule is built around fully-symmetrical π-extended porphyrin in which 2P active *g*-states are stabilized below the B-state level, ensuring efficient 2P excitation without inducing direct S_0-T_n transitions. The latter may possess non-negligible dipole strengths in phosphorescent metalloprhyrins due to their strong spin-orbit coupling. In addition to more than 50-fold increase in performance, the new probes can be synthesized much more efficiently, thereby reducing synthetic costs and making the method available to a broader range of researchers across different fields.

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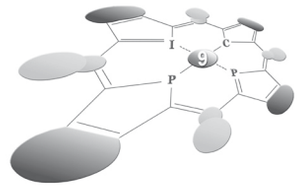

Tautomerism in Porphyrin Isomers

Jacek Waluk

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Well defined, rigid geometry of the inner cavity in porphyrins makes these compounds excellent models for the studies of intramolecular hydrogen bonds and tautomerism. Of particular importance are such issues as the correlation between the structural parameters and the strength of the H-bond, the mechanism of intramolecular double hydrogen transfer (stepwise *vs*. concerted), contribution of tunneling and the role of vibrational modes in the tautomerization pathway. Over the years, we have studied hydrogen transfer in porphycenes in the electronic ground and excited states under various conditions, from molecules in condensed phases,[1] isolated in supersonic jets[2] and helium nanodroplets,[3] to a single molecule regime.[4-7]
In this work, porphyrin (**1**) and its structural isomers, porphycene (**2**), corrphycene (**3**), and hemiporphycene (**4**) will be compared with respect to their H-bond and tautomerism characteristics. It will be shown how variations in geometry and symmetry of the inner cavity affect the H-bond parameters and tautomeric behaviour.

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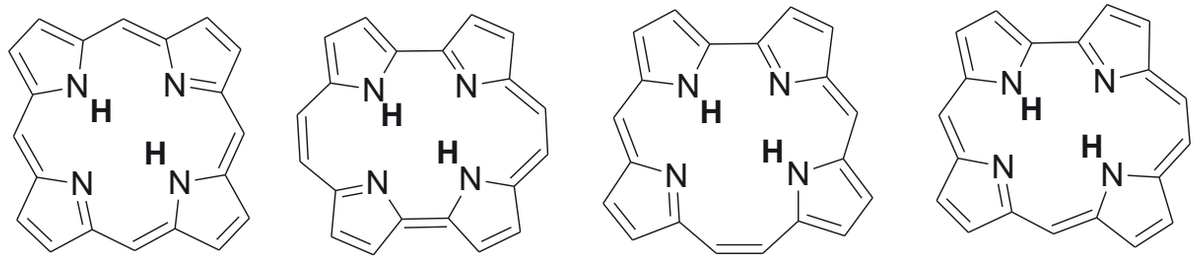

1 **2** **3** **4**

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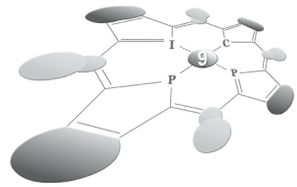

Functionalization of Π-Extended Porphyrins

R. G. Waruna Jinadasa,[a] Siddhartha Kumar,[a] Yuanyuan Fang,[b] Karl M. Kadish,[b] Christopher Ziegler,[c] Yi Hu,[a] Xiaoqin Jiang,[b] Hong Wang[a]

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Pi-extended porphyrins possess an unique set of photophysical and optoelectronic properties due to their extended *pi* structure. *Pi*-extended porphyrins promise broad application in various areas ranging from biomedicine to organic electronics due to their much broadened and red-shifted UV-Vis absorption and emision bands..[1-4] In this presentation, we report methodolgy development for the synthesis and functionalization of several series of *pi*-extended porphyrins including *push-pull* dibenzoporphyrins,[5, 6] A_2B_2 *push-pull* tetrabenzoporphyrins, and porphyrins oligomers linked through porphyrin *beta*-positions. New *push* (electron-donating groups) and *pull* (electron-withdrawing) groups were introduced at the porphyrin *beta*-positions and *push-pull* effects were studied. The electronic and optical properties of these *p*-extended porphyrins were measured using UV-Vis spectroscopy, steady state fluorescence spectroscopy, and cyclic voltammetry. DFT calculations were also performed for these porphyrins.

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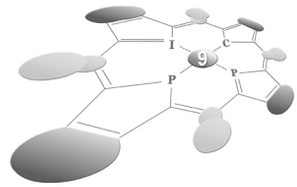

Metalloprotein Design Using Genetic Code Expansion

Jiangyun Wang

Key Laboratory of RNA Biology Institute of Biophysics, Chinese Academy of Sciences Beijng China

One aim in our laboratory is to use small, soluble protein scaffold, and the genetic incorporation of unnatural amino acid to design easy-to-characterize, easy-to-produce, and easy-to-optimize metalloenzymes which catalyze these important reactions with equal or greater efficiency/selectivity than that of the natural systems. Through the genetic incorporation of the Tyr-His ligand and CuB site into myoglobin, we recapitulated important features of HCO into this small soluble protein, which exhibits selective O2 reduction activity while generating less than 6% ROS, at more than 1000 turnovers. These results support that Tyr-His crosslink is indeed important for HCO function, and creates the exciting opportunity to rapidly evolve better HCO model proteins to achieve higher activity and selectivity, which may be suitable as alternatives to precious metal catalyst in fuel cells.
Another aspect of our ongoing research is the development of new methods for precise attachment of functional metal complexes on biomolecules, which is an important strategy for metalloprotein design. Bioorthogonal chemical reactions together with genetic code expansion technique have provided exciting new means for protein labeling in living cells. The main advantages of photoclick reaction are its fast rate (up to 50 M-1S-1), and that it has no need for toxic copper catalyst.

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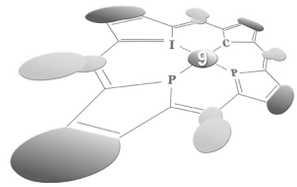

Unprecedented Heteroleptic Tetrapyrrole-fused Dimeric and Trimeric Skeletons

Yuehong Zhang,[a] Juwon Oh,[b] Kang Wang,[a] Chao Chen,[a] Wei Cao,[a] Kyu Hyung Park,[b] Dongho Kim,*[b] and Jianzhuang Jiang*[a]

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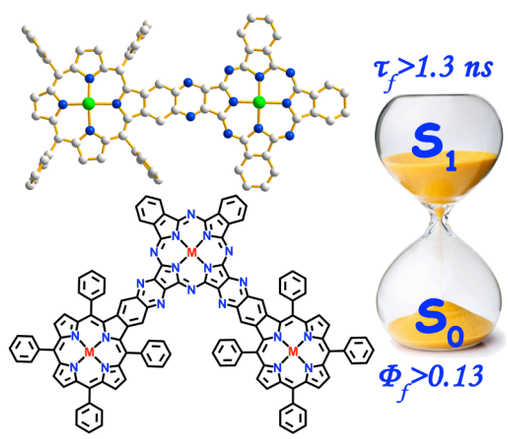
Phthalocyanine and porphyrin chromophores have been fused *through* the benzo[α]pyrazine moiety, resulting in the unprecedented heteroleptic tetrapyrrole-fused dimers and trimers. The hetero-tetrapyrrole nature has been clearly revealed based on the single crystal X-ray diffraction analysis of the zinc dimer for the first time. Electrochemical analysis, theoretical calculations and time-resolved spectroscopic results disclose that the two/three-tetrapyrrole-fused skeletons behave totally as one π-conjugated system due to the strong conjugative interaction between/among the tetrapyrrole chromophores. In particular, the effectively extended π-electron system through the fused-bridge induced strong electronic communication between Pc and Por moieties and large transition dipole moments in the hetero-Pc-Por-fused systems, providing high fluorescence quantum yields and relatively long excited state lifetime in comparison with their homo-tetrapyrrole-fused analogues.



heteroleptic-tetrapyrrole-fused skeletons

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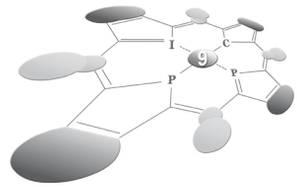

Dye-Sensitized Solar Cells: the Present Status, Challenges, and Future Chances

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Dye-sensitized solar cells (DSCs) [1] have been attracting a large amount of research interest in view of the extreme potential of converting solar and artificial light to electricity at low cost, and have recently reached a power conversion efficiency (PCE) record of 14.5% measured under the simulated AM1.5G sunlight.[2] This glorious accomplishment embodies over 10 years intense studies on metal-free organic dyes, single-electron redox shuttles, molecular-scale interface engineering, and device physics. Predictably, the development of more powerful metal-free organic dyes could well address the economic efficiency of a DSC, on primary account of copious raw materials and versatile synthetic methodologies. To further raise the PCE of a DSC, the realization of harvesting photons in the infrared region of the solar emission spectrum will be of paramount importance in the future explorations, mainly via narrowing the optical energy gap of a dye molecule. However, a reduction of HOMO/LUMO energy gap of a dye molecule is certainly concomitant with either a stabilized LUMO energy level or a destabilized HOMO energy level, or even both. These energetic changes are very much possible to exert unfavorable influences on the yields of generating long-lived charge carriers and thus lower external quantum efficiencies (EQEs), although many published papers claimed ultrafast electron injection kinetics or even femtosecond kinetics. Recent studies by several international groups have also indeed questioned these observations. While the widely used femtosecond transient visible/near infrared absorption measurements are not easy to make clear the dynamic picture, femtosecond broadband photoluminescence experiments do suggest that the electron injection kinetics are not so fast as previously thought. This issue could be better clarified in future studies by ultrafast vibrational spectroscopy techniques to unveil the kinetic picture and pave the way for coming materials development. Additionally, the open-circuit photovoltage of a DSC is notably dominated by the thickness and pinhole defect of self-organized dye layers, lying spatially at the boundary of electron-transporting titania and hole-transporting redox electrolyte. In this talk, I will select several examples[3-7] from our studies to address these issues.

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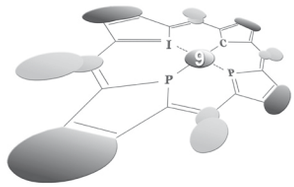

A new sensitizer DVDMS combined with multiple focused ultrasound treatment: an effective antitumor strategy

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Key Laboratory of Medicinal Resources and Natural Pharmaceutical Chemistry, Ministry of Education, National Engineering Laboratory for Resource Developing of Endangered Chinese Crude Drugs in Northwest of China, College of Life Sciences, Shaanxi Normal University, Xi'an, Shaanxi, People's Republic of China

Sonodynamic therapy (SDT) has been developed as a promising noninvasive approach. The present study investigated the antitumor effect of a new sensitizer, sinoporphyrin sodium (referred to as DVDMS), mediated multiple ultrasound treatment on sarcoma 180 both *in vitro* and *in vivo*. *In vitro* the combined treatment significantly suppressed cell viability, obviously potentiated apoptosis, and markedly inhibited angiogenesis. *In vivo*, fifteen days after sonication-thrice plus DVDMS treatment, the tumor weight inhibition ratio reached 89.82%, which was obviously stronger than ultrasound alone-once (32.56%) and sonication-once plus DVDMS (59.33%). DVDMS combined with multiple focused ultrasound treatment could more easily initiate tumor tissue destruction, induce cancer cell apoptosis, inhibit tumor angiogenesis, suppress cancer cell proliferation, decrease VEGF and PCNA expression levels. Moreover, the treatment did not shown obvious sign of side effects and body weight drop. These results indicated that DVDMS combined with multiple focused ultrasound is a promising strategy against solid tumor.

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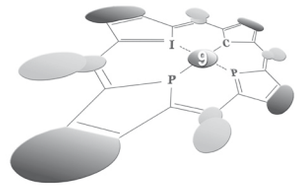
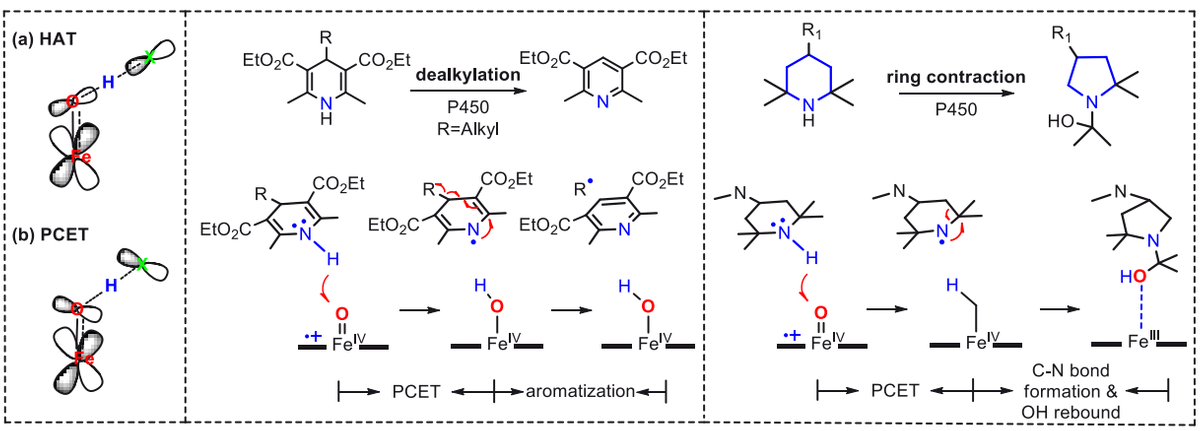


Cytochrome P450-Catalyzed reactions triggered by X-H (X = N, O) bond activation: A tale of the PCET mechanism

Yong Wang

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

The ubiquitous cytochrome P450 (CYP450) enzymes are considered to be "the most versatile biological catalysts known", owing to their vital roles in the metabolism of xenobiotics, such as drugs, and in the biosynthesis of endogenous compounds, such as steroids. Recently, we have performed systematically theoretical investigations on the mechanism of reactions involving X-H (X = N, O) bond activation. Firstly, the mechanism of dealkylation of 4-alkyl-substituted 1,4-dihydropyridines (DHP) was found to be initiated by N-H bond activation via proton-coupled electron transfer (PCET), following C-C bond cleavage to release an alkyl radical. Aromatization makes a difference in the last step. Secondly, Ring contraction of 2,2,6,6-tetramethylpiperidine (2,2,6,6-TMPi) was studied by means of the traditional DFT and the multistate DFT method (cooperated with Jiali Gao's group). This reaction was found also via initial N-H bond activation via the PCET mechanism and the following by stepwise ring-opening C-C cleavage and ring-fusing C-N bond formation, etc. Finally, CYP19-catalyzed estrogen formation was found (cooperated with Hajime Hirao's group) to involve the active intermediate Cpd I, by means of the QM/MM method. The initial O-H bond activation by Cpd I via the PCET mechanism triggers following C-C homolysis and beta hydrogen elimination. In summary, our theoretical results indicate that X-H (X=N, O) bond activation prefers a proton coupled electron transfer (PCET) mechanism, not via the long presumed HAT mechanism.



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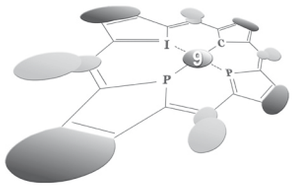

Biosynthesis of corrins

Andrew D Lawrence and Martin J Warren

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The biosynthesis of corrins such as adenosylcobalamin represents one of the most complex biochemical pathways found in Nature, requiring around thirty enzyme-mediated steps. We have managed to clone the complete cobalamin biosynthetic pathway to allow for not only the production of adenosylcobalamin but also for a range of biosynthetic intermediates. Manipulation of the pathway and the application of chemical biology means that we can also make a number of novel corrin-derivatives and analogues, which we have investigated for their ability to act as coenzymes and cofactors in B_{12}-dependent processes. Moreover, we have also used these compounds to investigate the uptake of cobalamin in both prokaryotic and eukaryotic systems. Together, this research is providing new insights into the chemistry and biology of the corrin ring system.

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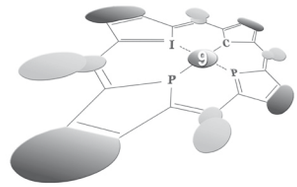

Charge transfer dynamics and electrocatalytic activity of porphyrin based hangman complexes on electrodes probed via surface enhanced vibrational spectroscopy

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Hangman complexes consist of a metal porphyrin and a functionality hanging group that is separated from the metal center by a flexible linker [1]. Depending on the type of metal and the acidity of the hanging group these complexes have proven to be efficient catalysts for reduction of oxygen and hydrogen peroxide as well as evolution of hydrogen. Catalytic activity for these compounds has been tested mostly in organic solution. However, to utilize them as electrocatalysts i.e. in hydrogen fuel cells, they have to be adsorbed on electrodes and should work efficiently in aqueous solution. Under these conditions the functionality of the molecules might drastically change, thus analytic techniques are needed that are able to study the catalysts when bound to electrode surfaces and in aqueous environment.

To get mechanistic insight into the reaction processes of hangman complexes under in situ conditions we apply a combined spectroscopic and electrochemical approach [2]. While electrochemistry monitors the catalytic activity of the surface bound molecules, surface enhanced resonance Raman scattering (SERRS) and surface enhanced infrared adsorption (SEIRA) is used to analyse the structure of the catalyst under turnover and non turnover conditions. The two different spectroscopic techniques give hereby complementary information. While SERRS probes the redox and conformational state of the metal porphyrin, SEIRA gives information on the protonation state of the hanging group. Using potential dependent SERRS spectroscopy we determined the structural state of Fe and Co hangman complexes as a function of potential, pH and oxygen concentration. Applying time resolved SERRS spectroscopy we were able to correlate the heterogeneous electron transfer rates between electrode and metal with the protonation degree of the hanging group [3].

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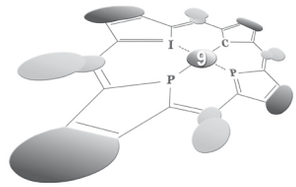

Oxygen-Dependent Globin Coupled Sensor Signaling - submitted to the International Conference on Porphyrins and Phthalocyanines

Emily E. Weinert[a], Justin L. Burns[a], Shannon Rivera[a]

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Recent studies have suggested that heme proteins play roles in sensing the bacterial environment and controlling cellular responses to stress, including the switch between motile and sessile (biofilm) states *(1-3)*. Globin coupled sensors are heme proteins that consist of a globin domain linked by a central domain to an output domain, such as a diguanylate cyclase or STAS domain. Diguanylate cyclase domains synthesize c-di-GMP, a major regulator of biofilm formation, while STAS domains modulate protein-protein interactions involved in signaling within stressosome complexes *(4)*. Current efforts to elucidate the signal transduction mechanisms of these enzymes have found that activity is controlled by ligand binding to the heme within the globin domain *(5)*. Gaseous ligand binding to the heme and c-di-GMP binding to an inhibitory site both control diguanylate cyclase-containing GCS oligomerization state, which regulates catalytic activity. In STAS domain-containing GCSs, ligand binding to the heme controls signaling of the associated kinase within the stressosome complex. Interactions between globin domains are key determinants of the accessible oligomerization states of the full-length proteins; however, despite similarity between both globin domains and full-length proteins, closely related GCS proteins adopt different oligomerization states. Furthermore, protein oligomerization affects heme pocket conformation, leading to altered hydrogen bonding and oxygen affinity. Recent work also has shown that GCS proteins control O_2-dependent bacterial virulence. These studies provide insight into the mechanism by which heme ligand binding controls activity of globin coupled sensors, as well as highlight the biological relevance of the pathways they control.

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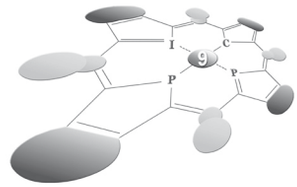

Metalloporphyrin Catalyzed Carbene Transfer – Scope and Mechanistic Aspects

Taiwo O. Dairo and L. Keith Woo

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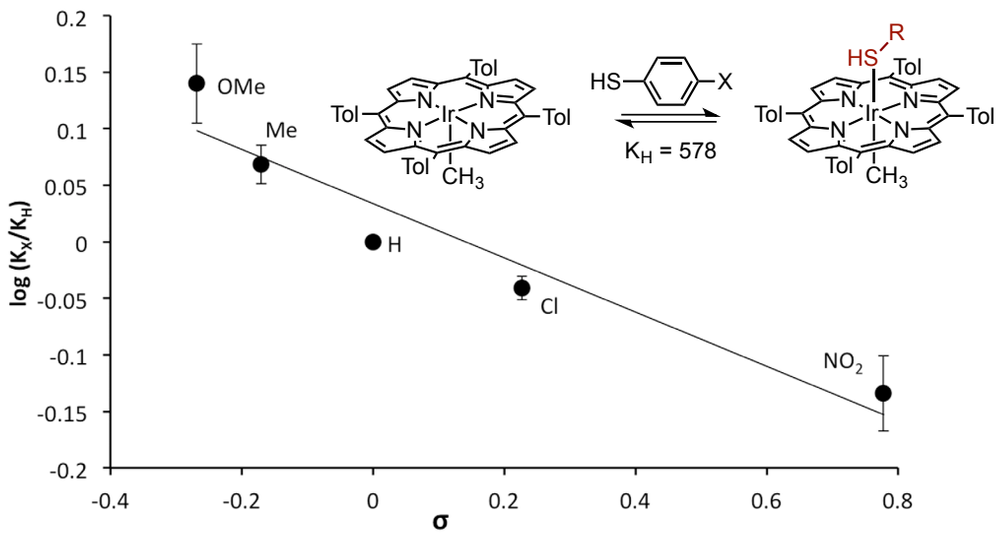
Metalloporphyrins are useful, atom-efficient catalysts for the generation of new carbon-carbon and heteroatom bonds using diazo carbonyl compounds.[1] Tetratolylporphyrinatomethyliridium, Ir(TTP)CH_3, was shown to be an active and robust catalyst for the cyclopropanation of olefins using diazo reagents as carbene sources.[2] Ir(TTP)CH_3 also catalyzes N–H insertion reactions between ethyl diazoacetate (EDA) or methyl phenyldiazoacetate (MPDA) and a variety of aryl, aliphatic, primary, and secondary amines.[3] Previous work with thiols demonstrate that group 8 metalloporphyrins efficiently catalyze S–H insertion reactions.[4,5,6] Aromatic thiols coordinate to iridium porphyrins with binding constants in the range of 400-800. Ir(TTP)CH_3 also catalyzes S–H insertion reactions with EDA or MPDA. Mechanistic aspects of these reactions with iridium porphyrins are evaluated.



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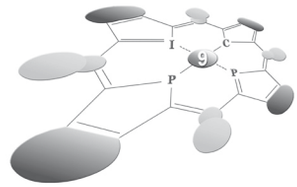

Discovering Highly Efficient DSSC Sensitizers Based on the Calculation of the First Transition Dipole Moment

Chengming Li,[a] Liang Luo,[a] Di Wu,[a,*] Ruilin Wang,[b,*] Jingsong You[a,*]

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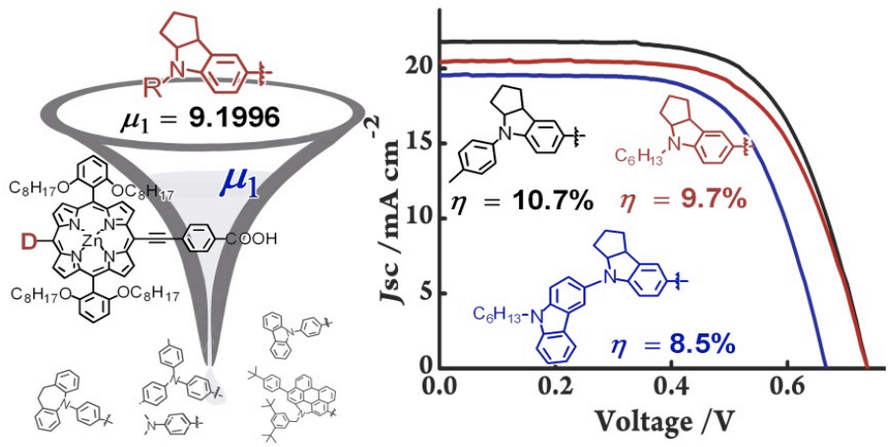

The enhancements of dye-sensitized solar cells (DSSCs) efficiency are often accompanied with considerable time and cost consumption in trial-and-error experiments. Quantum chemistry has effectively promoted the discovery of various functional molecular materials. However, it remains less developed to design well-performed sensitizers in DSSCs on the basis of quantum mechanical calculations. This work demonstrates a novel calculation-based strategy to discover highly efficient sensitizers for DSSCs.[1]
The first transition dipole moment (μ_1) is disclosed to have the function of predicting sensitizers with good molar absorptivity, enhanced light harvesting efficiency and overall efficiency. DFT calculation of μ_1 is used for the first time to screen sensitizers. Out of a library of donor-porphyrin-acceptor type sensitizers with single bond connecting donor and porphyrin fragments, indoline-conjugated porphyrin is screened out for its large μ_1 value and exhibits high overall efficiency of 10.7% in DSSCs without using cosensitizers or coadsorbents, which is comparable to the most efficient iodine-based DSSCs.[2] These results manifest the efficiency of this calculation-based strategy for the discovery of high-performance sensitizers. We anticipate that this strategy would efficiently accelerate the discovery of new sensitizers and open a new page of DSSCs.

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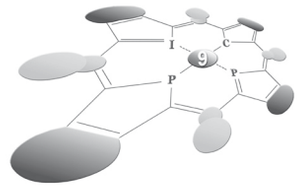

Porphyrin and BODIPY Based Diradicaloids

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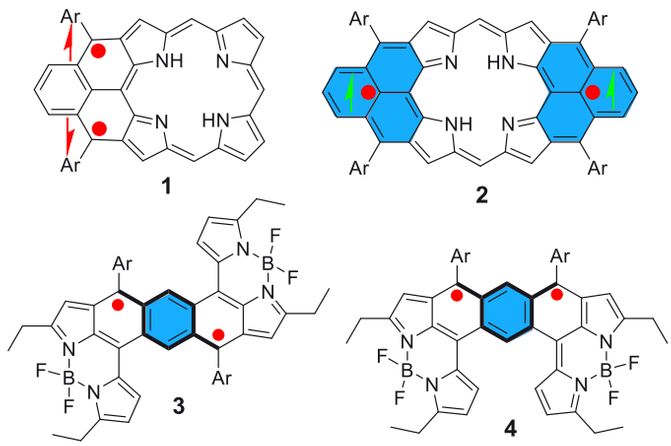
We will report how to synthesize porphyrin and BODIPY based stable diradicaloids which unique electronic and magnetic properties. Compound **1** has a closed-shell ground state but **2** is a persistent triplet diradical at room temperature. The *p*-quinodimethane and *m*-quinodimethane bridged BODIPY dimers **3** and **4** with small diradical characters exhibit intense absorption around 1100 nm. They both can be used for selective detection of hydroxyl radicals.



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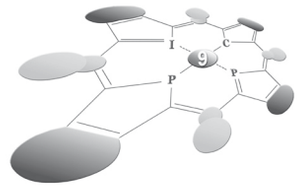

Porphyrins and Analogues for Optoelectronic Applications

Yunyu Tang[a], Pingchun Wei[a], Masatoshi Ishida[b], Hiroyuki Furuta[b], Yongshu Xie[a]*

[a]Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, Shanghai 200237, P. R. China; [b]Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka 819-0395, Japan.

Pophyrins and their analogues exhibit rich structural diversity and interesting properties.[1] In this work, based on a combined approach of structural optimization and co-sensitization, we synergistically improved the photovoltage and photocurrent of dye-sensitized solar cells (DSSCs), and thus achieved a photovoltaic efficiency of 11.5% based on the traditional iodine electrolyte.[2] We also synthesized porphyinoids containing directly linked confused pyrroles and investigated their macrocycle transformations and the applications as ion sensors.[3]

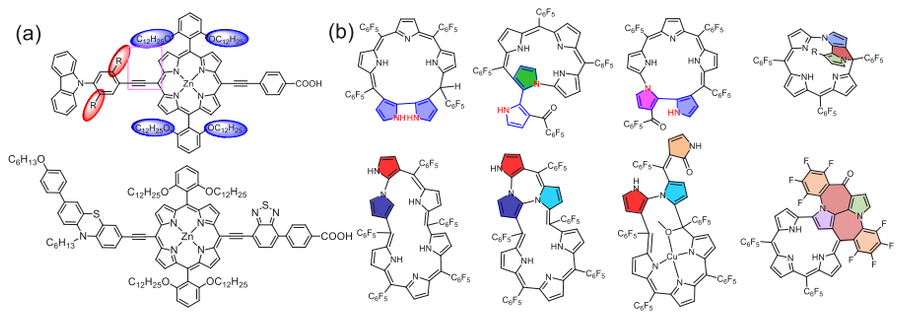

Fig. 1 Molecular structures of (a) porphyrin dyes; and (b) porphyrin analogues.

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Design Synthesis and Activity of Small moleculer Targeted Anticancer Photosensitizer

Fengling Zhang, Jun Li, Qi Huang, Xiaoqin Zhou, Mingjun Zhang, Jinping Xue*

State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350002, P. R. China

Photodynamic therapy (PDT) is a non-aggressive, with some targeted, minimally invasive method for tumor therapy [1]. PDT targeting generally refers to the area illuminated by the treatment bring a selected locality kill injury. In recent years, research of PDT targeting based on photosensitizer has got extensive attention. In this paper, small molecule targeted anticancer photosensitizers, which can target to epidermal growth factor receptor (EGFR) that can be overexpressed in some cancer cells, were designed and synthesised. These photosensitizers may specifically choose to combine carcinogenic sites of cancer cell, PDT role of tumor cell-specific death, but will not affect the normal tissue surrounding the cancer cells.

Experimental results show that the 12 novel photosensitizers are capable of targeting cancer cells overexpressing EGFR and cancer tissues at the cellular level and the level of the mice. The in vitro photodynamic inactivation of tumor cell experiments have shown a very high photodynamic activity, and no obvious dark toxicity. Tumor cell uptake of the photosensitizer, the generation of reactive oxygen species, photodynamic inactivation aganist tumor cells show a correlation on the structure of photosensitizers.

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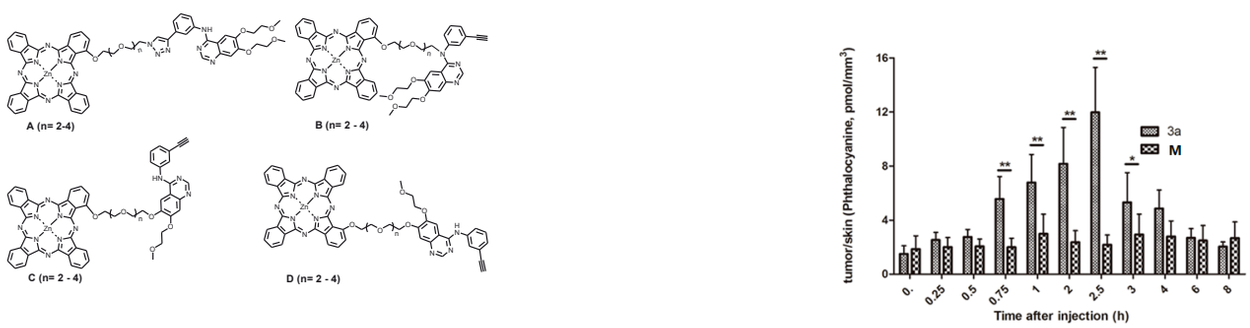

Fig. 1 Struction of smallmolecular target-based anticancer photosensitizers (left), in vivo FMT image of photosensitizers α-3c and control pthalocyanine M, by tail vein injection with α-3c (right,a), M (right, b), comparison of the average value of the tumour/skin biodistribution ratio of 3a and M (right,c). Values are means± SD. Statistical significance **($P < 0.01$), *($P < 0.05$).

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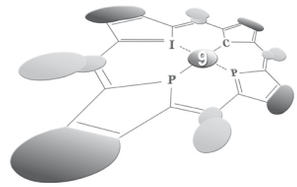

Synthesis of Oxatriphyrin[2.1.1] and its Boron complex

Daiki Kuzuhara[a], Shinsuke Kawatsu[a], Songlin Xue[a], Naoki Aratani[a], Hiroko Yamada[a,b],

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[b]*CREST, JST, Japan*

[14]Triphyrin(2.1.1) is a ring-contracted porphyrin with a 14π-electron aromatic system and acts as a monovalent ligand[1]. As a result of its metal-free composition, it can be converted to bowl-shaped Mn(I), Re(I), Ru(II), Pt(II), Pt(IV), and B(III) complexes. In 2013, we have reported a thiatriphyrin(2.1.1) and its protonated derivative as a first example of core-modified [14]triphyrin(2.1.1)[2]. Then, Latos-Grażyński reported thiphene– and *o*-phenylene–fused oxatriphyrins(2.1.1) and their B(III) complexes[3].
Here we will report the synthesis of *meso*–aryl–oxatriphyrin(2.1.1) and their boron complexes. The oxatriphyrin was obtained by intramolecular McMurry coupling of compound **1** followed by an in-situ oxidation (Scheme 1). The neutral state was not stable and the protonated structure (**3**) of oxatriphyrin(2.1.1) was confirmed by ^{1}H NMR and single crystal X-ray diffraction analysis. The boron complex was obtained by the reaction of protonated **3** with $PhBCl_2$ in the presence of triethylamine. Then the boron complex of the reduced oxatriphyrin **4** was obtained. The detail of the synthesis and properties of the oxatriphyrins(2.1.1) will be discussed in this presentation.

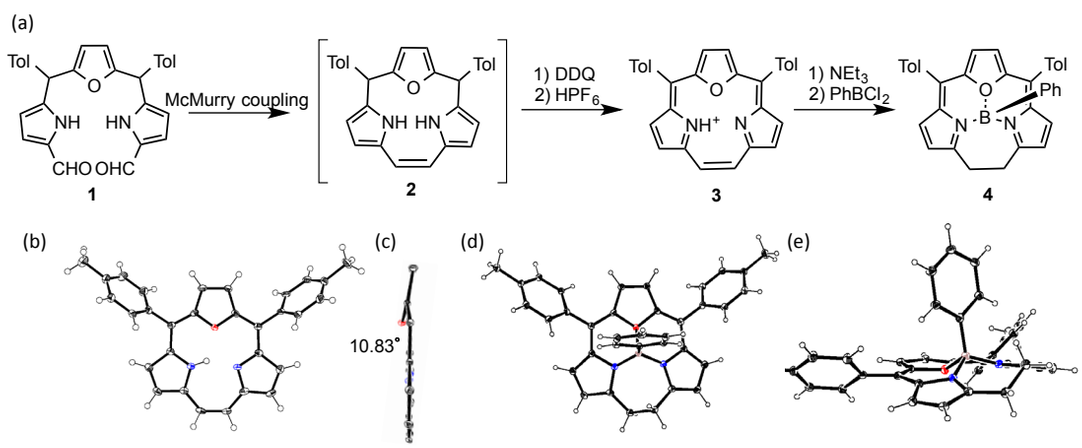

Fig. 1. (a) Synthetic scheme of oxatriphyrins; (b) top and (c) side views of oxatriphyrin **3** and (d) top and (e) side views of oxatriphyrin B(III) complex **4**.

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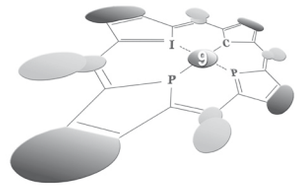

Cooperative Self-assembly of Simple Peptides and Porphyrins into Complex Synthetic Systems with Functional Properties

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Self-assembly is ubiquitous at various length scales throughout biology and is a key process of life. Inspired largely by biological systems, self-assembly has been developed as a dominant technique towards creation of complex synthetic systems [1,2]. However, how to achieve controlled self-assembly of functional structures towards biomimetic fabrication and biomedical application by key small biomolecules such as peptides and porphyrins remains a remarkable challenge. In this presentation, we will first report how multifunctional architectures with order at different length scales are created by hierarchical co-assembly of simple dipeptides and porphyrins [3-5]. Dependant on hydrophobic/hydrophilic property of dipeptides used, the resulting assemblies can be well controlled by tuning intermolecular interactions between dipeptides and porphyrins. Light-harvesting can be achieved within the assemblies including porous microspheres and fiber bundles. Following this, we will show how simple dipeptides and even amino acids can be used to tune self-assembly of photosensitive drugs for formation of well-defined nanoparticles as a future nanomedicine towards antitumor photodynamic therapy (PDT). Due to advantages of easy availability, structural simplicity, functional flexibility and effective cost of amino acids and dipeptides, such delivery systems based on co-assembly with drugs on themselves will provide a new alternative pathway for enhanced PDT against cancers.

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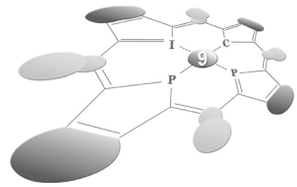

UV resonance Raman study on Indoleamine 2,3-dioxygenase

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Indoleamine 2,3-dioxygenase (IDO) is one of the two known heme containing dioxygenases found in human body. IDO catalyses direct incorporation of two oxygen atoms from molecular oxygen into tryptophan resulting in N-formylkynurenine. This reaction is the first and rate limiting step of main tryptophan metabolic pathway in our body. Being rare and unique as a heme enzyme, the reaction mechanism has been studied since IDO was reported. Structural information including the crystal structures of IDO with an inhibitor (*1, 2*) and the binding geometries of heme active site during catalytic reaction (*3, 4*) helps a lot to understand the reaction mechanism, which is still unclear yet. On the other hand, in the very end of the last century, participation of IDO in immune system was reported and the importance of Trp degradation in the peripheral immune tolerance has been massively studied in the last decade (*5*). IDO is one of the determinant of the local tryptophan concentration. Therefore, inhibitor of IDO has been one of the most important drug target (*2*). These studies to design inhibitor are usually based on crystal structures of IDO.

We have identified the binding geometries of IDO catalytic intermediates using visible resonance Raman with isotope labelling technic (*4*). Based on these and other biochemical results, we have proposed that the IDO reaction at the active site is as follows; $Fe^{2+} + O_2 + Trp \rightarrow Fe^{3+} - O_2^- + Trp \rightarrow Fe^{3+} - O_2^- - Trp \rightarrow Fe^{4+}{=}O + Trp\text{-}O \rightarrow Fe^{2+} + NFK$. At the moment we do not have any structural information about the bound substrate or intermediate products. We assume that the unique reaction catalyzed by heme must be enabled with assistant from substrate itself. We have also determined structural changes in heme side chains likely due to the structural alteration of protein upon binding of substrate or inhibitor. Furthermore, Raman shift of Fe-His, the only bond between protein and heme, stretching mode differs between with and without substrate, which indirectly binds to heme iron (*6*). This implies that protein changes its structure during reaction, where substrate changes its structure to each intermediate and final products, and finely tunes its reactivity. Therefore, we believe that it is imperative to determine the structure of substrate and intermediate products during reaction. In this study, we have established a method to extract UV resonance Raman spectra of bound substrate and successfully obtained the UV resonance Raman spectra of bound substrate in a binary- and a ternary- complexes, respectively. We will compare the UV resonance Raman spectra of Trp in solution and Trp as substrates.

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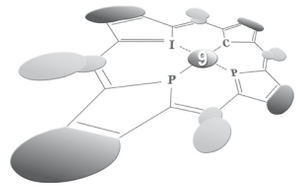

Structures and Signaling Mechanism of Modular Phytochrome Photoreceptors

Heewhan Shin, Zhong Ren and Xiaojing Yang

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Photosynthetic organisms such as cyanobacteria and plants employ a variety of photoreceptors to sense environmental light conditions to ensure optimal light harvesting and efficient photosynthesis. Phytochromes are a superfamily of photoreceptors that utilize linear tetrapyrrole (bilin) chromophores to perceive light signals. Like many signaling proteins, phytochromes adopt modular architecture to transmit light-induced structural changes over long distance to modulate the activity of the remote effector domain, thereby generating a light-dependent biological signal[1]. The N-terminal photosensory core module of classical phytochromes such as plant phytochromes and bacteriophytochromes (BphP) consists of three modular domains (PAS, GAF and PHY). Although the bilin chromophore is embedded in the GAF domain, all three domains are required in both plant phytochromes and BphPs to achieve full photoconversion between the red-absorbing (Pr) and far-red-absorbing (Pfr) states[2,3]. In contrast, a single bilin-bound GAF domain is often sufficient for photoconversion in newly characterized cyanobacteriochromes (CBCRs), which collectively confer sensitivity to light signals in a wide wavelength range from UV to red[4]. Small photosensory domains together with modular architecture of CBCRs allow us to dissect the molecular mechanisms of photoconversion and long-range signaling using X-ray crystallography. We will present a new crystal structure of red/green CBCR that features an unique domain combination. This structure sheds light on how signal integration is achieved at the molecular level. We will also discuss the general signaling mechanism based on joint analysis of a collection of phytochrome structures determined in various signaling states.

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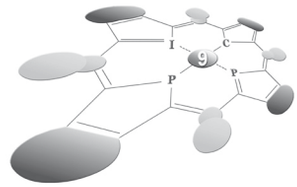

Small Molecule Activation Mediated by Porphyrin and Corrole Complexes

Shengfa Ye[a], **Huayi Fang**[a,b], **Christina Römelt**[a], **Thomas Weyhermüller**[a], **Penelope J. Brothers**[c], **Eckhard Bill**[a], **Serena DeBeer**[a], **Xuefeng Fu**[b], **Frank Neese**[a]

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Porphyrin and corrole are well known redox active noninnocent ligands, which may exhibit different oxidation levels in transition metal complexes. This peculiar property confers them an ability to function as an electron buffer in chemical transformations. Herein, I present our recent work on small molecule activation mediated by porphyrin and corrole complexes.

(TPFC)Ge(TEMPO) (TPFC = tris(pentafluorophenyl)corrole, TEMPO$^{\bullet}$ = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl) shows high reactivity toward E–H (E = N, O) bond cleavage in R_1R_2NH and ROH under visible light irradiation.[1] Our combined experimental and theoretical mechanistic study reveals the E–H bond activation by $[(TPFC)Ge]^0$/TEMPO$^{\bullet}$ radical pair, generated by photocleavage of the labile Ge–O bond in (TPFC)Ge(TEMPO), involving two sequential steps: (i) coordination of substrates to $[(TPFC)Ge]^0$ to form the corresponding substrate adduct containing a Ge^{IV} ion chelated by a $TPFC^{4-\bullet}$ radical and (ii) E–H bond cleavage induced by TEMPO$^{\bullet}$ through proton coupled electron transfer rather than H-atom transfer.

It has been reported that electrochemical CO_2 activation catalysed by $[Fe(TPP)]^{2-}$ exhibits drastically high turnover frequency with a low over-potential.[2] We recently performed a detailed study on its electronic structure using various spectroscopic techniques, and found that this formal Fe^0 species in fact consists of an intermediate spin ferrous center (S_{Fe} = 1) that is antiferromagnetically coupled to a porphyrin diradical tetraanion yielding an overall singlet ground state, viz. $[Fe^{II}(TPP^{4-\bullet\bullet})]$. Further mechanistic study show that the two electrons required for CO_2 reduction all stem from the porphyrin ligand while the iron oxidation state is unchanged during the reaction.

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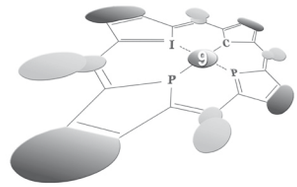

Porphyrins for New Generation Solar Cells

Chen-Yu Yeh, Chi-Lun Mai, Chiranjeevulu Kashi, Hsien-Hsin Chou, Hsuan-Wei Lee, Bo-Cheng Guo, Po-Cheng Su

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We report here the functionalized porphyrins for use in new generation solar cells. Porphyrin dyes with a push-pull framework have been prepared and used in dye-sensitized solar cells (DSSC), their spectral, electrochemical and photovoltaic properties were investigated. The photovoltaic measurements show that **YD2-*o*-C8** achieves a record power conversion efficiency ~12% using Co(II)/Co(III) as the electrolyte. Based on the structure of **YD2-*o*-C8**, a new porphyrin **GY50** with more red-shifted absorption has been synthesized. The device of **GY50** gives a power conversion efficiency of 12.75% under standard AM 1.5 sunlight. To improve the long term stability of the devices, pyridine-type anchors have been tested. It was demonstrated that 2-carboxypyridine is an efficient and stable anchoring group as **MH1** showed better cell performance and long-term stability than **YD2-*o*-C8** under light soaking conditions. We found that introduction of push and pull units to *meso*-positions is demonstrated to be achievable. Furthermore, bulky donors are compatible with cobalt-based electrolytes and yield high V_{OC}, long alkyl chains at *meso*-phenyls successfully reduce dye aggregation and decrease charge recombination rate, and the benzoic acid acceptor is superior to the cyanoacrylic acid counterpart. These push-pull porphyrin dyes are promising candidates for highly efficient DSSC. We also synthesized porphyrin dimers for organic solar cells (OPV). Compared to the single porphyrin, the porphyrin dimers exhibited a large improvement on the power conversion efficiency. In addition, porphyrins have been synthesized for application in perovskite solar cells as efficient hole-transporting materials.

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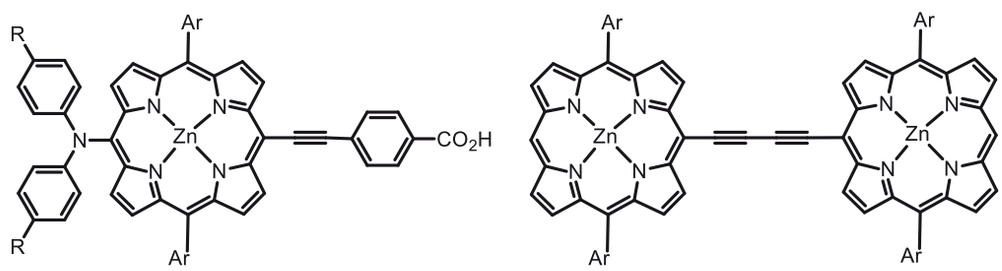

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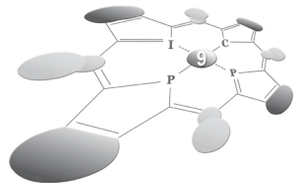

Oxygen Intermediate of Human Tryptophan 2,3-Dioxygenase: From Structure to Function

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Tryptophan 2,3-dioxygenase (TDO) is a homotetrameric hemeprotein that catalyzes the oxidative cleavage of Trp to N-formylkynurenine (NFK). TDO function has been linked to a variety of important diseases including cancer, making it an attractive target for drug discovery. QM/MM studies have suggested a two-step ferryl-based mechanism, initiated by dioxygen addition to the C_2 of the Trp.[1] But so far there is no direct experimental data to support the mechanism. In this talk, I will discuss the new crystal structure of an oxygen intermediate of human TDO (hTDO) obtained by exposing the deoxy Trp-bound binary complex crystal to an O_2-containing buffer. The structure provides four snapshots of the enzyme along the trajectory of the dioxygenase reaction, including two O_2- and Trp-bound ternary complexes and two NFK-bound adducts. In the ternary complexes, the heme iron-bound O_2 is located in a unique oxyanion hole, which strategically positions its terminal oxygen atom at 2.8 Å from the C_2 atom of the Trp, supporting the previously proposed two-step ferryl-based mechanism. In the NFK-bound adducts, the formyl group of the NFK is directly coordinated to the heme-iron; in addition, an active site loop (JK-Loop), which is critical for positioning the Trp for the dioxygenase chemistry, is fully disordered in one of the two subunits. Structure guided mutagenesis studies show that the conformational state of the JK-Loop is regulated by another active site loop, the F-Loop; together, they control the multiple turnover efficiency of the enzyme by gating product release and substrate entry. The new data also reveal two previously unknown structural features of hTDO, including (i) a novel exosite ~42 Å from the active site, which binds a second Trp, and (ii) a glutamate-rich Helix-loop-Helix domain, which protrudes out of the exosite. The implications of these unique structural data of hTDO on its functional properties will be discussed. This work is supported by NIH grant GM086482.

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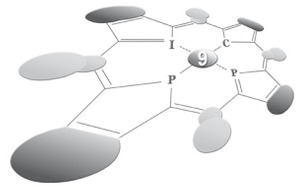

Schiff Base Complexes Functionalized Phthalocyanines for Oxidation Catalysts in Bleaching System

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Oxidation reactions are of great importance in the chemical industry. In particular, development of oxidants as bleaching agents in the processes play a major role for pulp and paper production, waste water treatment and industrial and domestic laundry for stain removing [1].
Main bleaching systems in oxidative bleach is based on destroying unwanted stains from the fabric surface in order to achieve the desired cleaning effect. In further studies, chemists have been trying to improve laundry bleaching at lower temperatures as low as 20 $^{\circ}$C by using catalysts instead of activators together with hydrogen peroxide. The first introduced bleach catalyst was Mn-1,4,7-trimethyl-1,4,7-triazacyclononane (Mn-TMTACN) allowing to substitute 5% of bleach activator (TAED: tetra acetyl ethylene diamine) by using only 0.05 % of the catalyst in 1994 [2].
To incorporate hydrogen peroxide/catalyst combination into the detergent formulations is expected to reduce the amount of chemicals and the costs [3]. So far, several novel coordination compounds of salen, saltren, terpyridine-type ligands and triazole derivatives have been synthesized and tested, possessing significant potential in activating hydrogen peroxide in bleach process [4]. Several transition metal complexes were also reported for the mentioned purpose.
We have developed some novel phthalocyanine derivatives as transition-metal catalysts for laundry cleaning applications. A series of phthalocyanine complexes in which two Schiff base Mn(III) and Co(III) complexes substituents directly linked through oxygen bridges to the phthalocyanine cores were synthesized and characterized [5]. We measured the oxidative bleach performance of the prepared complexes at room temperature in presence of H_2O_2 by online spectrophotometric method [6].

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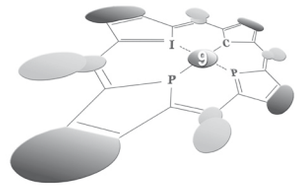

Oxidative Relationships of High-valent Metal Oxo and Hydroxo and Their Implications

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Active redox metal intermediates play the key roles in versatile biological and chemical oxidation events. In nature, certain metalloenzymes select high-valent metal oxo form as the key intermediate in oxidations, while others prefer a hydroxo form. However, selection of a metal oxo or hydroxo form of the active intermediate in a specific enzyme cannot be random; due to the complexity of biological systems, their redox mechanisms have not been fully elucidated. Alternatively, clarifying the reactivity differences and similarities of metal oxo and hydroxo moieties in oxidation with synthetic models may help to understand their roles in enzymes, thus benefit understanding their elusive mechanisms, and designing the selectivity catalyst.

In this talk, we will introduce our recent works in investigating the oxidative relationships of high-valent metal oxo and hydroxo using one manganese(IV) model. It was found that Mn(IV)=O and Mn(IV)-OH have very comparable hydrogen abstraction ability due to the compensation effect between the redox potential and pKa which determine the thermodynamic driving force in hydrogen abstract of an active metal ion. Moreover, their transition state information is also very similar in hydrogen abstract except that the Mn(IV)=O demonstrates a faster hydrogen abstract rate than the corresponding Mn(IV)-OH moiety. Through product analysis, it was further found that, after hydrogen abstraction, the reduced Mn(III)-OH from Mn(IV)=O can rebind the OH group back to the substrate radical to generate the hydroxylation product, and it may also abstract the second hydrogen to offer dehydrogenation product, while the Mn(III)-OH_2 from Mn(IV)-OH cannot perform hydroxylation through rebinding, and only offer dehydrogenation product. In electron transfer, the protonated Mn(IV)-OH demonstrates more efficient electron transfer rate than the corresponding Mn(IV)=O due to its positively increased net charge. After detailed investigating the oxidative relationships of Mn(IV)=O and Mn(IV)-OH, we have summarized the how the oxidative reactivity of an active metal intermediate changes with the change of its physicochemical properties. These findings have been applied to rationalize the selection of a high-valent metal oxo or hydroxo functional group in a specific enzyme, and it also benefit some unknown oxidative phenomena. Based on observed the fact of that increasing the positive net charge can accelerate its rate in electron transfer, we further explored non-redox metal ions as Lewis acid promoted catalytic oxidation by redox catalysts, and found that, in addition to the redox properties of copper(II), its Lewis acid properties also play significant role in Pd(II)-catalyzed Wacker-type oxidations.

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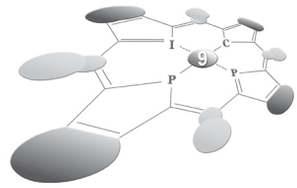

Water-Soluble Ionic Liquid Type Photosensitizers for Photodynamic Therapy

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Generally, most of the photosensitizers (PSs) are hydrophobic, which may afford disadvantages to make the PSs insoluble under physiological conditions and hinders to reach the accumulation in the tumor sites. For clinical application, it is need to prevent making aggregation of PS molecules in aqueous media. There are many efforts to make soluble the PSs in water by using various types, such as, cationic (pyridinium, ammonium), anionic (sulfate, phosphonate, carboxylate with sodium), saccharide, cyclodextrin, peptide, polyethylene glycol, polymeric micelles, polymers (starch, dextran, polyallylamine,[1] polyvinylpyrrolidone), and etc. Our group has developed water-soluble gold nanorod(GNR)-PS complex for controllable photodynamic therapy (PDT) effect.[1]

Ionic liquids (ILs) are useful materials based on good advantages, such as, negligible vapor pressure, high thermal stability, property improvement upon slight changes in the chemical architecture. IL type PS (IL-PS) may help PSs capable of increased solubility in aqueous system as well as support attachment of PSs on gold nanoparticles (GNPs) surface through stable electrostatic interactions between ILs and PSs.[2] In order to increase uptake of PSs into tumor cells, PSs should not highly water soluble (hydrophilic) to penetrate the tissue and cell membranes. Therefore it is very important to keep suitable hydrophobic/hydrophilic balance of PSs, for which use of GNPs has a great interest as an efficient carrier of IL-PS.

We developed various kind of ILs, such as morpholinium, cholinium, imidazolium, and ammonium type, of purpurin-18 (**IL1PSs**~**IL4PSs**) were used to prepare GNP complexes of **IL1-PS-GNPs**~**IL4-PS-GNPs** and their PDT effect was investigated.[3] The hydroxyl group of each IL-PS has important roles as a reducing agent to make Au(0) as well as a stabilizer through the electrically charged functional groups (i.e. carboxylate and amine groups) in forming the GNPs complexes without any additional reducing agents and surfactants. The GNPs complexes were characterized by a combination analysis of ^{1}H-NMR and UV-Vis spectroscopies, TGA and TEM measurements. UV-Vis spectra show that long wavelength absorptions (λ_{max} 715~762 nm) of the IL-PSs and IL-PS-GNPs. TGA spectra show the formation of the IL-PS-GNPs, result in directly measured amount of organic content of 37~48% and metallic Au of 52~63%. TEM images showed that the IL-PS-GNPs nanospheres have a size range of 20~80 nm.

All the IL-PS-GNPs showed better cell viability than that of the corresponding IL-PS, which result clearly reveal that the GNPs is an useful carrier for this IL-PS. PDT efficacy of the complexes IL-PS-GNPs and the corresponding IL-PSs were investigated by MTT assay against A549 and Hela cell lines. The IL-PS-GNPs complexes showed higher cell viability compared to the corresponding free IL-PSs, respectively, due to higher cell penetration based on excellent delivery effect of the GNPs, and relative PDT activity difference among the complexes was depend on the property of the IL-PSs. The IL-PS-GNPs complexes could be delivered into cancer cell by endocytosis result in high penetration and intracellular localization, which was confirmed by confocal laser scanning microscopy (CLSM) images. This result may useful for design and synthesis of new water-soluble IL-PSs and PS-GNPs complexes for enhanced PDT effect.

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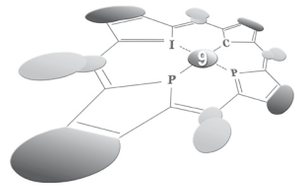

Triply Diarylamine-, Diarylmethane-, or Diarylborane-fused π-Extended Porphyrins

Kenichi Kato[a], Keisuke Fujimoto[a], Norihito Fukui[a], Hideki Yorimitsu[a,b], Atsuhiro Osuka[a]

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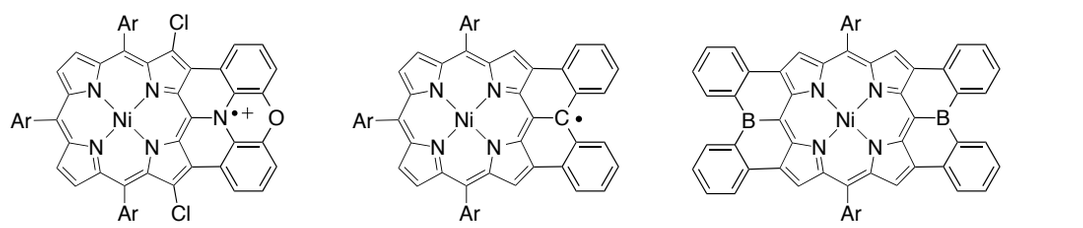
Stepwise oxidative fusion reactions of *meso*-phenoxazinoporphyrin followed by electrophilic *β*-chlorination provided the corresponding fused porphyrin **1** as a highly planar diarylamine-fused porphyrin.[1] Fused porphyrin **1** readily underwent one-electron oxidation to afford the corresponding radical cation $\mathbf{1}^{\bullet+}$. This radical cation was remarkably stable under ambient conditions, being compatible with silica gel column purification and dichloromethane/water partition. A solution of $\mathbf{1}^{\bullet+}$ shows apparent absorption in the NIR region.
β,meso,β-trichloroporphyrin[2] reacted with diphenylmethyllithium to yield *β,β*-dichloro-*meso*-diphenylmethylporphyrin through an S_NAr process. This dichloroporphyrin was then subjected to twofold palladium-catalyzed intramolecular C-H arylation. This C-H arylation was expected to give triply *β,meso,β*-diphenylmethane-fused porphyrin **2**. To our surprise, we isolated the corresponding dehydrogenated radical **2–H**, owing to facile oxidation of **2**.[3] Radical **2–H** displays NIR absorptions which correspond to HOMO–SOMO transitions.
Bis(diphenylborane)-fused porphyrin **3** was prepared from the corresponding *β,β*-bis(2-trimethylsilylphenyl)-substituted porphyrin through Si-B exchange with boron tribromide followed by an intramolecular bora-Friedel-Crafts reaction. Diboryl porphyrin **3** was robust owing to the structural constraint of the boron atoms embedded in the rigid and planar π-skeleton, and shows red-shifted absorption reaching the NIR region and positively shifted reduction potentials due to the effective interaction of the vacant *p*-orbitals of the borons with the porphyrin π-electronic circuit.



$\mathbf{1}^{\bullet+}$ **2–H** **3**

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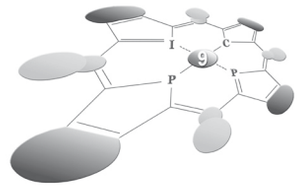

Efficient Catalytic Epoxidation by Mn-Porphyrins within Polyaromatic Capsules

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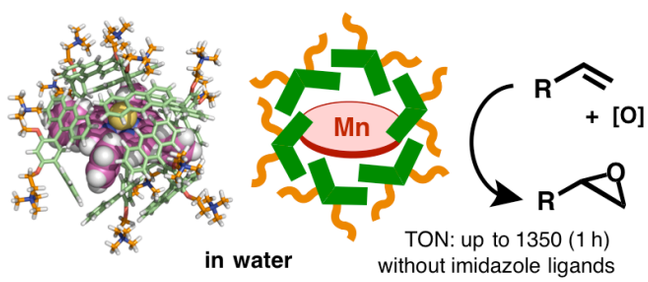
Cytochrome P450 provides a metallo-porphyrin catalyst in the pocket surrounded by large protein assemblies.[1] The confined microspace of the pocket is of essential importance to enhance the selectivity and efficiency of the enzymatic reaction in water. Inspired by such biological catalysts, a great deal of attention has been paid to the synthesis of various metallo-porphyrin compounds surrounded with bulky substituents.[2] On the other hand, the encapsulation of metallo-porphyrin compounds in the cavity of synthetic cages and capsules would be highly expected to develop novel bio-inspired catalysts but remains uncommon due to the difficulty of binding the large porphyrin frameworks. We recently reported that a polyaromatic amphiphile composed of a bent bis-anthracene framework with two hydrophilic groups forms a micelle-like polyaromatic capsule.[3,4] The capsule enables hydrophobic compounds (e.g., fluorescent dyes, fullerenes, and carbon nanotubes) to dissolve in water upon encapsulation.[5,6] Here we report (i) the encapsulation of metallo-porphyrins (M = Mn, Zn, Ni, and Co) within the aqueous polyaromatic capsule and (ii) the efficient catalytic epoxidation of styrenes in water by the encapsulated Mn-porphyrins without imidazole ligands under ambient conditions. The keys of the efficient catalytic cycle are the enforced proximity of the manganese catalyst and substrates through hydrophobic effects and also the smooth replacement of the products by substrates in the hydrophobic cavity of the capsule.[7]



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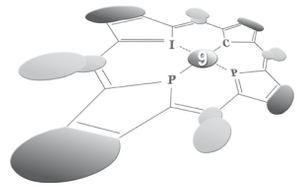

A Disassembly-Based Approach for Analyte Detection

Zelder F.,[a] Gasser G.,[a] Chao, H.,[b] Huang, H.[b] Kumari, N.[a]

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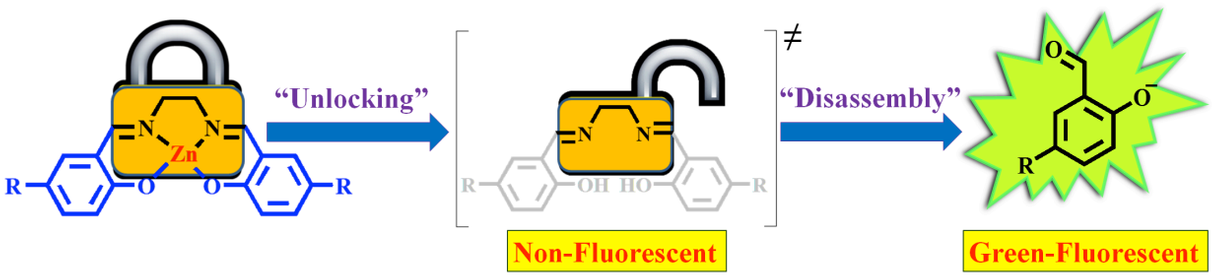
This talk presents a stimulus-induced disassembly approach in water.[1] In particular, the selective fluorometric detection of polyphosphates in water and biological media is described.
In this method, an analyte selectively sequesters a metal ion from a metal-chelate complex. The "unlocked" ligand subsequently hydrolyses into its molecular subunits. Since the optical properties of the disassembled ligand and its ancestor are distinguishable, the anylate induced depletion of the metal-complex is leading to a detectable signal.



The concept is described for the selective detection of pyrophosphate with metal-salen complexes.[1-3] Initially the intrinsic fluorescence of the salicylaldehyde signaling units is suppressed, but is unfolded during the disassembly of the molecule. Applications of this strategy for analyte detection in cells are presented.

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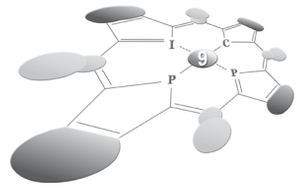

A Novel Biomimic Catalyst for the Aerobic Oxidation: Metal Corrolazines

Bingguang Zhang*, Peng Zhou, Yang Liu, Xuanmu Zhou, and Kejian Deng

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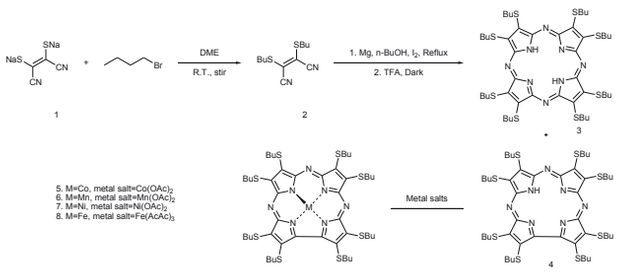
Triazacorrole or corrolazine(Cz), as a member of the porphyrinoid family, is distinguished since a meso-N is deleted from the porphyrazine ring while the number of π electrons remains 22[1]. These macrocycles exhibit some spectacular properties that differ dramatically from their porphyrin counterparts[2]. A novel porphyrinoid, triazacorrole or corrolazine (Cz), with contracted 20-electron conjugated macrocyclic system and one single internal hydrogen, as well as its different metal corrolazines (MCzs) were synthesized and characterized. And their catalytic activities were evaluated by the aerobic oxidation of benzyl alcohol and several important reaction parameters were optimized. With optimal condition, the impact of central metal on catalytic efficiency was investigated and the result showed that MnCz exhibited the highest activity with conversion and selectivity reaching 84% and 99% respectively. Other MCzs also exhibited good conversion and excellent selectivity with catalytic activity in an increase order of MnCz>CoCz>FeCz≈NiCz. A possible mechanism involving highly active metal-oxo was proposed in light of the *in-situ* UV-Vis spectra, in which a possible characteristic absorbing peak of metal-oxo was observed. With contracted structure, the catalytic efficiency is nearly 2 times higher than the corresponding symmetric metaloporphyrazines(CoPz) although their TON/TOF values are still unsatisfactory. This work provided an idea for designing thioporphyrazinoid with excellent catalytic efficiency.

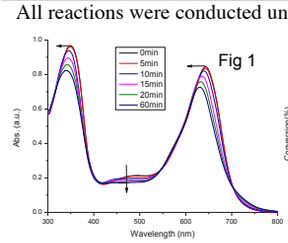


Scheme 1 Synthesis of freebase corrolazine and their metal complex

Table 1 The effect of central metal on efficiency of catalysts

Entry	Catalyst	oxidation		Conv.	Product (%)	
		1st(V)	2nd(V)	(%)	aldehyde	acid
1	Co	0.511	0.885	65	>99	<1
2	Mn	0.514	0.879	84	>99	<1
3	Fe	0.639	0.972	40	>99	<1
4	Ni	0.750	-	39	>99	<1

All reactions were conducted under optimized condition for 3h.



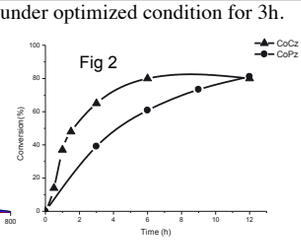


Fig 1 The in-situ UV-Vis spectra recorded in aerobic oxidation of benzoin at 30°C and air atmosphere as different time intervals.
Fig 2 The effect of reaction time on the efficiency of catalysts catalyzed by CoCz and CoPz respectively.

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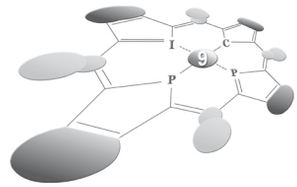

Design of NIR emissive lanthanide porpholactones

Ji-Yun Hu[1], Ying-Ying Ning[1], and Jun-Long Zhang[1]*

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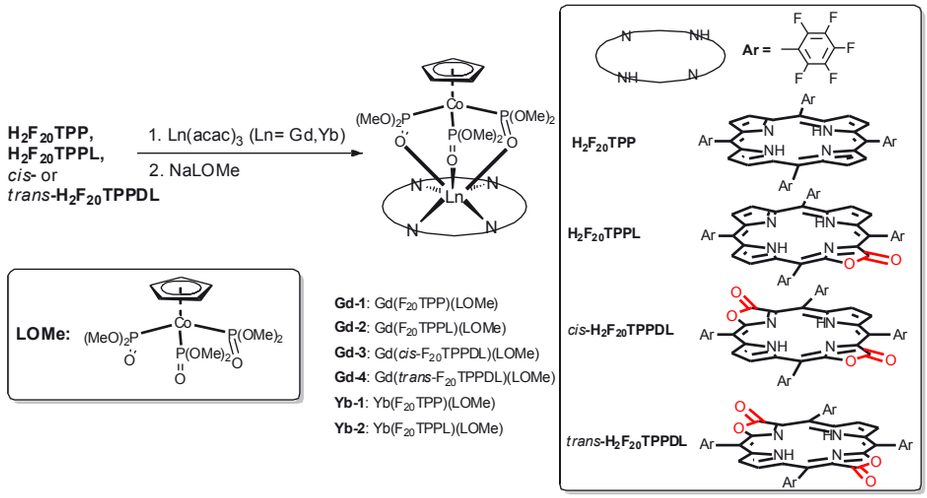
Porpholactones (TPPLs) are an important but relatively unstudied class of tetrapyrroles, which combine some of the features of porphyrins and chlorins, exhibiting increased intensity of the lowest-energy UV-visible absorption band near 650 nm and "porphyrin-like" chemical properties.[1] Based on the skeleton of unusual lactone, we derived a series of porpholactols, porphodilactones and porphodilactols to mimic the biosynthesis of chlorophylls and bacteriachlorophylls from protochlorophyllide.[2] The lactonization of beta-periphery of porphyrins renders the lower triplate excited states compared to those in porphyrins, which enhances the NIR emission of Ln ions. More importantly, through beta-fluorination of porphyrin periphery, the life time of NIR emission is significantly increased, which is considered to block the non-irradtive pathway. Taken together, the beta-modification of porphyrin represent an effective approach to enhance the NIR emission of Ln ions, which has the potential to further improve the practical application of Lanthanide chemistry.



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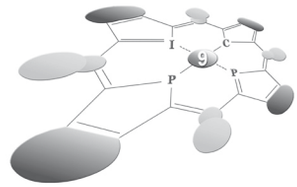

New Applications of Cobalt(II) Porphyrin-Based Metalloradical Catalysis

X. Peter Zhang[a]

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Organic synthesis has been dominated by chemical reactions that are based on 2e ionic processes, either stoichiometrically or in catalytic fashion. While 1e radical chemistry is equally rich, its application in organic synthesis has been hampered by several enduring challenges. Over the past decade, we have been in the process of formulating metalloradical catalysis (MRC) as a powerful new concept to guide the development of effective approaches for controlling both reactivity and stereoselectivity of radical reactions while catalytically generating carbon- and nitrogen-based radicals from common organic precursors. For achieving enantioselective radical reactions via MRC, we have developed a family of unique chiral metalloradical catalysts based on structurally well-defined cobalt(II) complexes of D_2-symmetric chiral porphyrins with tunable electronic, steric, and chiral environments. These cobalt(II) porphyrin-based metalloradical catalysts have been shown to be highly effective for a wide range of stereoselective organic reactions, including alkene cyclopropanation, alkene aziridination, C–H alkylation and C–H amination. Due to their distinctive radical mechanisms that involve unprecedented a-metalloalkyl radical (also known as metallocarbene Radical) and a-metalloaminyl radical (also known as metallonitrene radical) intermediates, the cobalt(II) porphyrin-based metalloradical systems enable addressing some long-standing problems in these important organic transformations.

We will present our progress on further applications of MRC for stereoselective carbene and nitrene transfers, including recent developments of new radical cascade processes by cobalt(II) porphyrins. Some new insights on mechanistic aspects of these cobalt(II) porphyrin-based new catalytic processes will also be presented.

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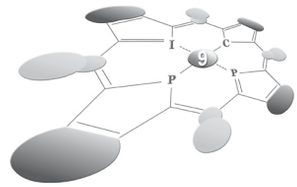

Functionalized Triazatetrabenzocorroles: Synthesis, Photophysics, Electrochemistry and Photovoltaic Applications

Xian-Fu Zhang[a,b], **Hao Geng**[a], **Xulin Lu**[a]

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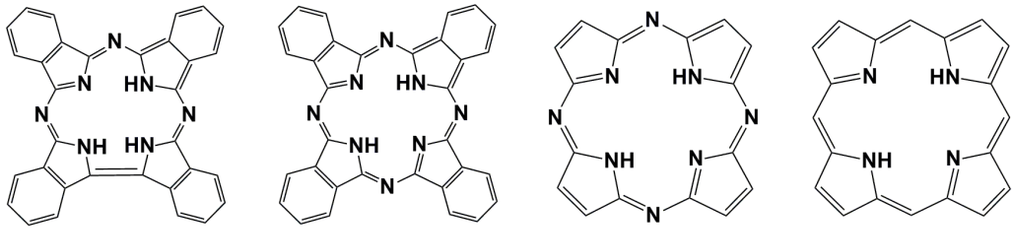
Triazatetrabenzocorrole complexes (TBCs) belong to the well-known phthalocyanine (Pc), corrole and porphyrin families.[1] TBCs show very strong light absorption in both the blue (400–450 nm) and the red region (620–660 nm).[1-4] TBCs also exhibit lower oxidation potential and higher reduction potential than its corresponding Pc complexes.[1] TBC macrocycles have a significantly smaller cavity diameter (0.44A˚) than that of Pc compounds (0.76 A˚) due to the ring contraction. These unique chemical and physical properties makes it possible for them find important applications in stabilizing high valent meta-stable metal ions, being good electron donors and good light harvesting antenna for organic photovoltaics, acting as good photosensitizers for photodynamic therapy of tumors (PDT).



TBC phthalocyanine tetraazaporphin porphin

In this report, P(V), Si(IV) and Ge(IV) TBC complexes functionalized with electron donating or electron withdrawing units were synthesized and characterized. Their UV-Vis absorption, fluorescence and excited triplet state properties, singlet oxygen generation and photoinduced electron transfer efficiency as well as electrochemistry were studied.

Organic solar cells based on TBC materials are fabricated by thermal evaporation coating method. IPCE and IV curves were measured. The results show that TBCs are promising candidates for photovoltaics and PDT.

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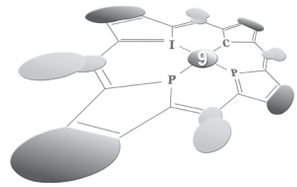

Catalytic and Biocatalytic Iron Porphyrin Carbene Formation: Effects of Binding Mode, Carbene Substituent, Porphyrin Substituent, and Protein Axial Ligand

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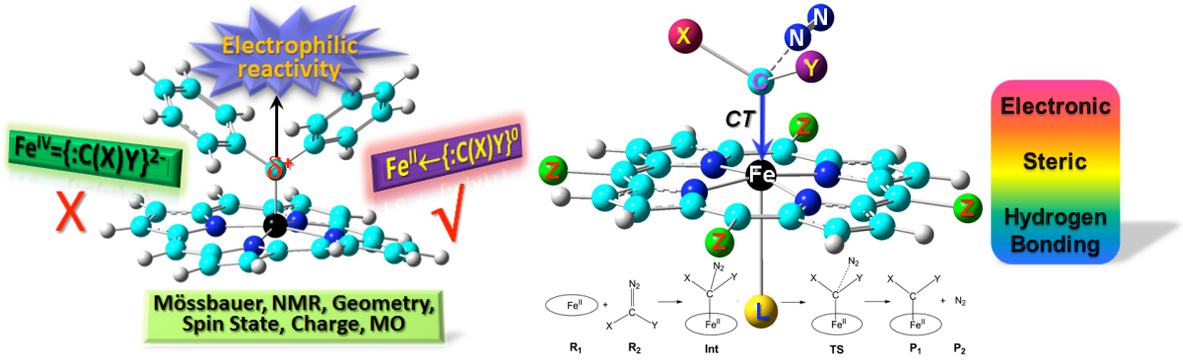
Iron porphyrin carbenes (IPCs) are important intermediates involved in various chemical reactions catalyzed by iron porphyrins and engineered heme proteins, as well as in the metabolism of various xenobiotics by cytochrome P450.[1-5] However, there are no prior theoretical reports to help understand their formation mechanisms and identify key information governing the binding mode, formation feasibility, and stability/reactivity. Following our recent quantum chemical investigation of their Mössbauer, NMR, geometry, spin state, charge, and MO properties to resolve the major resonance structure for reactivitiy,[6] a systematic quantum chemical study was performed to investigate the effects of carbene substituent, porphyrin substituent, and axial ligand on IPC formation pathways.[7] Results not only are consistent with available experimental data,[1-5] but also provide a number of unprecedented insights into electronic, steric, and hydrogen bonding effects of various structural factors on IPC formation mechanisms. These results shall facilitate research of IPC and related systems for sustainable chemical catalysis and biocatalysis.



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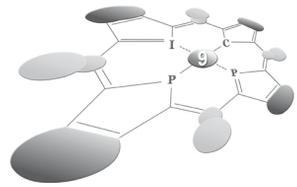

Design of Bodipy-Based Triplet Photosensitizers and Applications in Triplet-triplet Annihilation Upconversions

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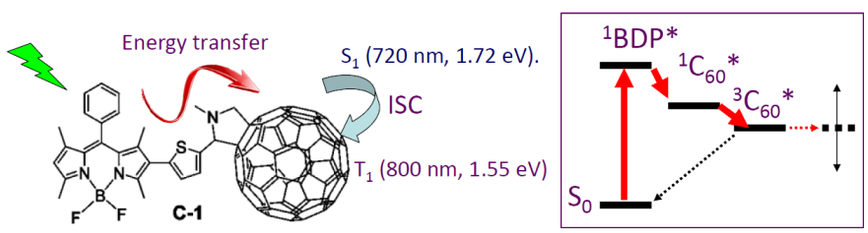
Triplet photosensitizers (PSs) are the compounds showing strong absorption of visible light, efficient intersystem crossing (ISC) thus high triplet state yield and good photostability.[1] Triplet PSs are widely used in photocatalysis, photodynamic therapy (PDT), and recently the triplet-triplet annihilation upconversion (TTA UC).[2] However, the conventional triplet photosensitizers are limited to the porphyrin complexes and Ru(II), Pt(II) complexes, and some halogenated xanthane dyes, such as Eosin Y. It is still a major challenge to design a new triplet photosensitizer which show predictable ISC, especially for those contain no heavy atoms because the intersystem crossing (ISC) of metal-free organic chromophores is usually unpredictable.

TTA UC has attracted much attention, due to the strong absorption of the photoexcitation energy, high upconversion quantum yields, and low photoexcitation threshold (excitation light power density can be as low as 5 mW cm^{-2}. Solar light is sufficient). However, most of the conventional triplet photosensitizers are Pt(II)/Pd(II) porphyrin complexes.[1] These complexes are difficult to prepare and to purify, and the molecular structures are unable to be modified feasibly. We proposed a few new approaches to prepare triplet PSs, such as to use Bodipy as the chromophore in heavy atom-containing compounds, or with C_{60} as the electron spin converter heavy atom-free organic photosensitizers.[3]



Scheme 1. A strategy to prepare heavy-atom-free organic triplet photosensitizer.

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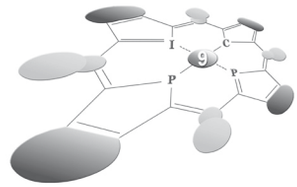

New far-red and near infrared fluorescent proteins derived from biliproteins

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Fluorescent proteins have become invaluable tools in life sciences. Of particular interest are far-red and near-infrared (NIR) emitting dyes. Light is absorbed and scattered minimally in this region by mammalian and most other tissues, therefore, such dyes allow for deeper penetration. Biliproteins are emerging candidates because of their intense absorption and bright fluorescence in this region. They are either derived from the naturally fluorescent cyanobacterial light-harvesting pigments, phycobiliproteins, or from sensory photoreceptors of the extended phytochrome family where, by engineering, the photoreaction is suppressed in favor of fluorescence. Phycobiliproteins usually bind the bilin chromophores covalently, thereby shortening their conjugation system. The covalently bound chromophores fluoresce in the orange and red region, with a limit at ~670 nm for the allophycocyanin B and the core-membrane linker, L_{CM}. In certain near infrared photoacclimated cyanobacteria, L_{CM} can bind bilins non-covalently. Depending on the chromophore bound, the resulting phycobiliproteins show far-red and NIR fluorescence, due to their more extended conjugation compared to the respective covalently bound bilins. These phycobiliproteins can be molecularly engineered to become monomeric, soluble, smaller and more strongly fluorescent. We will present new developments how L_{CM} and other non-covalently bilin-binding phycobiliproteins can by tailored for fluorescence biolabeling at wavelengths up to 725 nm.

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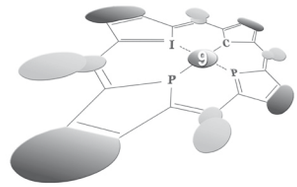
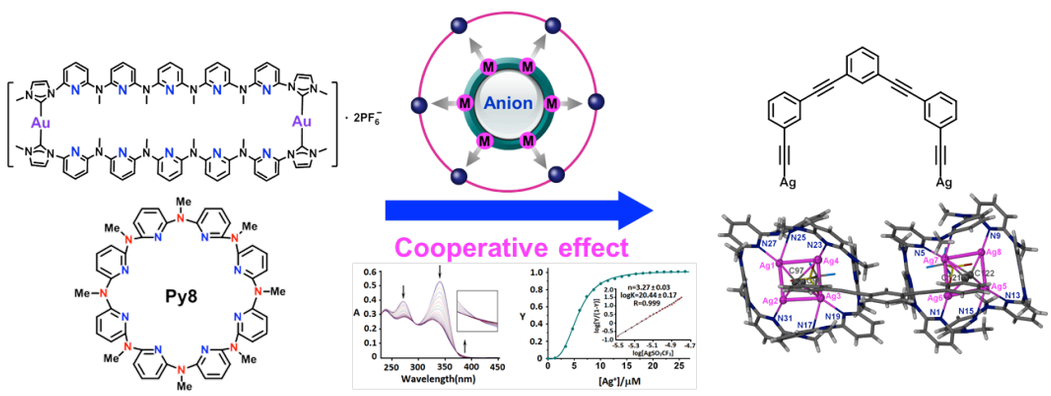


Macrocycle-Directed Controllable Synthesis of Polynuclear Metal Clusters

Liang Zhao

Department of Chemistry, Tsinghua University

Polynuclear metal clusters, featured by the aggregation of several interacted metal atoms through metal-metal interactions/bonds, have been deemed as an elusive intermediate in the catalytic process of some organic transformations under homogeneous or heterogeneous conditions. The difficulty in understanding the functions of metal cluster aggregates in catalytic process and in building detailed structure-property relationship mainly lies in the fluxional nature of the structures of metal clusters. In order to achieve controllable synthesis of multinuclear organometallic clusters with specific nuclearity numbers, we have endeavored to establish a general synthetic strategy by using organic or organometallic multidentate macrocyclic compounds as a template.[1] A variety of metal clusters can be fabricated inside the cavity of differently sized azacalixpyridines, giving rise to metal cluster-centered capsule, rotaxane, catenane and polygon assemblies. Mechanistic studies have revealed that the cooperative effect inherent in multidentate macrocycles plays a pivotal role in the synthesis of metal clusters.[2] By virtue of this effect and the established macrocycle-directed metal cluster synthetic approach, we have successfully achieved a plethora of metal clusters (Ag, Cu etc.) with different anionic centers (such as halides, chalcogenides etc.).[3] The acquired metal clusters can be further applied in the fabrication of cluster-based functional materials.[4] Electrochemical and catalytic properties of the acquired metal clusters have been investigated.



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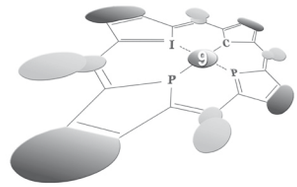

From nano to micro, and back: Explore porphyrin supramolecular chemistry for cancer imaging and therapy

Gang Zheng[a,b], **Juan Chen**[b]

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[b]*Princess Margaret Cancer Center, Toronto, Canada*

Porphyrins are aromatic, organic, light-absorbing molecules that occur abundantly in nature, especially in the form of molecular self-assemblies. In 2011, we first discovered 'porphysomes', the self-assembled porphyrin-lipid nanoparticles with intrinsic multimodal photonic properties. The high-density porphyrin packing in bilayers enables the absorption and conversion of light energy to heat with extremely high efficiency, making them ideal candidates for photothermal therapy and photoacoustic imaging. Upon nanostructure disruption, fluorescence and photoreactivity of free porphyrins are restored to enable low background fluorescence imaging and activatable photodynamic therapy. Metal ions can be directly incorporated into the porphyrin building blocks of the preformed porphysomes thus unlocking their potential for PET and MRI. By changing the way porphyrin-lipid assembles, we developed porphyrin lipoprotein nanoparticles, microscopy-controlled porphyrin protocells, and hybrid porphyrin-gold nanoparticles, thus expanding the purview of porphyrin nanophotonics. Most recently, we created trimodal (ultrasound/photoacoustic/fluorescence) porphyrin shell microbubbles. Upon ultrasound exposure, porphyrin microbubbles form nanoparticles that possess the same optical and therapeutic properties as the original microbubble, thus providing an interesting opportunity to overcome the Achilles' heel of cancer nanotechnology, where the over reliance of the enhanced permeability and retention effect has consistently resulted in promising efficacy in mouse models but poor clinical track record. By closing the nano-micro-nano loop, the simple yet intrinsic multimodal nature of porphyrin self-assembly represents a new frontier in cancer imaging and therapy.

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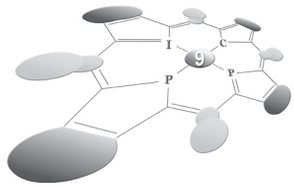

Human mass balance study of the novel anticancer agent photocyanine using accelerator mass spectrometry

Xin Zheng[a], Yiming Zhang[b], Jinping Xue[c], Xinxiang Zhang[b], Naisheng Chen[c], Ji Jiang[a]

[a]*Peking union Medical College Hospital*
[b]*Peking University*
[c]*Fuzhou University*

PHOTOCYANINE, is a fully chemically synthesized anti-cancer photosensitizer, which is an amphiphilic di-sulfonic-di-phthalimidomethyl zinc phthalocyanine di-potassium salt. In phase I clinical trial, the human plasma pharmacokinetics of photocyanine have been described. However, the excretory pathways and contribution of metabolism to photocyanine elimination have not been determined. The parent drug recovery is less than 3%. To investigate the elimination pathways of photocyanine we initiated a mass balance study in cancer patients. Due to the ethical reasons, cancer patients could not be exposed to high radiation doses. This necessitated the use of much lower levels of [14C]-labeling and an ultra-sensitive detection method, Accelerator Mass Spectrometry (AMS). Four patients with advanced cancer received an intravenous dose of 0.1 mg/kg, 300 nCi of [14C] photocyanine over 1 h. Plasma, urine and faeces were collected up to 14 days after administration and total radioactivity (TRA) was determined using AMS. photocyanine in plasma and whole blood was quantitated using a validated LC-MS/MS method. Mean recovery of photocyanine -derived radioactivity was investigated. And both fecal excretion and urinary excretion were identified. Only a minor part of TRA is accounted for by unchanged photocyanine in both plasma and urine, which indicates that metabolism is a major elimination mechanism for this drug. Future studies should focus on structural elucidation of photocyanine metabolites and characterization of their activities.

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Templating Isoindoline Units to Make Chelates: Constructing Half of a Porphyrazine

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Templates are very frequently used to construct macrocycles, and the phthalocyanines in particular are archetypal examples of compounds made via metal templated reactions. Over the past several years, we have been exploring the construction of isoindoline-based chelates, rather than macrocycles, using both transition metal and main group templates. This talk will present some of our recent work in this area, including the construction of aza(dibenzopyrro)methenes using $Re(CO)_3$ compounds and phenyl boron reagents. Additionally, we can construct "half-hemiporphyrazines" using similar methods involving heterocylic amines and diiminoisoindoline. In addition to discussing synthetic methods, this talk will also present investigations into the electronic structures of these compounds, which are markedly different from similarly structured chelates, such as the aza(dipyrro)methenes and the BODIPY class of fluorophores.

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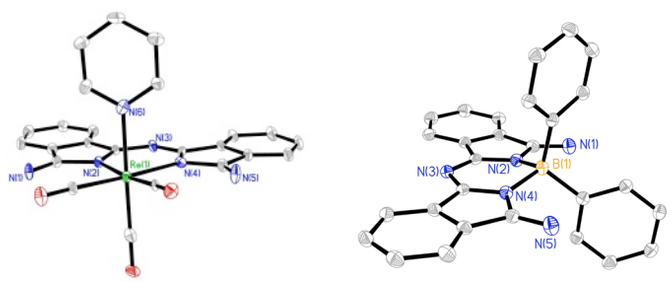

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Water Soluble Non-aggregating Phthalocyanines for Photodynamic Therapy

Petr Zimcik, Veronika Novakova, Miloslav Machacek, Jan Kollar, Antonin Cidlina

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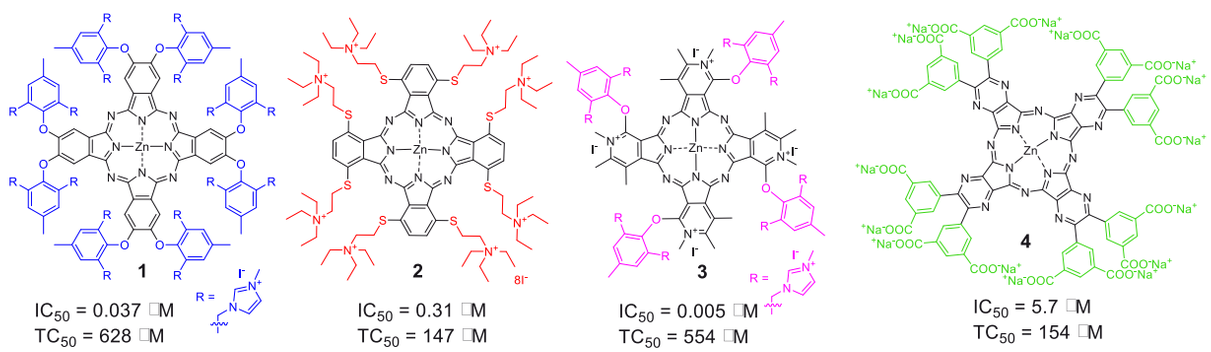
Phthalocyanines (Pcs) are widely studied photosensitizers in photodynamic therapy (PDT) with advantageous photophysical properties such as strong absorption in area close to or above 700 nm and strong singlet oxygen production. However, their planar hydrophobic core makes them water insoluble and prone to the aggregation that substantially decreases their potential in PDT. Introduction of charged peripheral substituents on Pcs increases their water-solubility and, at the same time, may prevent the self-aggregation.

Introduction of the cationic substituents, in particular in the rigid arrangement like in **1**, decreased the aggregation and *e.g.* **1** was completely non-aggregating in water up to maximum tested concentration of 100 mg / mL. It was reflected in high photodynamic activity (λ > 570 nm, 11.2 J cm^{-2}) with IC_{50} values on HeLa cells about 37 nM with low toxicity in the dark (TC_{50} = 628 μM).[1] Detailed *in vitro* studies were performed for derivative **2** with more flexible linker to understand the mechanism of action on the subcellular level.[2] The experiments revealed that cationic Pcs are located in lysosomes leading to redistribution after irradiation with subsequent influence of other subcellular organelles with final destruction of the nucleus. Recent developments in synthesis of substituted tetrapyridoporphyrazines[3] allowed us to design compound **3** with rigid cationic substituents and quaternized nitrogens in the core that exerted interestingly high photodynamic activity with IC_{50} in range of nanomols. On the other hand, anionic **4** that was also fully non-aggregating in water at neutral pH was much less active than all the cationic compounds due to important effect of pH inside the lysosomes and significant binding to serum proteins.

This work was supported by Czech Science Foundation (reg. No. 13-27761S).



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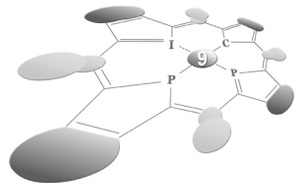

Nitroxyl (HNO) Derivatives via Hydride Attack at the Coordinated Nitrosyls in Ferric Porphyrins

Erwin Abucayon,[a] Rahul L. Khade,[b] Yong Zhang,[b] and George B. Richter-Addo[a]

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Nitroxyl (HNO; nitrosyl hydride) is an important biologically active species. HNO elicits several biological responses that complement those attributable to its redox related nitric oxide (NO). For example, HNO elicits responses such as vasodilation and muscle constriction, but its actions are distinct from those elicited by NO. Significant efforts have been placed in the last decade on the design of HNO donors for use in physiology and biochemistry. Importantly, HNO is also an intermediate in various processes catalyzed by heme proteins. Such heme-HNO intermediates have been proposed to form during the enzymatic detoxification of NO by fungal cytochrome P450 nitric oxide reductases (P450nor), and during nitrite reduction by cytochrome *c* nitrite reductase. We have prepared heme model compounds containing the Fe-HNO moieties from hydride attack on the ferric heme model nitrosyl precursors. For example, the (OEP)Fe(HNO)(5-MeIm) (OEP = octaethylporphyrinato dianion) product has been characterized by infrared and ^{1}H NMR spectroscopy. This product, however, decomposes to the known five-coordinate ferrous (OEP)Fe(NO) and dihydrogen. We have utilized DFT methods to probe the mechanism of hydride attack on the cationic $[(\text{porphine})\text{Fe(NO)(5-MeIm)}]^{+}$ precursor (porphine = unsubstituted porphyrinato dianion). We show that the N-pathway, namely direct attack of the hydride at the nitrosyl N atom rather than attack at the nitrosyl O atom, is the preferred pathway for the formation of the Fe-HNO derivative.

Importantly, this (OEP)Fe(HNO)(5-MeIm) compound represents the first report of hydride attack at a ferric heme-model nitrosyl group to generate a Fe-HNO product, and the first spectroscopic characterization of the HNO ligand in a heme model Fe-HNO derivative (*J. Am. Chem. Soc* **2016**, 138, 104-107). The preparation, spectroscopic characterization, reactivity, and DFT investigation of the (OEP)Fe(HNO)(5-MeIm) derivative will be presented and discussed.

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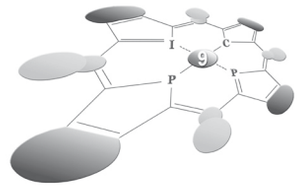

Novel nanocomposites of graphene quantum dots and phthalocyanines for nanosensors fabrication

Ojodomo J. Achadu and Tebello Nyokong*

*Department of Chemistry, Rhodes University, Grahamstown, 6140, South Africa. *email: t.nyokong@ru.ac.za*

Recently, graphene quantum dots (GQDs) show strong and tunable photoluminescence (PL), excellent photostability, high biocompatibility (solubility in aqueous media) and non-toxicity [1]. The supramolecular assembles of GQDs and macrocycles with extended π-conjugated systems such as phthalocyanines (Pcs) could considerably extend GQDs-based nanosensors fabrication due to the excellent optical properties of phthalocyanines [2]. Graphene quantum dots (GQDs) and zinc phthalocyanines interactions are reported for the first time. Metal free-2,(3)-tetra-(2-mercaptopyridine) phthalocyanine; 2,(3)-tetra-[(2-mercaptopyridine) phthalocyaninato] zinc (II); quaternized 2,(3)-tetra-[(2-mercaptopyridine) phthalocyaninato] zinc (II) were separately adsorbed onto the planar structure of graphene quantum dots (GQDs) via π-π interaction to form GQDs-Pcs nanocomposites, Fig. 1. The GQDs fluorescence emission was substantially quenched by the mercaptopyridine-substituted phthalocyanines and was "switched ON" in the presence of Hg^{2+} as a test analyte. The novel nanoprobes were highly sensitive and selective towards Hg^{2+}. Our novel method employs the fluorescence "turn ON" process which is more reliable than the widely reported "turn OFF" process.

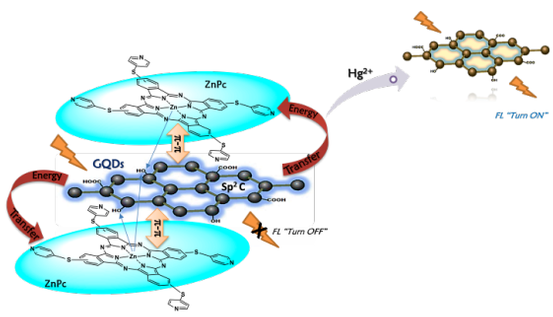

Fig. 1. Representation of GQDs conjugates with phthalocyanines

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Novel Fluorescent Zwitter-ionic BODIPYs: Water-soluble small molecular bio-markers for living cells

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The ease with which the resolution and sensitivity achieved by fluorescent techniques make small fluorescence organic dyes preferred choice than other available modalities. One crucial challenge to this approach is the insoluble nature and self-quenching due to aggregation of the organic fluorophores in water[1]. Circumventing these problems needs a tethering approach such as sulphonylation or bio conjugation with multi-step synthesis includes harsh protocols. Owing to their tunable optical and chemical properties, high fluorescence quantum yield, make BODIPY as potential fluorophore for practical utilization in biomarkers, protein tags and biosensors [2, 3]. Here we report a couple of water soluble small molecular fluorescence zwitterionic BODIPY by a simple two step synthesis.

Two new small molecular zwitterionic fluorescent BODIPYs show high fluorescence quantum yield and good solubility in aqueous media. The zwitterionic nature of molecules was probed by single crystal XRD. Their optical properties were envisaged by UV-Visible, fluorescence and TCSPC spectrometry.

Figure 1. Fluorescence of water soluble zwitter-ionic BODIPYs in water as solvent

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Aliphatic amine discrimination by Pentafluorophenyl-dibromo BODIPY

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Aliphatic amines constitute one of the most important and abundant classes of amines found in nature. They also play crucial roles in synthetic chemistry, biology and atmospheric sciences. With these considerations along with characteristic properties specified to various degrees of aliphatic amines (primary, secondary and tertiary), there should be a potential need for direct discrimination of these amines in a wide range of environments[1]. Molecular recognition provides an effective and promising approach sufficing most of the above requirements. It affords fast and convenient read-out signals in the form of colour and fluorescence. However, owing to the range of sizes, conformations, shapes in amines besides high polarity, it is really challenging to design a molecular scaffold providing aliphatic amine discrimination and analysis in both aqueous and organic media. Our target was to achieve a molecular system which exhibits fluorescence along with a chromogenic response for amine discrimination. The BODIPY backbone was chosen because of its excellent fluorescence, colour and it is structurally robust.

Two new fluorescent BODIPY dyes (**R_a** and **R_b**) have been designed and synthesized. Their selective reactivity towards an Ar-S_N2 reaction[2] has been explored as a potential basis for colorimetric and fluorescent discrimination of various degrees of aliphatic amines. This recognition event is unprecedented, dual-mode and instantaneous. The recognition mechanism was probed by NMR titration studies and single crystal XRD analysis.[3]

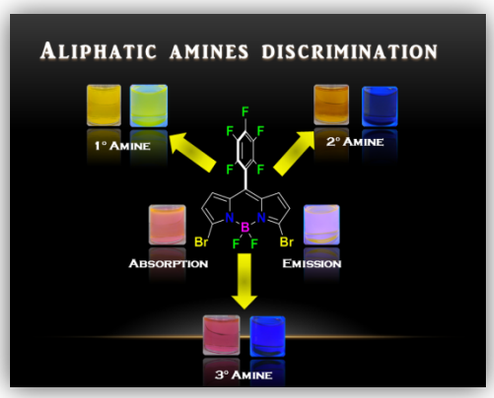

Figure 1. Visible absorption and emission changes of **Ra** in DCM upon additions of various types of amines.

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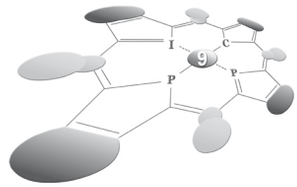

First Developments of Phthalocyanine-Based Bridged Silsesquioxane Nanoparticles

Vefa Ahsen,[a] Serkan Alpugan,[a] Deniz Kutlu Tarakci,[a] Chiara Mauriello Jimenez,[b] Magali Gary-Bobo,[c] Marie Maynadier,[c] Marcel Garcia,[c] Laurence Raehm,[b] Fabienne Dumoulin[a] and Jean-Olivier Durand[b]

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Nanomedicine is an extremely promising anti-cancer strategy and receives accordingly institutional support.[1] Photodynamic therapy is itself an alternative cancer treatment with numerous advantages over more conventional modalities (radiotherapy, chemotherapy or surgery). The third generation of photosensitisers includes numerous photosensitizing nanoparticles.[2-3] Porphyrin-based Bridged Silsesquioxane Nanoparticles have already proved to be of high interest in photodynamic nanomedicine.[4] In order to benefit from the peculiar properties of phthalocyanines, and in particular their maximum intense absorption centered at 700 nm close to NIR wavelengths, the preparation of phthalocyanine-based Bridged Silsesquioxane Nanoparticles has been planned. The first developments obtained in the preparation and characterization of these novel materials will be presented.

ACKNOWLEDGEMENTS
The Scientific and Technological Research Council of Turkey (TUBITAK) and the French Embassy in Turkey are gratefully acknowledged for the bilateral Parteneriat Hubert Curien between Turkey and France (project Bosphorus 115Z864 / 35666WL).

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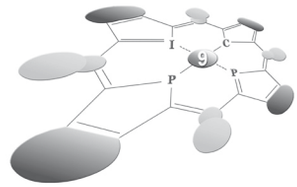

Heme-based displacment of a redox active signalling trigger

Justin A. Grennell[a], and Mehnaaz F. Ali[a]

[a]*Xavier University of Louisiana*

Point-of-care systems require highly sensitive, quantitative and selective detection platforms for the real-time multiplexed monitoring of target analytes. To ensure facile development of a sensor, it is preferable for the detection assay to have minimal chemical complexity, contain no wash steps and provide a wide and easily adaptable detection range for multiple targets. Towards this end, electrochemical detection can be integrated towards this need for real-time monitoring of analytes without requiring wash-steps, since the electron transfer event is triggered only when the electro-active species is proximal to the signalling electrode. We have designed a label-free detection strategy for relevant small-molecules and nucleic acids using aptamers as our molecular recognition probe. The aptamer consists of both the molecular recognition component and the signalling trigger, which is released upon target binding. In this case we describe a Heme selective aptamer that is temporarily bound to a redox active (suboptimal target) molecule. Upon the specific binding of Heme the redox active tag is released and detected electrochemically. To this end we show successful binding of the redox active trigger to the Heme binding aptamer. We also show efficacy of a secondary method involving a conjugate between Heme and the signalling trigger to serve as a suboptimal target. The detection strategy is based on a decoupled approach between the electrochemical signalling surface and the molecular recognition surface, which is immobilized, on a 3D surface to enhance reaction kinetics and reduce mass transfer limitations. Further studies include Heme based displacement of the signalling trigger showing efficacy for the development of a sensor for the selective detection of Heme which will further the diagnostic value of this robust aptamer-based electrochemical sensor.

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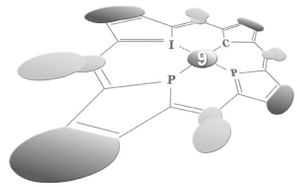
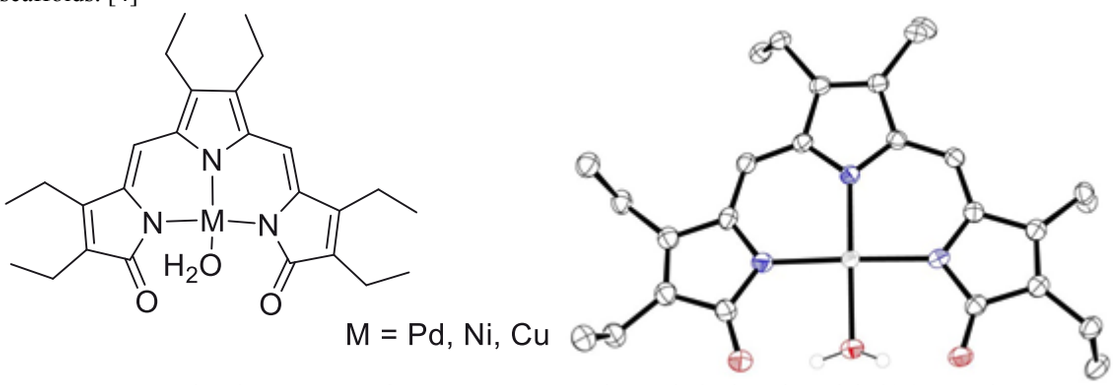


Metal complexes of Tripyrrindione - A non-innocent ligand

Stefanie Bahnmüller[a], **Prof. Dr. M. Bröring**[a]

[a] *University of Braunschweig ▫ Institute of Inorganic and Analytical Chemistry*

Tripyrrindiones represent a new class of tridentate dianionic *N,N,N*-pincer ligands which have a addressable redox activity in contrast to the closely related monoanionic ligand tripyrrin. [1]
The reaction of the hexaethyl derivative of tripyrrindione with a series of metal salts has given access to the corresponding neutral aquo metal(II) complexes with palladium, nickel and copper. These show a hypsochromic shift in the absorption spectrum due to the electron withdrawing carbonyl groups in both α-positions. [2] [3]
EPR-spectroscopic analyses of the corresponding aquo metal(II) complexes confirm the radical nature of the ligand and indicate the existence of a dimeric copper complex that has not been described before in similar ligand scaffolds. [4]



Molecular structure of aquo-2,3,7,8,12,13-hexaethyl-tripyrrine-nickel(II)-complexes.

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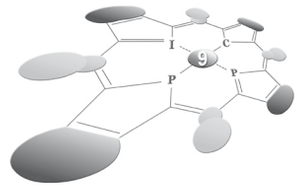

Enhanced Nonlinear Optical Responses of Zinc Diamino Pyrimidin-2-ylthio Phthalocyanine-Ag_xAu_y Composites

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The invention of modern lasers has promoted a growing interest in the development of optical limiting devices against laser-induced damage of light sensitive materials. The unique optical and electronic properties of phthalocyanines and metallic nanoparticles make them suitable candidates for photo-driven applications like nonlinear optics [1,2]. It is expected that composites of phthalocyanine-Au-Ag nano-alloys will give rise to materials with enhanced photophysical and optical limiting (OL) behavior compared to individual molecule. The present work describes for the first time the enhancement of photophysical and OL response of zinc diaminopyrimidin-**2**-ylthio phthalocyanine (**2**), in presence of Ag_xAu_y alloys. The conjugates of **2** and Ag-Au are termed **2**-Ag_1Au_3 and **2**-Ag_1Au_3 corresponding to the mole ratio of Ag and Au atoms in the alloy mixture. Figure 1, shows electronic absorption spectra of **2**, **2**-Ag_3Au_1, **2**-Ag_1Au_3 (in DMSO) and unconjugated Ag_3Au_1 and Ag_1Au_3 alloys (in hexane). No shifts in the Q-bands of **2** before and after conjugation to Ag_xAu_y.

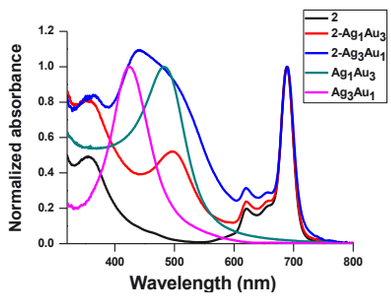

Fig. 1. Absorption spectra **2**, **2**-Ag_3Au_1, **2**-Ag_1Au_3 (in DMSO), Ag_3Au_1 and Ag_1Au_3 (in hexane).

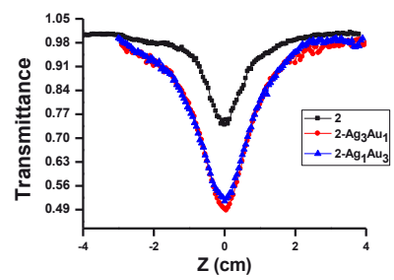

Fig. 2: OA Z-scan curves for evaluating β_{eff} for **2,** **2**-Ag_1Au_3 and **2**-Ag_3Au_1. I_{00} ~55.4 MW cm^{-2}, Absorbance = 0.5 in DMSO.

Optical limiting (OL) responses of the samples were evaluated using Z-scan at 532 nm and 10 ns in DMSO. Reverse saturable absorption (RSA), which is a direct consequence of triplet absorption of already excited molecules was observed as the dominant mechanisms for nonlinearity of the samples. **2**-Ag_xAu_y composites were found to exhibit stronger and better OL responses than **2**, Fig. 2. Large third-order susceptibility (2.14 x 10^{-9} and 2.60 x 10^{-9} esu) and β_{eff} (910.5 and 1108.8 cm GW^{-1}) were estimated for complex **2**-Ag_3Au_1 and **2**-Ag_1Au_3, respectively. β_{eff} increases in magnitude with positive slopes as the concentration increases suggesting direct relationship between the nonlinear optical responses and the concentration of each sample.

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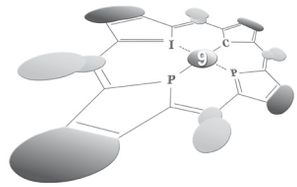

Equitorial Thioester Anchor – Towards Ordered Phthalocyanine Monolayers on Au(111)

Malcolm A. Bartlett[a], **Michael Kothe**[b], **Jörg Sundermeyer**[a] **and Gregor Witte**[b]

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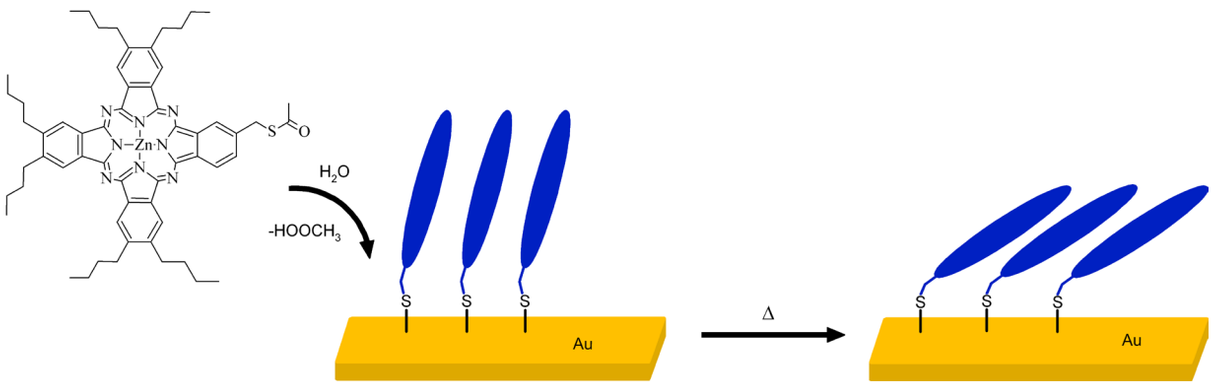
[b]*Philipps-Universität Marburg, Fachbereich Physik, 35032 Marburg, Germany, gregor.witte@physik.uni-marburg.de*



The understanding and tuning of charge transfer dynamics at interfaces is crucial for the efficiency of electronic devices based on organic molecules, and forms the basis for the current collaborative research centre of the DFG's "Sonderforschungsbereich" (SFB) 1083. In this context, we use functionalized phthalocyanines, which can be anchored to a gold substrate. This enables control of molecular orientation and electronic coupling and, thereby, on charge transfer dynamics.

A phthalonitrile derivative bearing a single thioester group was synthesised *via* an environmentally friendly and high-yielding radical bromination, and was co-cyclised with 4,5-di-^{n}butylphthalonitrile[1] and $Zn(OAc)_2$ to yield a mixture of isomers. Separation of the mixture involves chemical transformations, *viz.* salt formation and protection of the thiol group, which aid chromatographic separation to yield the desired complex.

We analyzed its ability to anchor covalently on the well ordered Au(111) surface by means of XPS while NEXAFS provided information on the molecular orientation. We determined that thiolate bonds are formed, but additional oxidized sulfur-species occur. The molecules are initially standing on the as-prepared sample and switch to a lying orientation upon heating in vacuum.

In conclusion, we have synthesised a zinc phthalocyanine that forms ordered monolayers on Au(111) surfaces; this allows for further studies of the charge dynamics at this metal-molecule interface.

Acknowledgement: We thank the DFG for funding within the SFB 1083 research cluster Marburg.

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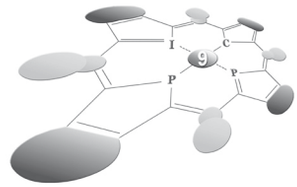

Isomeric, N-Substituted and Contracted Porphyrinoids: Tautomeric and Acid-Base Equilibria, Thermal and Acid Media Stability and Electrocatalysis by Metallocomplexes

Dmitry B. Berezin[a], **Vu Thi Thao**[a], **Olga V. Shukhto**[a], **Anastasiya E. Talanova**[a], **Nadezhda M. Berezina**[a], **Mikhail A. Krestyaninov**[b], **Alexander S. Semeykin**[a]

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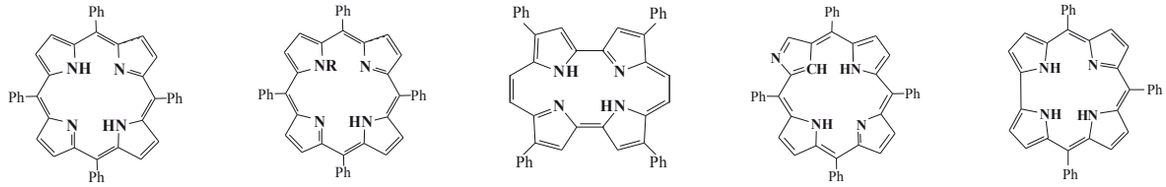
Porphyrin analogs are extensively synthesised and investigated compounds within last two decades. Their unique properties such as specific acid-basic and tautomeric equilibria, metal coordination ability, catalytic, sensor, optic properties are driven by unusual for common porphyrins (H_2P) asymmetrical structure of these molecules. These properties are different as differ individual structural features for porphyrinoids of various classes. The aim of this work is to compare some of them with H_2P of closely related structures. N-substituted {H(NR)P}, inverted {[^{2}N,^{21}CH]H_2P}, *ms*-bridge isomeric (porphycenes, H_2Por) and contracted (corroles, H_3Cor) porphyrin analogs bearing *meso*-aryl substituents are considered.



H_2P *H(NR)P* *H_2Por* *{[^{2}N,^{21}CH]H_2P}* *H_3Cor*

In contrary to H_2P many porphyrin analogs, for instance, inverted isomers, tend to both inner-cyclic tautomerism and inner-outer conversion. Meantime the first one is usually slowed or nearly blocked because of inner-cyclic H-bonds formation (H_2Pors, etc.). The series of compounds related to the ability for various tautomerism is: {H(N-R)P} < H_2Por < H_2P < H_3Cor < [^{2}N,^{21}CH]H_2P.

The main feature of acid-basic properties of porphyrinoids is the selective multi-centered reactivity; one of the reaction centers is normally much more basic or acidic in relation to anothers. So, basicity of porphyrinoids increases in the series: H_2Por < H_2P < H_3Cor < [^{2}N,^{21}CH]H_2P < H(N-R)P. This sequence determines the main property of aromatic macroheterocycles – an ability to the metal coordination, which also has the same regularity. As for thermodynamic stability of metalloporphyrinoids, it seems to change in other series of macroheterocycles: {(X)Zn(N-R)P} < Zn[^{2}N,^{21}CH]P < ZnPor < ZnCorH < ZnP, where common metalloporphyrins (MP) are the most stabilized. The thermal stability of studied complexes in a solid state is quite close and has the next tendency:{(X)M(N-R)P} < M[^{2}N,^{21}CH]P < MCor < MPor << MP.

The main feature of metalloporphyrinoids formation and dissociation is a difference in a size and composition of coordination centers which implies an ability to stabilize metals in different oxidation state {Co(II) or (III); Cu(II) or (III); Fe(II), (III) or (IV)} which can be lower or higher in relation to complexes of MP. This property of metalloporphyrinoids, in turn, plays a key role in electrocatalysis. Electrocatalitic function of d-metal complexes of porphyrin analogs in an indicator reaction of oxygen reduction is described by the following regularity of a half-wave potential $E_{O2}^{1\backslash 2}$ from the structure of the aromatic macrocycle, for instance: CoPor < CoP <{(X)Co(N-R)P} < CoCor.

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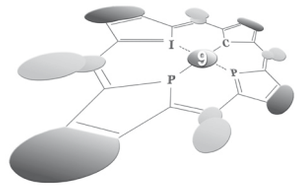

Coordination-Induced Contraction, Thiophene Inversion, Electron Configurational Isomerism, and More – 23-Thiaazuliporphyrin

Michał J. Białek, Lechosław Latos-Grażyński

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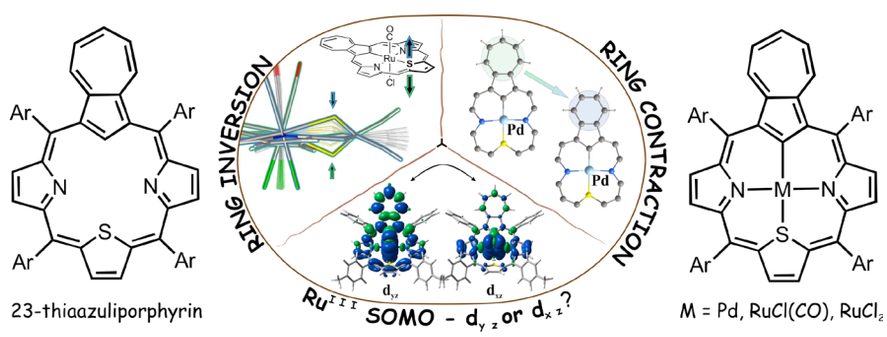
Azuliporphyrins, carbaporphyrin family members, pesented their versatility in exploration of electronic structures and unique coordination reactivity.[1,2] We continue to explore metal-carbon interactions stabilized by azuliporphyrin ligand.[3,4]

In presented studies[5] *meso*-tetraaryl-23-thiaazuliporphyrin (SAz) was synthesized using a simple [1+3] reaction between nonfunctionalized azulene and thiatripyrrane. The generated macrocyclic ligand possesses a singly anionic *CNSN* cavity, which significantly alters coordination properties in comparison to regular azuliporphyrin. **I**) An insertion of palladium(II) into SAz yields the cationic complex **[Pd(SAz)]**$^+$. An accumulation of positive charge on an azulene 7-membered ring induces the higher degree of macrocyclic aromaticity. The positively charged 7-membered ring is susceptible for nucleophiles attacks, which enables a transformation of palladium(II) 23-thiaazuliporphyrin to palladium(II) 23-thiabenzocarbaporphyrin counterpart. **II**) A six-coordinate ruthenium(II) of **[Ru^{II}(SAz)Cl(CO)]** acquires two different axial ligands - chloride and carbonyl. Consequently, the thiophene ring, tilted from the molecular plane, can be directed toward or outward of the axial chloride. Both conformational isomers were observed with variable temperature NMR and their unique transition through RuN_2C plane was also studied with DFT. **III**) A metal-centered one-electron oxidized product was also yielded - **[Ru^{III}(SAz)Cl$_2$]** - and exhibited the well-resolved ^{1}H NMR spectrum. The spin density delocalization was investigated in depth using DFT. Two different spin density patterns were obtained for $(d_{xz})^2(d_{yz})^1$ or $(d_{xz})^1(d_{yz})^2$ configurations and, when merged, revealed the important azulene participation in spin density delocalization fully correlated with NMR data.



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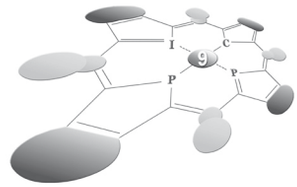

Poprhyrin-tetrakis Dithenylethene Scaffolds: Synthesis and Optical Switching Properties

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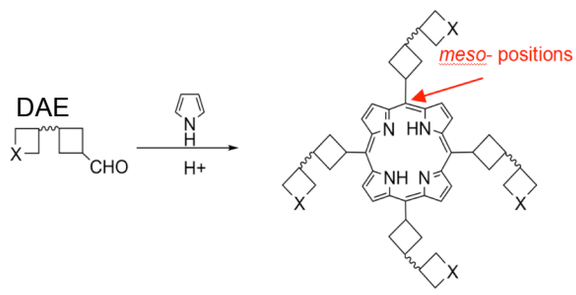
[a]*Institut de Chimie de Strasbourg (UMR 7177), Université de Strasbourg – CNRS, Strasbourg, France.*

Single molecular devices are essential to both the development of molecular electronics and extreme miniaturization[1] in order to enhance the density of information that could be treated or stored in molecular analogues of the actual silicon based devices. Because of the binary 1/0 treatment that is usually involved in the processing of any kind of information or signal by computers, molecular functions that can be switched on ("I") and off ("O") by an external stimulus have been the focus of attention over the last decade. A particular field that has expanded quickly and concerns the changes of geometry or conformation in molecules upon light irradiation or application of a redox potential.[2] We are developing new optically active molecular devices based on a porphyrin core substituted in meso- positions by various diarylethenes (DAE)[3] in order to study their interactions with magnetic surfaces as a function of the open or closed conformation of the DAEs.



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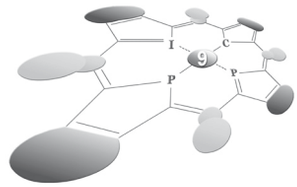

Selective Discriminating of Mercuric and Mercurous Ions with a Thiol-Functionalized Phthalocyanine

Ahmet T. Bilgiçli[a], M. Nilüfer Yaraşir[a], Mehmet Kandaz[a]*, Orhan Güney[b]

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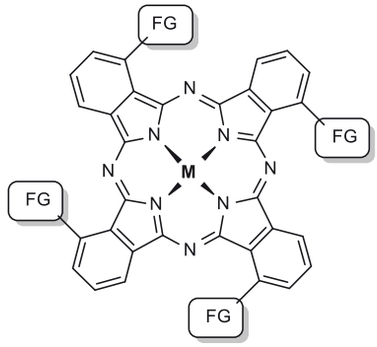
Mercury is one of the most dangerous and ubiquitous of pollutants in the global environment. It is derived from both natural sources and human enterprise, and exists in a variety of forms (elemental, inorganic, and organic mercury). Mercuric ion, Hg^{2+} much more common than mercurous ion, Hg^{+} is a caustic and carcinogenic material with high cellular toxicity[1-4]. Methylmercury, one primary form of organic mercury, can be formed naturally by biomethylation of mercuric ion in the aquatic environment. It is bio-accumulated in human body through biological food chains, and can cause brain damage and other chronic diseases[1-4]. Therefore, it is important to discriminate and monitor Hg^{2+} and Hg^{+} in many scientific fields, including medicine, environmental monitoring, etc.



In this work, the synthesis of a new zinc, cadmium phthalocyanines with thioalcohol functional substituents and detection of heavy metal ions were reported.

We thank to research funds of SAÜ (BAP-2015,02-04-001), and TUBİTAK (114Z448).

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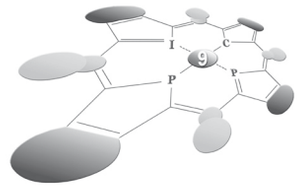

New phthalocyanines with thiol functional substituents for detection of heavy metal ions by induced aggregations

Ahmet T. Bilgiçli, Armağan Günsel, M. Nilüfer Yaraşır, Mehmet Kandaz

Department of Chemistry, Sakarya University, 54140 Esentepe, Sakarya, Turkey

Development of analytical tools for the detection of heavy metal ions has been a continuing endeavour. Efforts are ongoing to prepare rapid and inexpensive techniques for the detection of heavy metals. A number of popular current methods for detecting the presence of heavy metals require somewhat sophisticated analytical techniques, including atomic absorption spectroscopy, mass spectroscopy, X-ray fluorescence spectroscopy. However, these methods can be cumbersome and impractical for on-site testing and while they can be very precise, even in the ppt and ppq range, the instruments are often expensive to run. Therefore, the development of less expensive methods utilising smaller, more portable instruments for the sensitive detection of trace elements is desirable. The recognition of metals using an optical
response, which is seen upon a change in the environmental stimuli, is a well understood phenomena and the methods. The design and synthesis of a sensitive and selective fluorescent sensor molecule is a fundamental goal for organic and analytical chemists in fluorometric metal ion analysis. The development of practical fluorescent chemosensors for many heavy metal ions is still a challenge[1-3].
In this work, the synthesis of a new phthalocyanines (ZnPc, CdPc, NiPc and CoPc) with thiaalcohol substituents and detection of heavy metal ions were reported. A comparative study of the recognition property of the phthalocyanine derivatives for heavy metal ions have been carried out by absorption and fluorescence spectroscopy. Phthalocyanines exhibited spectral change in aggregation peak at UV-visible and fluorescence spectra upon complex formation with heavy metal ions. This means that heavy metal complexation with phthalocyanine derivative effects the concentration of monomeric units by causing intramolecular sandwich formation.

We thank to research funds of SAÜ (BAP-2015,02-04-001), and TUBİTAK (114Z448).

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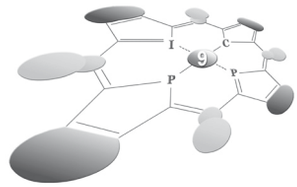

Spectroscopic Insights into Transient Heme Binding to Histidine- and Tyrosine-Based Protein Motifs

Hans Henning Brewitz[a], Nishit Goradia[b], Erik Schubert[c], Kerstin Galler[d,e], Toni Kühl[f], Ute Neugebauer[d,e], Jürgen Popp[d,g], Gregor Hagelüken[b], Olav Schiemann[c], Oliver Ohlenschläger[b] and Diana Imhof[a]

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Iron protoporphyrin IX (heme) is a co-factor of many important hemoproteins such as hemoglobin and catalases and acts as one of the major iron sources for pathogenic bacteria. During an infection enormous amounts of heme are required for bacterial growth. Therefore, bacteria developed sophisticated heme-acquisition and utilization systems including erythrocyte lysis and heme capture from host hemoproteins.[1] Due to the cytotoxicity of increased free heme levels, the cellular heme content requires strict regulation. In this context, heme acts as an effector molecule controlling e.g. transcriptional, biosynthetic and metabolic processes as has been observed in humans.[2] On a molecular basis, regulation is realized by transient heme association to small sequence stretches, named heme-regulatory motifs (HRMs), containing a heme iron coordination site such as cysteine, histidine and tyrosine.[2,3] However, electrostatic interactions, π-stacking and hydrophobic interactions of the porphyrin ring with adjacent amino acids relative to the coordination site considerably contribute to a sufficient ligand binding.[3-6] Since most of the HRMs described in the literature are cysteine-based,[2,5,6] we were particularly interested in histidine- and tyrosine-based motifs. We investigated heme-binding capacities of histidine- and tyrosine-based peptides derived from both, a high-throughput-screening[3] and a literature search. Most promising candidates were further investigated by NMR-, EPR- and resonance Raman spectroscopy to provide insights into the molecular basis and consequences of heme-peptide/protein interaction.[7] Using this knowledge we were able to predict and confirm heme binding to chloramphenicol acetyltransferase from *E. coli* as well as the inhibitory effect of heme on the enzyme activity.[7]

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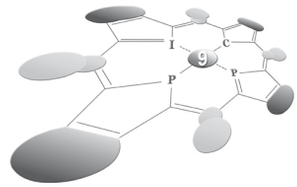

2D Nanostructures based on DNA-Porphyrin Hybrids

G. Chatelain,[a] C. Saint-Pierre,[b] D. Gasparutto,[b] and S. Campidelli[a]

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The use of DNA as support of information for the fabrication of supramolecular nanostructures has been extensively reported over the last decade. Different strategies were used for this purposes either based purely on oligonucleotides or by combining oligonucleotides with organic molecules. On the first hand, the approach based on pure oligonucleotide can be achieved using double crossover DNA strands[1] or *via* DNA origami.[2] The second strategy relies on the use of small organic molecules to define the angle in the nanostructures.[3] These organic molecules can be introduced in single stranded DNA (ssDNA) during its synthesis or functionalized afterward with functional DNA.
Recently, we reported the synthesis of porphyrin/DNA hybrids by copper-catalyzed *Huisgen* cycloaddition reaction (CuAAC). We synthesized four DNA/porphyrin derivatives (from the mono to the tetra adduct) containing a 14-mer single stranded DNA.[4] We tested the association of the tetra-adducts with gold nanoparticles, we proved this association but we realized that the formation of double stranded DNA using 14-mer oligonucleotides was not efficient enough under our hydridization conditions. In order to improve the stability and give rise to the formation of 2D nanostructure, we increased the number of bases of our ODN from 14 to 20.
Here, we report on the synthesis of two porphyrin/oligonucleotide polyadducts *via* CuAAC containing two complementary strands (**ODN-1**: 5'-GCA TTG GTA ACT GTC AGA CCU-3' and **ODN-2**: 5'-GGT CTG ACA GTT ACC AAT GCU-3') named respectively $\mathbf{P_n}$ (n = 1-4) and $\mathbf{P_{nc}}$ (n = 1-4). The hybrids were characterized by absorption spectroscopy and gel electrophoresis. The two complementary hybrids $\mathbf{P_4}$ and $\mathbf{P_{4c}}$ were associated to form a 2D nanostructure and studied by atomic force microscopy.[5]

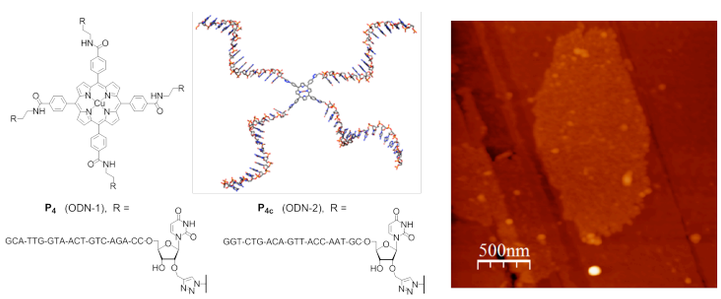

Figure. Representation of the tetra-adduct porphyrin-oligonucleotide hybrids and AFM image of a 2D nanostructure.

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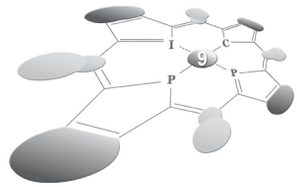

Recent Developments in the Synthesis and Characterization of N-Substituted Azacalixphyrins: A New Class of Porphyrinoids

Zhongui Chen[a], Lucien Lavaud[a], Gabriel Canard[a], Gabriel Marchand[b], Denis Jacquemin[b] and Olivier Siri[a]

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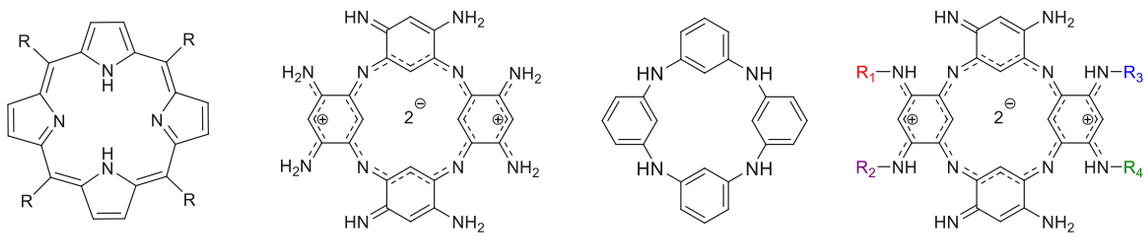
b) Université de Nantes, CEISAM (UMR 6230), 4322 Nantes, France and Institut Universitaire de France, 75005 Paris, France.

In 2013, the first "pyrrol-free" tetraaza-analogue of porphyrins (**1**) – named azacalixphyrin **2** – revealed unusual fundamental and applied aspects.[1] The preparation of **2** became possible thanks to recent developments on azacalix[4]arenes **3**, an emerging class of macrocycles in the calixarene family.[2] However, although azacalixphyrin **2** is a new extremely promising but yet unexplored macrocycle, its use appeared limited due its very poor solubility.



1 **2** **3** **4**

Herein, we wish to present the introduction of a series of typical N-substituents that modulates the absorption properties according to their nature and their position on the macrocycle. The substitutions were carried out at different stages of the synthesis, thereby introducing selectively different types of substituents on the peripheral nitrogen atoms and allowing the fine tuning of the properties (solubility, geometry, absorption...). Di- and tetra-substituted azacalixphyrins **4** with different substituents were developed for applications such as material science. The poster will present the mentioned syntheses and selected properties of the N-substituted azacalixphyrins.

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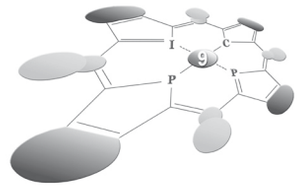

Realization of Three-Dimensional Aromaticity in Bridged Core-Modified Octaphyrin

Won-Young Cha, Taeyeon Kim, and Dongho Kim

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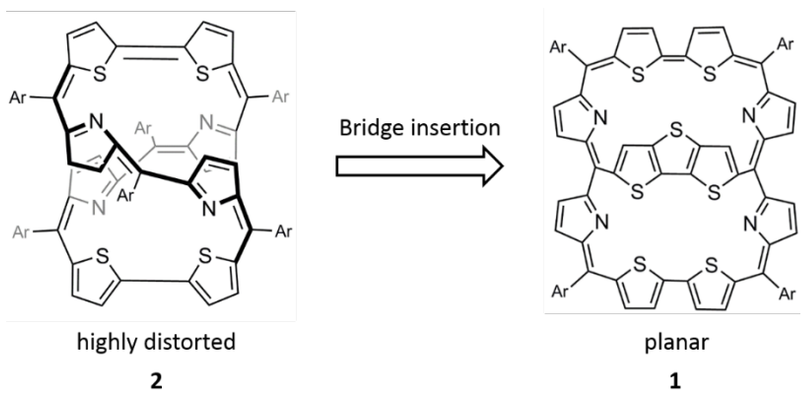
Over the years, a plenty of researches on the characterization of Hückel and Möbius (anti)aromaticity have been actively conducted by using various molecular systems. Recently efficient multiple π-electron delocalization can occur through allow effective three dimensional delocalization confronts a fascinating synthetic challenge.
In this respect, expanded porphyrins have attracted considerable attention from organic and physical chemistry due to their potential applications in light of their rich chemistry, especially such such as structural versatility and easy accessibility of [4n] and [4n+2] congeners for controlling the number of π-electrons through two-electron oxidation and reduction processes. Various modifications have been carried out on expanded porphyrins including core-modification and meso-meso connection with aromatic moieties. Throughout the studies on core-modifies and meso-bridged expanded porphyrins, we have observed the correlations between photophysical properties and three-dimensional aromaticity in measurements of the magnetic indices(chemical shift), temperature-dependent steady-state absorption and emission spectra, time-resolved excited-state dynamics, and computational calculations including NICS (nucleus-independent chemical shift), HOMA(harmonic-oscillator model for aromaticity) and AICD(anisotropy of the induced current density).



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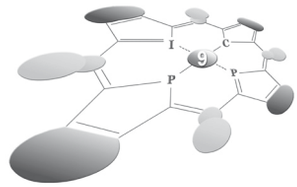

Formation of Self-assembled Artificial Antenna Nanostructures based on Diphenylalanine–Porphyrin Derivatives

Georgios Charalambidis[a], **Evangelos Georgilis**[b], **Anna Mitraki**[b], **Teodor Silviu Balaban**[c], **Athanassios G. Coutsolelos**

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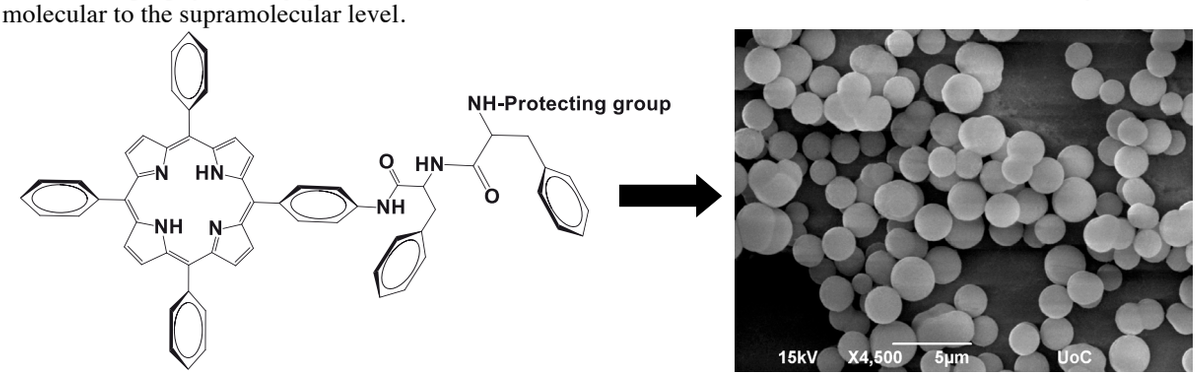
Artificial self-assembling light-harvesting systems are of interest in dye-sensitized solar cells where a large photon capture cross section can assure that efficient energy transfer occurs to a large band-gap semiconductor. Presently, all artificial antenna systems, either assembled *via* covalent syntheses as in elegant dendrimeric architectures, or the self-assembling BChl *c* mimics, lead to large architectures which are unable to be dismantled, once they were formed.[1] Self-assemblies of short peptides such as diphenylalanine [(*L*)F(*L*)F)] have been intensively studied in recent years and have shown promising luminescence or sensing applications.[2]
We have previously prepared diphenylalanine-porphyrin conjugates and have shown that these hybrid materials self-assemble upon drying into porous nanospheres.[3] By modifying the self-assembly conditions, and dissolving the porphyrin conjugates in dichloromethane which is then "injected" into a nonpolar solvent, we observed the formation of nanofibers. This porphyrin containing self-assembling antenna system can be reversibly assembled or disassembled by slightly changing only the solvent's polarity. Furthermore we synthesized the unnatural [(*D*)F(*D*)F]-porphyrin conjugate and have studied with circular dichroism the transfer of chirality from the molecular to the supramolecular level.



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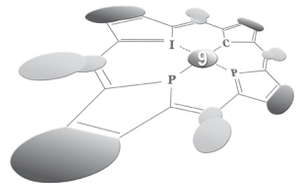

Facile Synthesis of Unsymmetrical *β*-substituted Porphyrins *via* Nucleophilic Substitution Reactions

Nivedita Chaudhri, Nitika Grover, Kumari Anshul and Muniappan Sankar

Department of chemistry, Indian Institute of Technology Roorkee, Roorkee-247667, Uttarakhand, India

The chemical transformation of *meso*-tetraarylporphyrins at the *β*-pyrrole positions has been explored as a way to prepare novel porphyrin derivatives for various biological and material applications.[1] The *β*-nitroporphyrins are versatile precursors to achieve such transformations due to their ease of synthesis and facile functionalization.[2] The *β*-functionalization by conjugate nucleophilic addition and substitution at 2-nitro-tetraarylporphyrins afford unique chlorin derivatives which further pay for new porphyrin derivatives under mild reaction conditions. Herein, we report the facile synthesis and characterization of 2,12,13-trisubstituted-5,10,15,20-tetraphenyl porphyrins, 2,12,13-trisubstituted-5,7,8,10,15,17,18,20-octaphenylporphyrins and their metal (Ni(II) and Zn(II)) complexes (Figure1a) *via* nucleophillic substitution reactions. Single crystal X-ray structure of $MTPPBr_2CH(COOEt)_2$ (M = Ni(II) and 2H) exhibited *ruffled* conformation of porphyrin core (Figure1b and 1c). The electronic spectral, photophysical and electrochemical redox properties of these porphyrins have been tailored by introducing various active methylene substituents at the *β*-pyrrole position. In this presentation, we will discuss about the regioselective synthesis, photophysical and electrochemical redox properties of unsymmetrical *β*-susbtituted porphyrins in detail.[3]

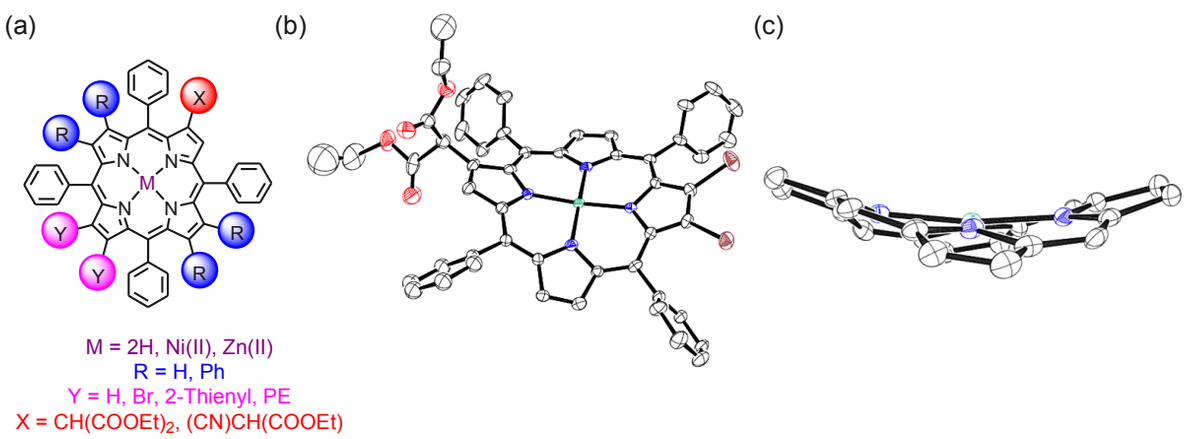

Figure 1 (a) Molecular structures of *β*-substituted-*meso*-tetraphenylporphyrins. ORTEP diagrams showing (b) top and (c) side views of $NiTPP(CH(COOEt)_2)Br_2$.

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3. N. Grover, N. Chaudhri, K. Anshul and M. Sankar (*Submitted for publication*).

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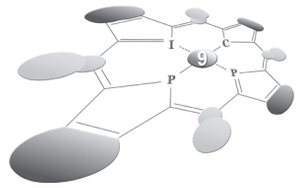

Colorimetric "Naked-eye" Selective Detection of CN^- ions by Porphyrinic Chemosensors and Chemodosimeters

Nivedita Chaudhri, Ravi Kumar, Mandeep K. Chahal and Muniappan Sankar

Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee-247667, India

CN^- is one among the toxic anions; even as little as 0.5 - 3.5 mg cyanide per kg of body weight is lethal to humans where it binds with cytochrome c inside the cells and interferes the mitochondrial electron transport chain, thus inhibiting cellular respiration causing hypoxia.[1a] Despite their toxicity, their outstanding applications in various industrial processes are inevitable which raises the risk for accidental or intentional release of cyanide ions into environment as a toxic contaminant. Nowadays, the most attractive approach focuses on highly selective colorimetric CN^- sensors, which allows "naked-eye" detection of CN^- ions by means of color change.[1b-c]

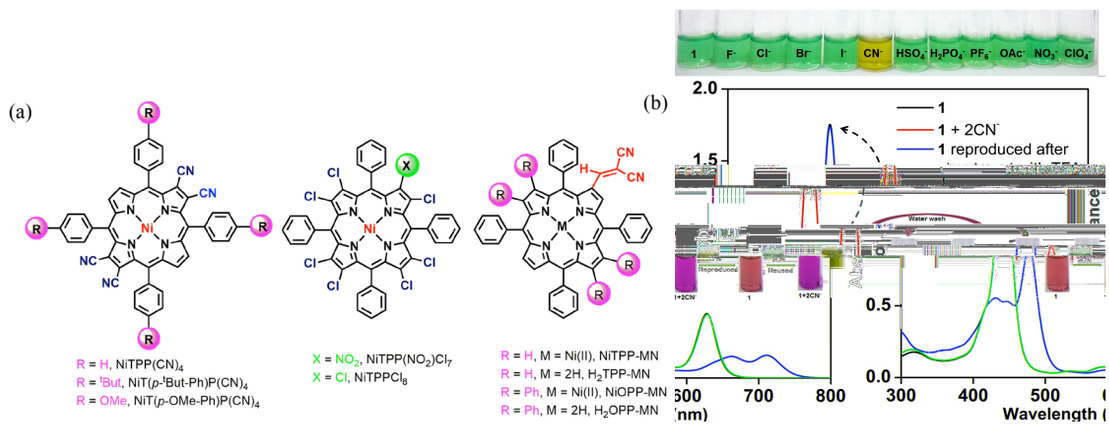

Figure 1. (a) Molecular structures of β-substituted porphyrinic sensors; (b) the colorimetric response and reversibility studies of $NiTPP(CN)_4$ with tested anions in toluene at 298 K.

In general, square planar Ni(II) porphyrins exhibited very weak axial ligation and extremely low binding constants (β_2 = 0.3 - 38 M^{-2}) with nitrogenous bases. Herein, we are presenting an easy, rapid, selective colorimetric detection of cyanide ions by highly electron deficient planar and nonplanar β-substituted Ni(II) porphyrin chemosensors. The β-cyano porphyrins exhibited extremely high binding constants (10^{16} - 10^{12} M^{-2}) (Fig. 1a) through axial coordination.[2a] These sensors can be recoverable from porphyrin•$2CN^-$ adduct by acid treatment and reused without loss of their sensing ability (Fig. 1b). Further, the dicyanovinyl appended β-substituted porphyrins have also been utilized as chemodosimeters for ratiometric and selective sensing of cyanide ions.[2b]

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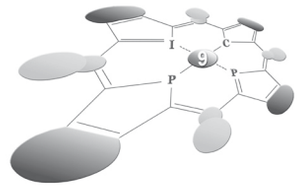

Modulation of Peripheral Substituents of Cobalt Thioporphyrazines and their Photocatalytic Activity

Lianqing Chen, Quan Zhou, Xu Shuai, Changjun Yang*, Kejian Deng

Key Laboratory of Catalysis and Material Sciences of the State Ethnic Affairs Commission & Ministry of Education, College of Chemistry and Material Sciences, South-Central University for Nationalities, Wuhan, 430074, China. Tel: +8627-67843930; Fax:+8627-67842752; E-mail: lqchen@mail.scuec.edu.cn;

Thioporphyrazine exhibited a high thermal stability and unique photocatalytic activity for activating H_2O_2 and O_2 [1]. Herein, the molecular structure of thioporphyrazine through modulation of peripheral substituents so as to define the final photocatalytic activity. A series of thioporphyrazines have been synthesized via cocondensation from 2,3-dicyano-1,4-dithiin (A) and 2,3-bis(butylthio) maleonitrile (B) and thoroughly characterized with UV-Vis, ^{1}H-NMR and MALDI-TOF MS. Through modulation of peripheral substituents of thioporphyrazines, both symmetrical and asymmetrical molecular structures in thioporphyrazines including B_4, *cis*-A_2B_2, *trans*-A_2B_2 and AB_3 were obtained, and were further used to react with cobalt acetate to form metal complexes, cobalt thioporphyrazines. Moreover, they were loaded on Al_2O_3 to form biomimetic catalysts for the photocatalytic activation of dioxygen, whose efficiencies were assessed by photodegradation of Rhodamine B (RhB) in an aerated suspension unde visible light irradiation. Importantly, it was found that the lower on the molecular symmetry of thioporphyrazine delivers the better on the photocatalytic activity. Electrochemical and theoretical studies demonstrated that lowering the molecular symmetry of the cobalt thioporphyrazines moderately decreased the HOMO-LUMO energy gap and increased the contribution of S atom in substitiuents to HOMO so as to enhance the photocatalytic activity. A possible mechanism to predict this reaction pattern was proposed through both detailed analysis of degradation products by HPLC and detection of the main reactive oxygen species (ROS) by ESR, indicating both energy transfer (major) and electron transfer (minor) to dioxygen to exist in the heterogeneous visible light photocatalytic system.

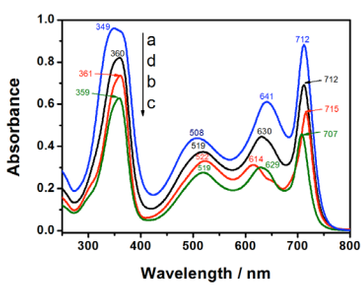

Figure 1. UV-Vis spectra of metal-free thio- porphyrazines in CH_2Cl_2.

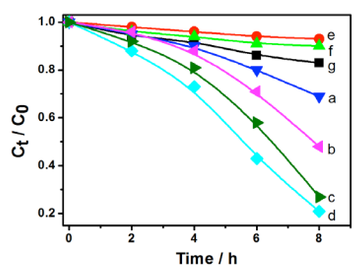

Figure 2. Comparative experiments on the photocatalytic degradation of RhB at pH 4. a: CoB_4@Al_2O_3/air/light; b: *trans*-CoB_2A_2@Al_2O_3/air/light; c: *cis*-CoB_2A_2 @Al_2O_3/air/light; d: CoB_3A@Al_2O_3/air/light; e: CoB_3A@Al_2O_3/N_2/light; f: CoB_3A@Al_2O_3/air/dark; g: air/light.

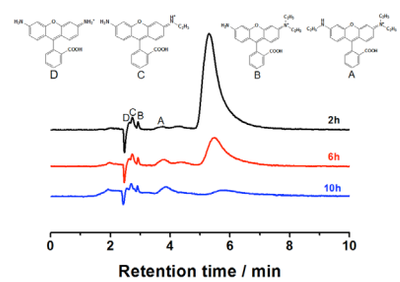

Figure 3. The HPLC changes of photocatalytic degradation of RhB (1×10^{-5} M) with different interval for 10h irradiation in an aerated suspension of pH 4 and in the presence of CoB_3A loaded on Al_2O_3 with loading amount of 4.0‰.

Acknowledgement: This work was financially supported by NNSFC(Nos. 20977115 and 21272281), the S&T Plan Innovation team for of Wuhan city (2015070504020220).

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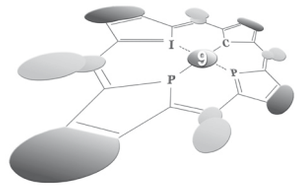

Nitrogen and sulfur co-doped anatase-phase TiO_2 hollow boxes with enhancing visible photocatalytic performance

Linbo Xie, Quan Zhou, Yufeng Huang, Xuan Zhao, Kejian Deng, Lianqin Chen*

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Owing to its chemical stability, nontoxicity, and low cost, TiO_2 has been recognized as an attractive photocatalyst for air and water purification, and solar energy conversion. TiO_2 as perfect semiconductor, it has a high photocatalytic activity under UV light, the electrons are arouses from the valence band to the conduction band form electron-hole pair under the UV light. However, due to the electron of TiO_2 are difficult arouse under visible light, and the electron-hole pair have high recombination rate lead to low utilization. So its limited photo catalytic activity in the visible light region, which is still one of its main drawbacks. In order to enhancing the TiO_2 utilization ratio in the visible light, we using $TiOF_2$ as precursor and DL-Methionine as nitrogen and sulfur source, through one-step calcinate synthesis of the nitrogen and sulfur co-doped anatase-phase TiO_2 hollow boxes(N, S-co-doped TiO_2) with different proportion of DL-Methionine of photocatalytic materials. The synthesized photocatalysts are characterization by TEM, SEM, XRD, UV-Vis DRS, XPS; and theirs activity were evaluated though photodegradation Rhodamine B(RhB) under the visible light irradiation. The photodegradation results indicate the N, S-TiO_2 photocatalyst exhibited the highest activity in the photodegradation reaction tests of RhB under visible light irradiation and the degradation rate is 60.82%. What's more, the 5-recycles test showed that N, S-TiO_2 photocatalyst could be reused and its activity kept stable.

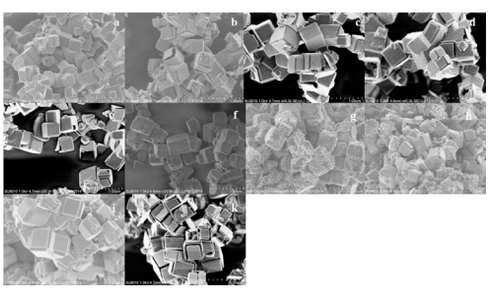

Fig. 1 The SEM of samples

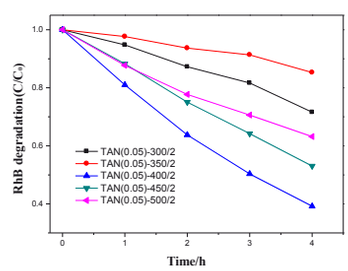

Fig. 2 RhB photodegradation

Acknowledgements: this work was supported by National Natural Science Foundation of China (No. 20702064, 21177161and 31402137), Hubei Province Science Fund for Distinguished Yong Scholars (2013CFA034).

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Preparation and enhancing photocatalytic performance of gold schottky embedded TiO_2 Hollow boxes

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The problem of energy shortage and environmental pollution has attracted wide attention, global's environmental pollution is very serious, environmental issues need to be resolved. Titanium dioxide, as a safe, non-toxic, friendly semiconductor material, has been got more and more attention and research. As we all know, TiO_2 has a larger band gap and it can not respond in the visible light range. And noble metal deposition can not only expand the range of the optical response of titanium dioxide, but also form Schottky barrier between the metal-semiconductor boundaries, which can effectively restrain the recombination of the carriers. In this paper, the photocatalytic activity of titanium dioxide was improved by the typical noble metal gold modified. The gold schottky embedded TiO_2 hollow boxes with different sizes nanoparticles was prepared by deposition-calcination method. The photocatalysts materials use XRD, TEM, SEM, DRS and XPS characterization, and the photocatalytic performance evaluation test though degradation RhB under visible light illumination. The experimental results show that the photocatalytic materials have high catalytic activity under visible light, and the catalytic activity increases with the decrease of the size of the gold nanoparticles.

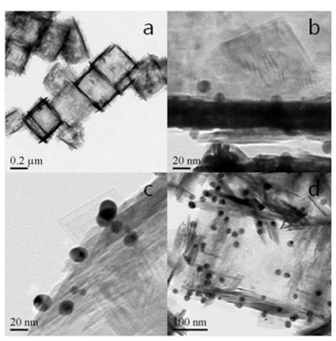

Fig. 1 The TEM of samples

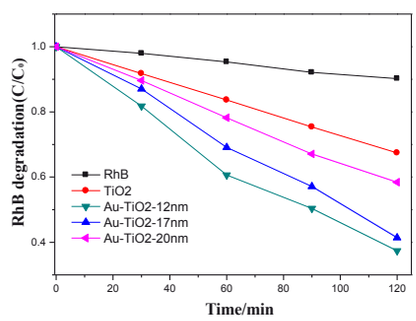

Fig.2 RhB photodegradation

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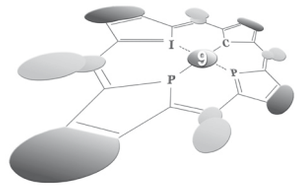


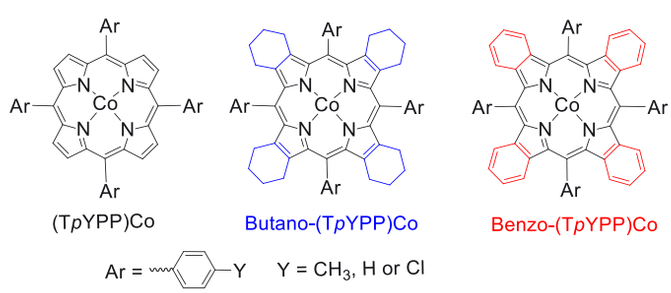
Nonplanar cobalt tetrabutano- and tetrabenzo-tetraaryl-porphyrins: Synthesis, electrochemistry and catalytic activity for reduction of molecular oxygen in acid media

Minyuan Chen[a], Lina Ye[a,b], Weijie Xu[a], Yuanyuan Fang[a], Zhongping Ou[a]*, Yang Song[c], Karl M. Kadish[c]*

[a]*School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China*
[b]*College of Computer, Jilin Normal University, Siping, China*
[c]*Department of Chemistry, University of Houston, Houston, TX 77204-5003 USA*

Three series of cobalt tetraarylporphyrins with general formula of (T*p*YPP)Co, butano-(T*p*YPP)Co^{II} and benzo-(T*p*YPP)Co^{II} (Chart 1) have been synthesized characterized by UV-vis spectroscopy as well as electrochemistry and spectroelectrochemistry. The T*p*YPP represents a dianion of the *meso*-substituted porphyrin, Y is a CH_3, H or Cl substituent on the *para*-position of the four phenyl rings, butano and benzo are the β,β'–substituted groups on each pyrrole ring of the compound. Each porphyrin undergoes three reversible oxidations and one or two reductions in CH_2Cl_2 and PhCN containing 0.1 M TBAP. The first electron addition and first electron abstraction of each Co(II) porphyrin are both mainly metal-centered to generate a Co(I) and Co(III) porphyrins. Each compound was investigated as catalyst for electoreduction of dioxygen when adsorbed on a graphite electrode in 1.0 M $HClO_4$. The number of electrons transferred (*n*) during the catalytic reduction was 2.0 for (TPP)Co and the butano-(T*p*YPP)Co^{II} derivatives, consistent with only H_2O_2 being produced as a product of the reaction. Other investigated monomeric T*p*YPP and benzo-T*p*YPP type of cobalt porphyrins exhibit *n* values between 2.4 and 3.1 under the same solution conditions, giving a mixture of H_2O and H_2O_2 as reduction products. The results indicate that both the meso- and β-substituents have significant effect on the catalytic activity of the porphyrins for reduction of dioxygen in acid media. Support from Jiangsu Province Ordinary University Graduate Student Research Innovation Project (KYLX-1064), Natural Science Foundation of China (21501070) and Foundation of Jiangsu University (15JDG131, 05JDG051).

Chart 1. Structure of examined catalysts



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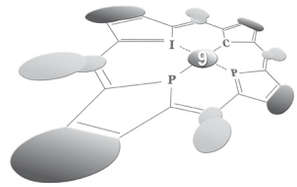

Push-Pull Phthalocyanine-Based Photosensitizers for Dye-Sensitized Solar Cells

Xiao-Fei Chen and Dennis K. P. Ng*

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Dye-sensitized solar cells (DSSCs) have emerged as promising alternatives of traditional silicon-based solar cells.[1] Being a key component, the photosensitizer plays a crucial role of electron injection to the semiconductor upon photoexcitation. Various classes of dyes have been explored as photosensitizers for DSSCs and to date the highest solar-to-electric power conversion efficiency (PCE) is achieved by the porphyrin-based photosensitizer **SM315**.[2] The introduction of a donor and an acceptor/anchoring group at the opposite *meso* positions of porphyrin allows the construction of a donor-π-acceptor structure and facilitates the electron injection to the TiO_2 electrode.

As porphyrin analogues, phthalocyanines are also promising photosensitizers which exhibit intense absorptions in the UV-visible region (ca. 350 and 670 nm for the Soret and Q bands, respectively), and their HOMO and LUMO levels are suitable for both electron injection to the TiO_2 and dye regeneration by the electrolyte. Despite with all these advantages, the performance of phthalocyanine-based photosensitizers is still lower than that of porphyrins so far due to their intrinsic strong aggregation tendency and lack of electron directionality caused by the large conjugated macrocycle. To circumvent the aggregation problem, bulky substituents have been introduced to the peripheral or axial positions of the phthalocyanine core.[3] Due to synthetic difficulties, the push-pull strategy that is commonly utilized for porphyrin photosensitizers has barely been realized in the phthalocyanine counterparts. We report herein the design and synthesis of a series of non-aggregated push-pull phthalocyanines in which the donor and acceptor/anchoring group lie at the opposite sides of the macrocyclic core, as well as their performance in DSSCs.

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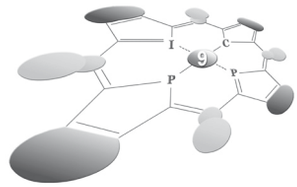

Synthesis of the First ABCD-Type Phthalocyanine *via* Intramolecular Cyclization

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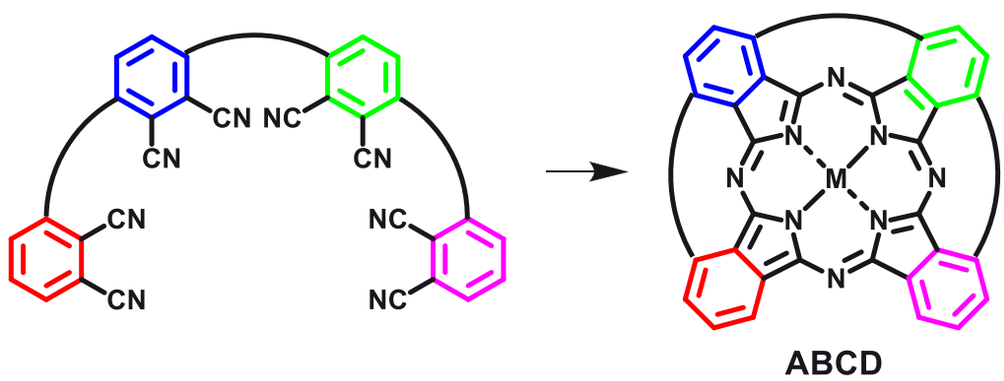
Phthalocyanines (Pcs) were accidentally discovered and subsequently characterized in around 1930.[1] Traditionally, their syntheses involve cyclotetramerization primarily of phthalonitriles, but also of a variety of other precursors.[2] The high thermal stability and favorable optoelectronic and photophysical properties of Pcs have enabled them to find practical applications in various disciplines, such as photoelectric devices, optical recording and limiting materials, and photodynamic therapy.[3] However, symmetric Pcs do not always provide the optimal properties for these applications. Hence, low-symmetry Pcs have received considerable attention.[2,3] The most commonly used synthetic method involves cross condensation of two different precursors, from which A_3B-type Pcs could be prepared readily by careful selection of precursors and adjusting the stoichiometric ratio of the reactants.[2] Several other strategies have also been used to control the sequence of the four isoindole units, including using pre-formed "half-phthalocyanine", introduction of steric control, and using pre-linked bisphthalonitrile.[4] Herein, we present the synthesis of the first example of ABCD-type phthalocyanines *via* a novel intramolecular cyclization reaction of a pre-linked tetrakisphthalonitrile. By optimizing the reaction conditions, this compound can be prepared in 7.2% yield.



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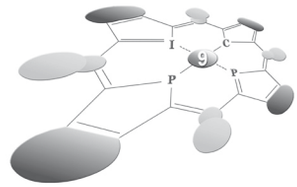

In depth analysis of photovoltaic performance of chlorophyll derivative-based "all solid-state" dye-sensitized solar cells

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Photovoltaic devices are currently the subject of intense research for low-cost conversion of sunlight into electrical power. In particular, dye-sensitized solar cells (DSSCs), which relies on the dye-sensitization of a semiconductor band gap (TiO_2, ZnO…) have emerged as a promising third-generation photovoltaic technology, leading to efficiencies of up to 13%.[1,2] Despite these good performances, they still require improvements due to several disadvantages such as the corrosive liquid electrolyte and their costly production (mainly due to the dye). In this context, natural dyes and their organic derivatives are ideal candidates for photovoltaic devices since they are non-toxic, low in cost, renewable and abundant.[2]
Based on this strategy, we focus here on the development of chlorophyll *a* derivatives as sensitizers to achieve solar energy conversion. Chlorophyll *a* can be easily and safely extracted from spirulina (~ 13 g/kg), an algae widely used as food supplement. The chlorophyll *a* derivatives were then integrated in "all solid-state" DSSCs to avoid the use of the liquid electrolyte which causes serious problems such as electrode corrosion and electrolyte leakage. In order to provide a comprehensive understanding of some parameters (structure, nature of the anchoring group, adsorption…) and their relation with the device photoconversion efficiency, a combination of TD-DFT calculations, quartz crystal microbalance with dissipation monitoring (QCM-D) measurements and optical and photovoltaic studies was performed.

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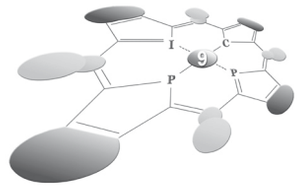

Electrochemical and spectroelectrochemical studies of phenylethynyl β-substituted corroles and porphyrins

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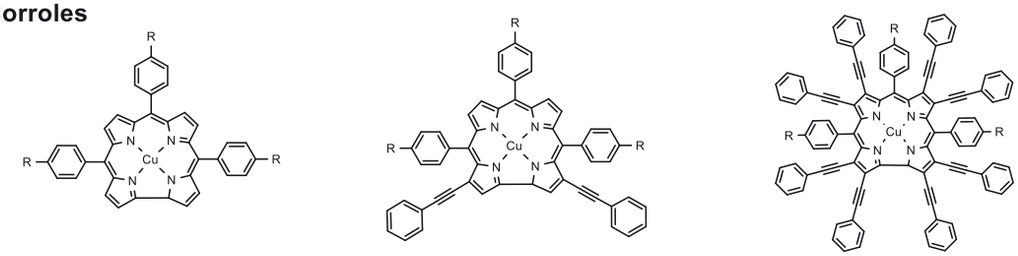
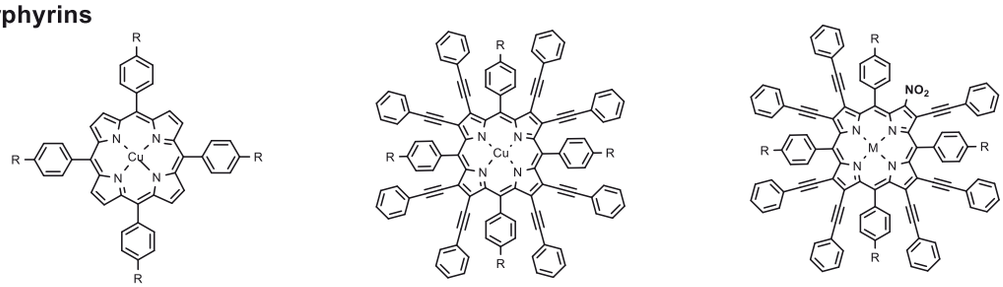
A series of phenylethynyl b-substituted metallocorroles and metalloporphyrins were investigated as to their electrochemical and spectroelectrochemical properties in nonaqueous media. Selected structures of the examined compounds are shown in Chart 1. Each phenylethynyl substituted corrole and porphyrin was shown to undergo multiply redox reactions, some of which involved the conjugated π-ring system and others the central metal ion. The potential for each redox reaction was measured by cyclic voltammetry and the UV-visible spectra were elucidated after oxidation and reduction by thin-layer UV spectroelectrochemistry.

Corroles



CuCor CuCor(PE)$_2$ CuCor(PE)$_8$

Porphyrins



CuPor CuPor(PE)$_8$ MPor(PE)$_8$

M = Ni, Cu, Zn, Co, 2H
R = CH_3, H

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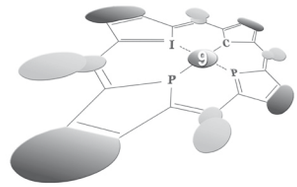

Ultrafast energy transfers in bis-porphyrin dyads

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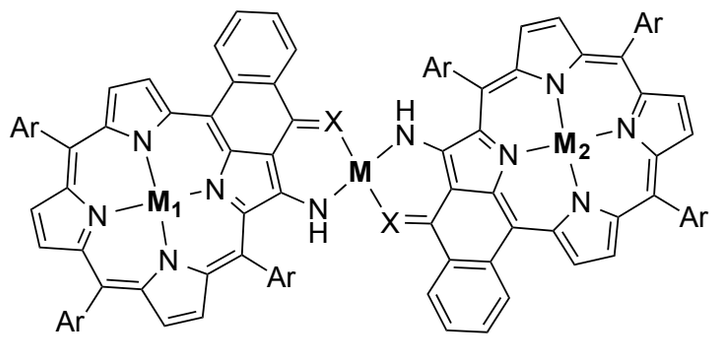
Energy and electron transfers are key photophysical events in photosynthetic bacteria and plants. Synthetic models for these processes often use covalent linkers between the individual chromophores. Several metallo-bridged homo- and hetero-oligoporphyrins are reported in the literature and some of them showed significant electronic communication between the subunits.[1-3] Recently, we have reported an ultrafast energy transfer in bis-porphyrin dyads held together by a palladium(II) linker.[4] New homodimers and dyads are herein reported where platinum(II) is used as linking ion. Their electrochemical and photophysical properties, supported by DFT calculations, are described and compared with earlier results. An increase in the electronic coupling has been evidenced when replacing the Pd(II) bridge with Pt(II) and the fastest singlet energy transfer ever recorded has been measured for the (Zn)porphyrin-(Fb)porphyrin dyad (~100 femtoseconds).



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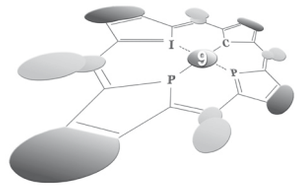

Synthetic strategy for preparation of corrole or porphyrin DOTA complexes as potential bimodal contrast agents in medical imaging

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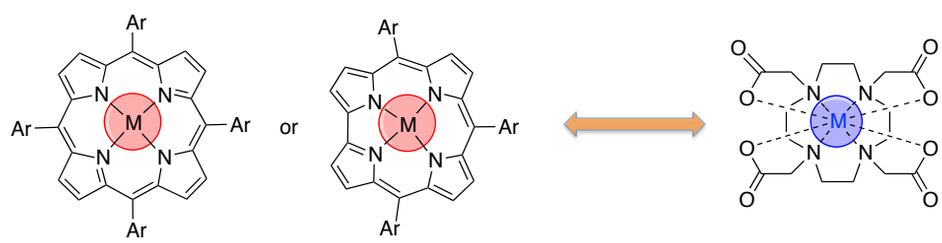
Magnetic resonance imaging (MRI), positron emission tomography (PET) or single photon emission computed tomography (SPECT) are actually the most commonly used imaging modalities. In the last decade, the concept of coupling different imaging modalities to exploit the complementarities between each technique has emerged. In this work, we have designed new multimodal porphyrinoids-DOTA-like agents incorporating different metals ions *e.g.* Mn, Ga, In and Gd of potential interest in medical imaging.[1-4] The preliminary relaxivity measurements show that the developed complexes are promising medical imaging agents for contrast enhancement in MRI techniques. These compounds can be also grafted onto folic acid derivative for biovectorization.



	Porphyrin/Corrole	DOTA
Bimodal contrast agents	Cu (PET) Ga (PET) In (SPECT) Mn (MRI)	Gd (MRI) Gd (MRI) Gd (MRI) Ga (PET)

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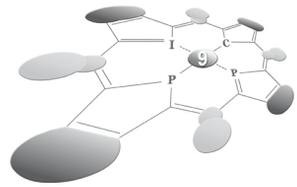

Design of porphyrins as G-quadruplex ligands

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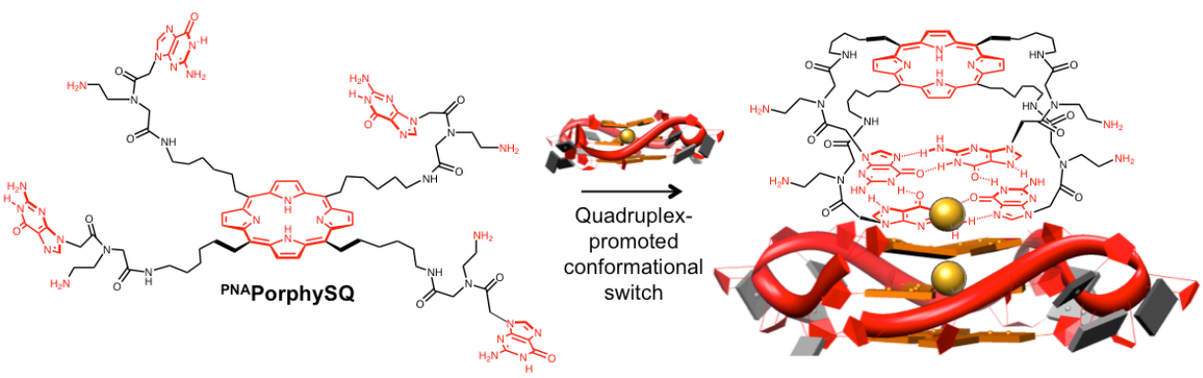
The recent demonstration of the existence of G-quadruplex DNA in human cells[1] is giving much impetus to the quest of efficient G-quadruplex ligands as promising therapeutic agents. We recently developed PorphySQ (for *Porphyrin-templated synthetic G-quartet*),[2] one of the first prototypes of biomimetic G-quadruplex ligands. Our strategy exploited the nature-inspired self-association of G-quartets, one native (from quadruplexes), one synthetic (from the ligand), responsible for the high G-quadruplex stability. PorphySQ provided the proof-of-concept that synthetic G-quartet might act as valuable quadruplex ligands, but displayed perfectible quadruplex-affinity and water-solubility. We thus developed ^{PNA}PorphySQ bearing guanines with amine pendant arms whose protonation at physiological pH improved both DNA affinity (on electrostatic basis) and solubility. ^{PNA}PorphySQ was one of the first prototypes of smart quadruplex ligands,[3] experiencing a quadruplex-promoted structural switch that ensures high affinity and selectivity. We also developed TEGPy,[4] an amphiphilic porphyrin whose higher-order assemblies disassembles upon interaction with quadruplexes only, thus being actively selective for its target.



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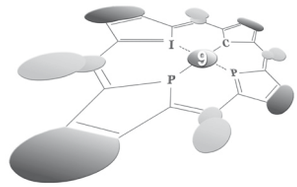

Aromatic Nucleophilic Substitution of *meso*-Nitroporphyrin with Azide and Amines

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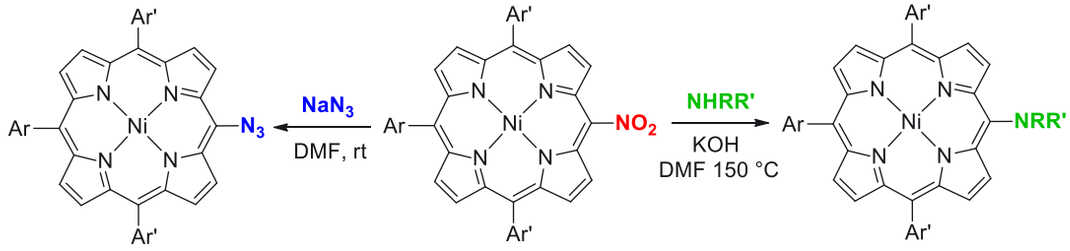
The grafting of a nitrogen atom at the periphery of the porphyrin core is a relatively well explored field since the conjugation of nitrogen induces new interesting electronic properties to exploit. Synthetic routes leading to nitrogen-substituted porphyrins consist in the chemical transformation of amino porphyrins[1] or the transition-metal catalyzed C-N (amine or amide) bond formation from haloporphyrins.[2] However, transition metal catalysts are sometimes expensive or not easily available. We will present herein the very simple S_NAr reaction of *meso*-nitroporphyrin (see Scheme below) with azide and amines to obtain the corresponding *meso-N*-functionalized porphyrin derivatives in fair to good yield.[3] It should be noted that this transformation was developed in parallel by Zhu, Zheng and co-workers for sulfur-, oxygen- and carbon-based nucleophiles.[4] Though *meso*-azidoporphyrin is not very stable, its crystallographic X-ray structure has been obtained and its reactivity towards Huisgen cycloaddition was tested. Besides, primary or secondary amines, aryl or alkyl amines, bearing electron-withdrawing or electron-donating groups have been successfully grafted at the *meso* position of the porphyrin core. Of particular interest is the possibility to synthesize very easily diporphyrinylamines using stoichiometric amount or slight excess of amino-porphyrins.



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Anodic Reactivity of Zinc(II) and Nickel(II) Tri-*Meso*-Aryl-Porphyrins with One *Meso*-Free Position

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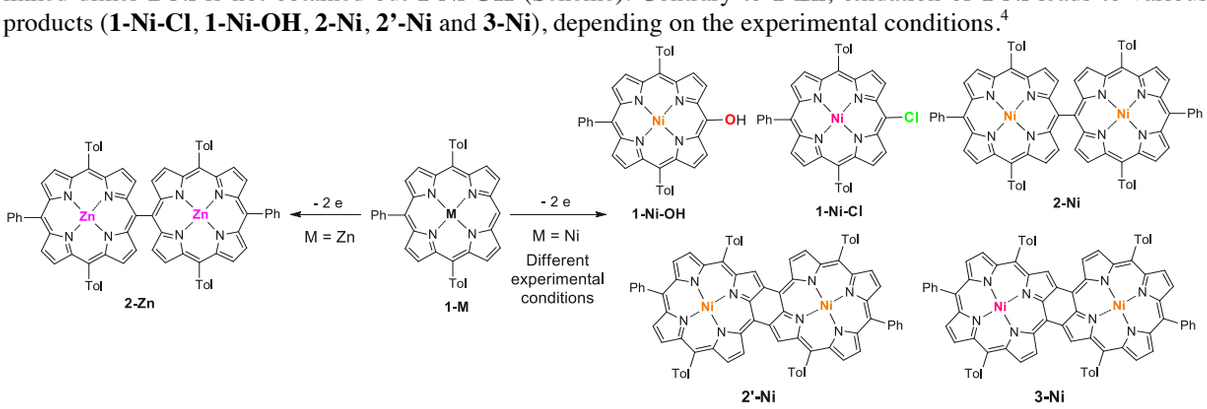
For many decades, porphyrins have been the subject of intense researches due to their versatile and outstanding physico-chemical properties and also to their implication in essential natural processes like photosynthesis, blood oxygen transport. One of our research fields is focused on the electrochemical functionalization of porphyrins. In particular, our work was first concentrated on the oxidative reactivity of magnesium(II) porphine, the fully unsubstituted porphyrin, in the presence of nucleophiles.[1] The efficient functionalization of the porphine ring was only performed in the presence of large excesses of nucleophiles since, with lower amount, a competition between functionalization and polymerization occurred. Besides, mechanism studies of the oxidative coupling were very difficult due to the presence of four *meso*-free reactive positions leading to a very rapid polymerization process.[2] To decrease the oxidative reactivity of the porphyrin core, three *meso*-position have been blocked with aryl substituents. We will present herein the anodic reactivity of zinc(II) and nickel(II) complexes **1-Zn** and **1-Ni** in presence or in the absence of nucleophiles (Scheme).
Thus, anodic oxidation of **1-Zn** leads to the *meso-meso* singly linked dimer **2-Zn** in nearly quantitative yield, after optimization of the experimental conditions.[3] In the same conditions, starting with **1-Ni**, the *meso-meso* singly-linked dimer **2-Ni** is not obtained but **1-Ni-OH** (Scheme). Contrary to **1-Zn**, oxidation of **1-Ni** leads to various products (**1-Ni-Cl**, **1-Ni-OH**, **2-Ni**, **2'-Ni** and **3-Ni**), depending on the experimental conditions.[4]



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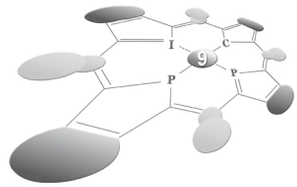

Mechanothermal control of the conformation of a small molecule

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The ability to control the conformation of small molecules using external stimuli, particularly mechanical force, is an intriguing, yet fairly unexplored area of research, with potentially far-reaching applications in a variety of fields. This contribution provides an example of the use of mechanical force, in conjunction with temperature, to modulate the conformational bias of a small molecule. Specifically, the conformational change (from the twisted to planar state) of a porphyrin dimer in a polyvinyl alcohol film upon stretching with and without heating is described.

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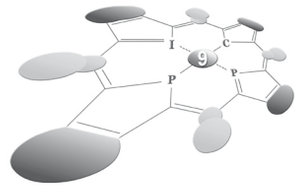

Synthesis, Characterization and Electrochemistry of meso-Substituted [14]Triphyrin(2.1.1) Rhenium(I) complexes

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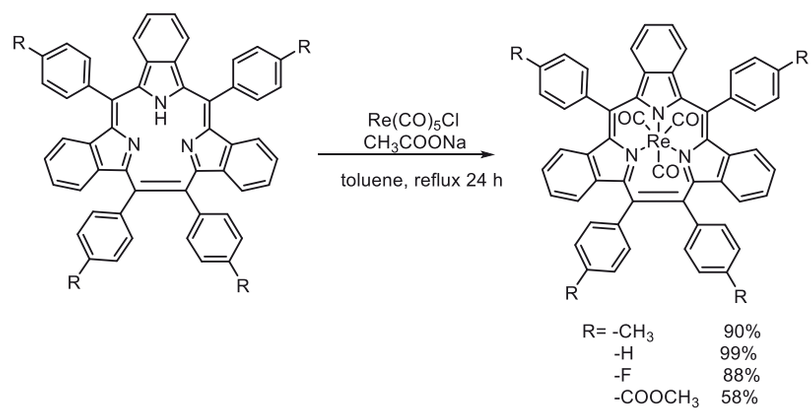
School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China

Subporphyrin which composed by three pyrrole rings linked with four meso-sp^2 carbon atoms is a 14-π-electron aromatic conjugated system. A facile synthesis of meso-aryl-substituted free-base [14]triphyrin(2.1.1) (TriP) by a modified Lindsay method was reported in 2008.[1] Over the past years, some groups have been already synthesized several kinds of [14]triphyrin(2.1.1) metal complexes such as ruthenium(II), platinum(II), platinum(IV), manganese(I), iron(II), iron(III) and palladium(II).[2-4] Here we want to report the synthesis, structural and electrochemical properties of TriP rhenium(I) tricarbonyl complexes (Scheme 1). These compounds were characterized by ^{1}H NMR spectroscopy, IR Spectra, UV absorption spectrum, X-ray crystal structures, electrochemistry and thin-layer UV-vis spectroelectrochemistry. The different properties of these complexes will be discussed.



Scheme 1 The synthesis routes of TriP rhenium(I) tricarbonyl complexes

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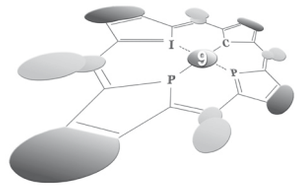

Supramolecular Assembly of Zinc Protoporphyrin Studied by Scanning Tunneling Microscopy

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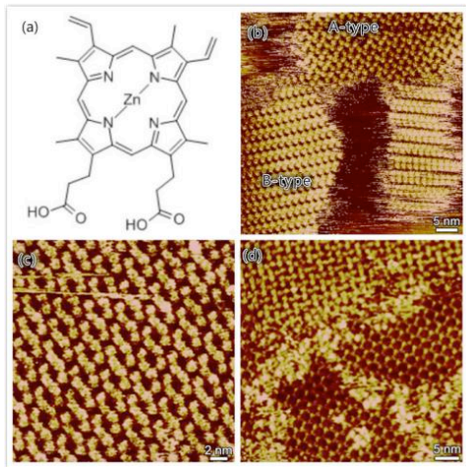
As a typical functional material, porphyrins present high potentials for their ample electronic, photonic, and catalytic properties. Formation of ordered porphyrin monolayers on surface is of much importance for both fundamental and technological points of view. Thus, the construction of supramolecular patterns of porphyrins has been extensively pursued in recent years. We present a scanning tunneling microscopy study on the supramolecular ordering of Zinc Protoporphyrin (ZnPP) molecules on a highly oriented pyrolytic graphite (HOPG) surface. Two forms of molecular assembly structures of ZnPP were observed. Specifically, we have successfully achieved the A-type structure of ZnPP adsorption on an hydrogen-bond monolayer of



triphenylene-2,6,10-tricarboxylic acid (H_3TTCA) on HOPG. Theoretical investigation indicates that the hydrogen-bond interactions between the porphyrin together with the van der waals interactions between porphyrins and substrates direct the assembly behavior of ZnPP.

Figure 1. (a) Chemical structure of Zinc Protoporphyrin. (b) Two assembly structures of ZnPP on HOPG substrate. (c) High resolution STM image of ZnPP A-type assembly structure. (d) ZnPP A-type structure on H_3TTCA nano-porous network.

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Influence of peripheral BODIPY-Substituents on the Solar Cell Performance of Porphyrazines

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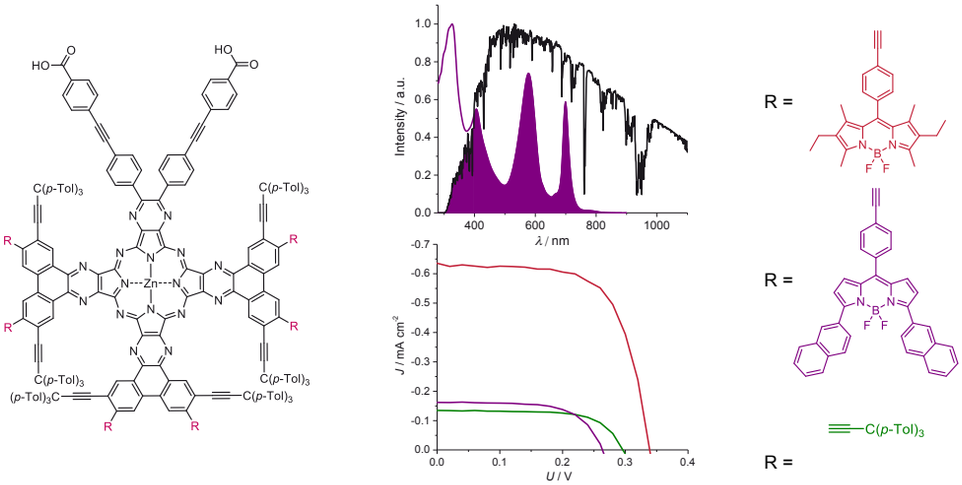
Although phthalocyanines (Pc) – or more general porphyrazines – possess properties that make them attractive for use in dye-sensitized solar cells (DSSC), the power conversion efficiencies of Pc-sensitized DSSCs are still limited compared to porphyrin-based DSSCs. Significant progress has been made to overcome these limitations, one factor being the implementation of peripheral substitution to prevent aggregation of the planar macrocycles.[1] In an effort to improve the light harvesting properties of the porphyrazines, we previously reported the preparation of tetrapyrazinoporphyrazines whose light-absorbing properties are augmented by peripheral BODIPY substitution. In addition to the panchromatic absorption profile of these hybrids, the chromophores feature a donor-bridge-acceptor structure with pronounced light-induced energy transfer properties.[2] In continuation of this work we have now developed [3+1]porphyrazines consisting of peripheral BODIPY groups and anchoring units for the attachment of the BODIPY-Pz chromophores to semiconductor surfaces. The synthetic approach that we have chosen allows for the easy variation of both entities around the Pz core. Therefore we report here on the performance of differently substituted tetrapyrazinoporphyrazines in TiO_2-based solar cells and will discuss the influence of BODIPY-variations on the photophysical and electrochemical properties of the panchromatic chromophores.



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Tetrapyrazinoporphyrazines as Photoelectron-Acceptors in noncovalent Assemblies to Graphene

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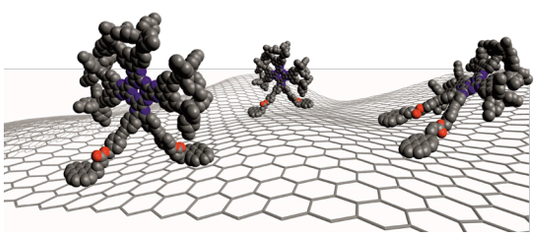
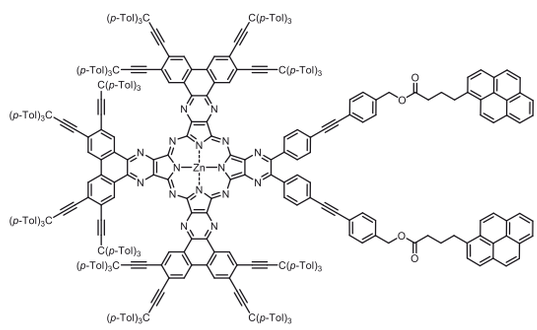
Due to its unique (opto-)electronic and mechanical properties, graphene is currently in the focus of extensive research efforts. In a recent development, the liquid-phase exfoliation of graphite has evolved as a yield- and cost-efficient method for the isolation of high quality graphene monolayers. Extended polycylic aromatic hydrocarbons (PAH) such as pyrene, that feature strong affinity towards graphene via π-π-stacking, have been shown to assist in the exfoliation process and in the stabilization of the isolated material.[1] The combination of the PAH-substructure with photo- and redoxactive chromophores like porphyrins and phthalocyanines (Pc) allows the isolation of nanohybrid materials with enhanced light harvesting and interesting charge transfer features. Whereas the Pc acts as the photoelectron donor in most of the reported Pc/graphene conjugates, DE LA TORRE, TORRES and GULDI *et al*. recently reported evidence for a graphene-to-Pc charge transfer involving an "electron-poor" alkylsulfonyl-substituted Pc.[2] Following up on this observation, we have explored pyrazino-fused porphyrazines (Pz) that are more electron deficient than the benzenoid Pc and that should therefore act as more efficient electron-acceptors in supramolecular graphene-conjugates. We report here the synthesis of a pyrene-functionalized pyrazino-fused Pz **1**, whose core has previously been used as an efficient electron acceptor in supramolecular conjugates.[3] We will discuss the photophysical properties and the intermolecular interactions of the graphene/Pz-nanohybrids.



Schematic representation of the graphene/Pz hybrid.



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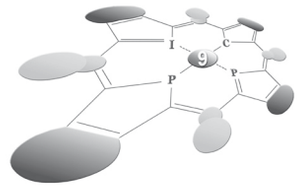

Synthesis of novel ABAB phthalocyanine-edged M_4L_6 cages

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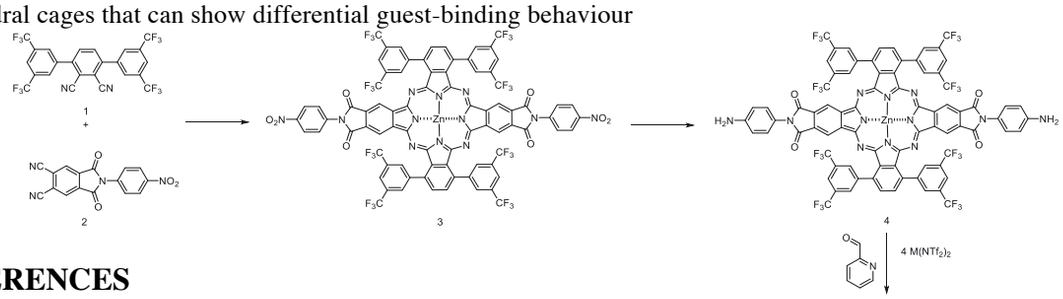
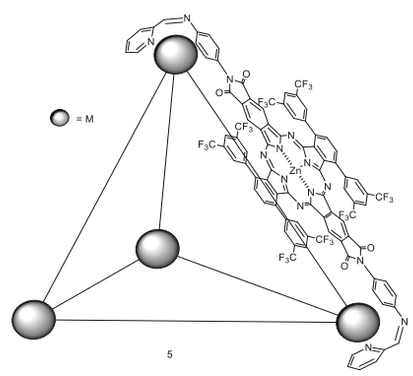
Metal-organic cages have attracted significant attention due to their many application fields.[1] In the last few years a wide variety of M_4L_6 architectures have been described using different kind of ligand, like pyrene,[2] perylene bisimide,[3] BODIPY[4] and porphyrin dyes.[5] In the literature there are very few examples of supramolecular architectures obtained using phthalocyanines (Pcs) as building blocks.[6] In this framework and in the search of new possible dyes to be used as ligands, we have synthesized a battery of face-to-face Pcs (the so-called ABAB Pcs) containing amine groups in the opposite isoindole units in order to self-assemble them with 2-formylpyridine and metal ions. First, a linear ABAB Pc **3** has been prepared by statistical condensation of bulky 3,6-(3□,5□-bis(trifluoromethyl)phenyl)phthalonitrile (**1**), with hampered self-condensation capabilities, and a dicyanophthalimide derivative **2**, *N*-functionalized with 4-nitrophenyl units, which are reduced in a further step to amino moieties to yield Pc **4**. Other face-to-face, diamino-functionalized Pcs have been also prepared, starting from an ABAB Pc reported in our group[7] that holds two opposite isoindoles containing iodine atoms, which were used for further chemical transformation into the target Pcs. In this case, separation of the two possible regioisomers was compulsory and, indeed achieved, thus yielding amino-containing ligands with defined geometries.

Self-assembly of octahedral metals ions and the prepared ABAB Pcs has been tested in the search of novel tetrahedral cages that can show differential guest-binding behaviour





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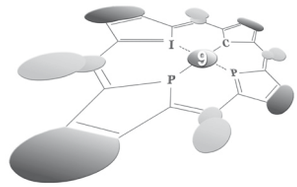

Ruthenium Phthalocyanines as potential photosensitizers for singlet oxygen generation

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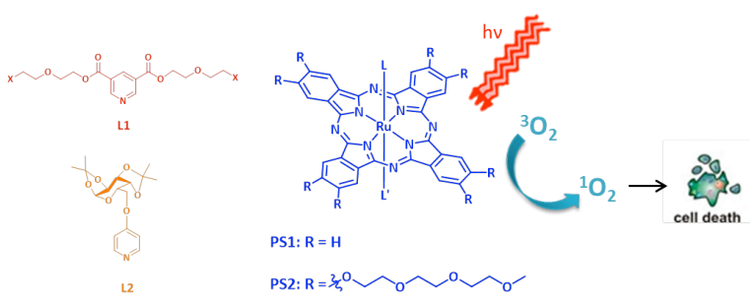
In recent years, there has been an increased interest in the synthesis of photosensitizers (PSs) to be applied in Photodynamic Therapy (PDT), a technique that uses $^1O_2$ for the treatment of cancer or as antimicrobial agent. PDT combines light, molecular oxygen and a PS for the production of reactive oxygen species (ROS), such as $^1O_2$ and free radicals that will induce cell dead, thus allowing for the non-invasive, selective and localized destruction of tumor or microbial cells with reduced side effects. Phthalocyanines (Pcs) are promising compounds to be applied as PSs for singlet oxygen generation.[1,2] However, a major drawback of these compounds is their low solubility in a physiological environment. This can be overcome through functionalization of the macrocycle at the peripheral and/or axial positions with appropriate hydrophilic functions. The introduction of axial ligands also reduces their aggregation in solution, thus improving their $^1O_2$ generation efficiency.[3]
Here, we present the synthesis of ruthenium phthalocyanines (RuPcs) to be applied as PSs. These PSs consist in RuPcs endowed with axial pyridyl ligands that provide the required solubility and/or selectivity. In this respect, several pyridine-based structures bearing polyether chains or carbohydrate units were synthesized and further coordinated to the central ion of RuPcs. Some of these axial ligands have been provided with charged functions specifically designed to render selectivity against Gram-negative bacteria. In addition, water solubility is enhanced through peripheral functionalization of RuPcs with polyether chains. All the prepared PSs have been studied with regard to two fundamental parameters in PDT, namely, water solubility and ability to generate singlet oxygen.



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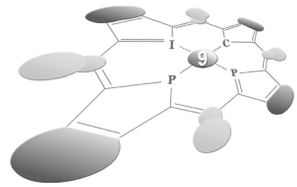


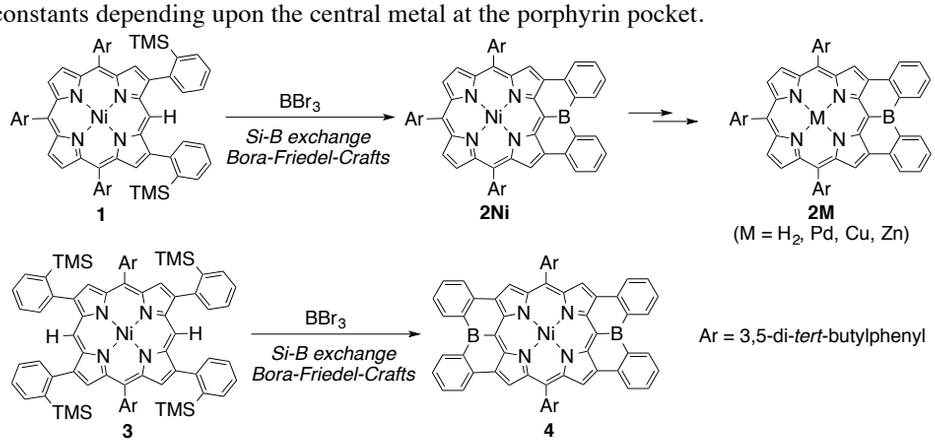
Synthesis and Characterization of Diphenylborane-fused Porphyrins

Keisuke Fujimoto, Hideki Yorimitsu, Atsuhiro Osuka

Department of Chemistry, Graduate School of Science, Kyoto University

Boron-containing π-conjugated compounds have attracted considerable attention in light of their fascinating features such as highly luminescent properties, large nonlinear optical responses, and anion-sensing properties. Among them, structurally constrained triarylboranes, in which the boron atom is embedded in a rigid and planar framework, exhibit intriguing properties such as high chemical stabilities and reversible coordination by strong Lewis bases with alteration of the structural and electronic properties.[1] Hence, the structurally constrained triarylboranes have become promising as stimuli responsive light emitting materials as well as a well-defined substructure of boron-doped graphene.[2]

Here, we disclose novel porphyrin-based structurally constrained triarylboranes. Diphenylborane-fused Ni(II) porphyrin **2Ni** was synthesized by one-pot reaction of bis(2-trimethylsilylphenyl)-substituted Ni(II) porphyrin **1** with BBr_3, which proceeded via Si-B exchange reaction, intramolecular bora-Friedel-Crafts reaction, and ring closing Si-B exchange reaction. Demetalation of **2Ni** efficiently gave the free base porphyrin **2H$_2$**, from which the corresponding metal complexes, **2Pd**, **2Cu** and **2Zn** were synthesized. Bis(diphenylborane)-fused Ni(II) porphyrin **4** was similarly synthesized from tetrakis(2-trimethylsilylphenyl)-substituted Ni(II) porphyrin **3**. **2M** and **4** are highly stable and tolerable to aqueous work-up and separation over a silica gel column owing to the structural constraint of the boron atom embedded in a rigid and planar π-skeleton. In these porphyrins, effective electronic interactions of the empty p-orbital of the boron atom with the porphyrin π-circuit lead to red-shifted absorption spectra, and substantially decreased LUMO energy levels. Pyridine adds at the boron center to cause a plane-to-bowl conversion with concurrent disruption of the electronic interaction of the boron atom with large association constants depending upon the central metal at the porphyrin pocket.



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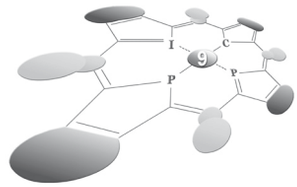

Synthesis of N-Confused Porphyrin-aza-Dipyrrin Conjugates: Porphyrin Analogues Bearing Exterior and Interior Coordination Sites

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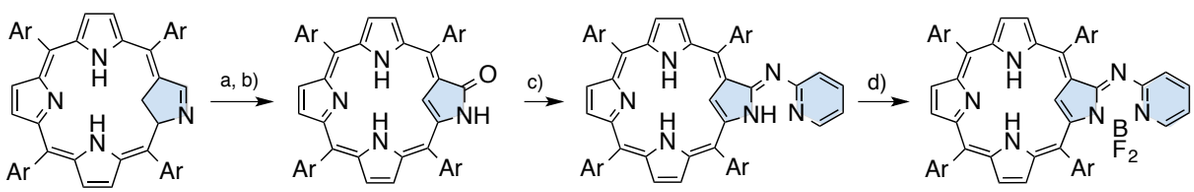
In recent years, intensive research interests have been devoted to N-confused porphyrin (NCP), in which one of the pyrrole rings is connected at α and β' positions to *meso*-carbons, due to its unique NH-tautomerism and metal coordination arising from the confused pyrrole ring.[1] The confused pyrrole ring also provides exterior metal coordination and anion binding sites. In order to further enhance the exterior coordination and anion recognition abilities, additional coordinating units were introduced in this study. A dipyrromethene (dipyrrin) unit was introduced to the periphery of NCP using a Schiff base forming reaction of lactam compounds, which was recently developed by us as a new synthetic method of aza-BODIPY.[2]

As shown in Scheme 1, the target NCP-aza-dipyrrin conjugate and its BODIPY derivative were synthesized from N-confused oxoporphyrin **2** bearing amide moiety in the confused pyrrole ring. A Schiff base forming reaction of **2** and 2-aminopyridine in the presence of titanium tetrachloride under basic conditions provided the NCP-aza-dipyrrin conjugate **3**, which was further converted into its BODIPY derivative upon coordination of a boron difluoride. Due the expansion of conjugated system through hybridization of NCP and aza-dipyrrin or aza-BODIPY, we observed a ca. 50 nm bathochromic shift of the absorption spectrum of **4** relative to regular NCPs and only a weak fluorescence. These results indicated that the conjugated system of NCP was effectively expanded upon fusion with the aza-BODIPY unit.



Scheme 1. Synthesis of NCP–aza–BODIPY (**4**). Conditions a) $SnCl_2$, b) HCl, c) 2-aminopyridine, $TiCl_4$, NEt_3, d) $BF_3{\cdot}OEt_2$

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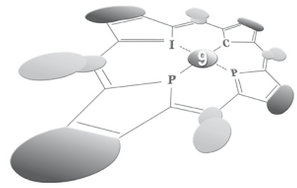

Highly Planar Diarylamine-fused Porphyrins and Their Stable Radical Cations

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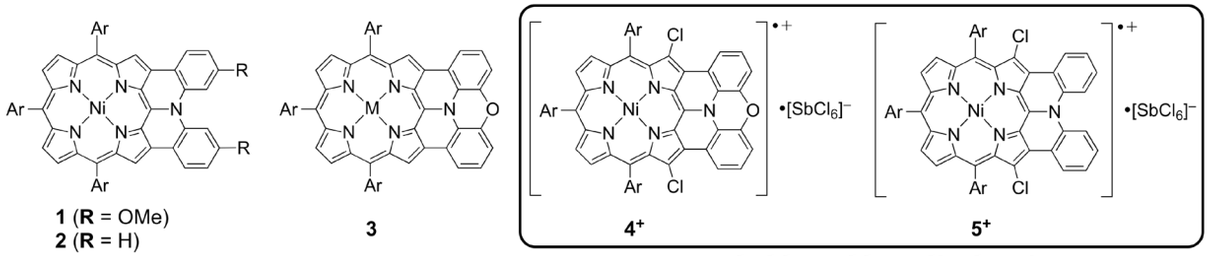
In the chemistry of porphyrins, their radical cations have been extensively studied as the central targets, since they are involved as key intermediates in crucial steps in photosynthesis. Many researchers accomplished the isolation and structural characterization of radical cations of metalloporphyrins. However, it required careful manipulations under strictly inert atmosphere without conventional work-up such as aqueous work up and silica-gel column chromatography in open air. The instability can be ascribed to the inherent high reactivity and insufficient kinetic protection toward a wide range of nucleophiles and reducing reagents. Therefore, synthesis and investigation of highly stable porphyrin radical cations have been quite limited.

A large π-system including a planarized amino nitrogen atom has been known to yield a stable organic radical cation upon oxidation. These results encouraged us to investigate the formation of highly stable radical cations from porphyrins including a fused diarylamine unit at the periphery. In recent years, diarylamine-fused porphyrins such as **1** and **2** were actually explored as a new class of electron-rich macrocycles, but their radical cations have not been studied yet.[1,2] In addition, it is well known that the planarity of radical cations plays a crucial role in the solid state magnetic properties. However, in the case of **1** and **2**, the slightly distorted structures caused by the intramolecular steric repulsion prevented the effective intermolecular interactions.

Here we report the first synthesis of phenoxazine-fused porphyrins **3** as highly planar diarylamine-fused porphyrins, which form π-π stacking dimers in solution and in the solid state. In addition, one electron oxidation of doubly *β*-chlorinated phenoxazine-fused porphyrin **4** and diphenylamine-fused porphyrin **5** allowed the isolation of the corresponding radical cations $\mathbf{4^+}$ and $\mathbf{5^+}$, respectively. They are extremely stable under ambient conditions, and can be manipulated as usual organic molecules as a rare case. Interestingly, these two radical cations display distinctly different intermolecular magnetic interactions to each other in the solid state.



1 (**R** = OMe)
2 (**R** = H)

3

$\mathbf{4^+}$ $\mathbf{5^+}$

remarkably stable radical cations

Ar = 3,5-di-*tert*-butylphenyl

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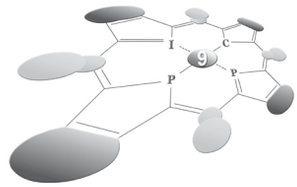

Vitamin B_{12} – a unique cobalt catalyst

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Cobalt-catalysis has been known for decades and reactions such as Co-catalyzed [2+2+2] cycloaddition, Nicholas or Pauson-Khand reactions are included in introductory organic chemistry courses. Nowadays, the area is growing rapidly and methodologies avoiding the use of noble metals (Pd, Rh, Ru, Ir, Au) gain in importance.[1]
In this regard, vitamin B_{12} is a compound of particular interests. As a natural cobalt complex it combines the benefits of transition metal catalysis with unique nontoxicity and environmental harmlessness.[2] Synthetic application of cobalamin is inherently connected with its ability to form alkyl derivatives *via* Co(II) and Co(I) reduced forms. To date, a large number of vitamin B_{12}-catalyzed reactions have been described with the addition to double bonds, halide and alkene coupling, ring expansion, rearrangement, cyclopropanation being the most representative.[3]

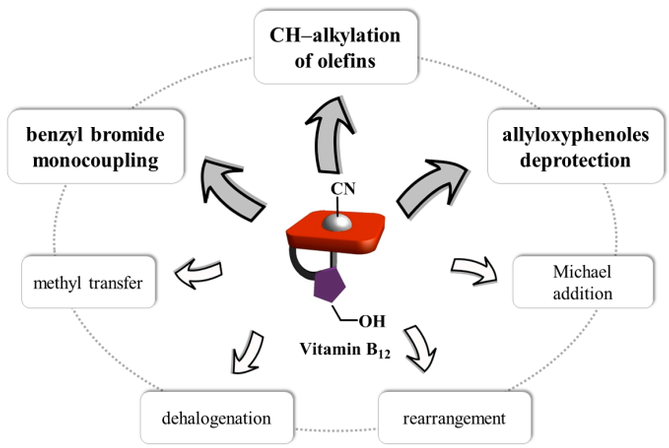

Figure 1. Reactions catalyzed by vitamin B_{12} and its derivatives

Recently, we have developed a few vitamin B_{12}-catalyzed methods involving a novel Co(I)-catalyzed reaction of diazocompounds with olefins leading to the unusual Heck-type functionalization of sp^2 C-H bonds.[4] We have also established an efficient procedure for the benzyl bromides monocoupling under microwave irradiation and deprotection of alliloxyarenes. Ultimately, the redox behaviour and structure-activity relationship of known B_{12} derivatives has been evaluated with the goal of finding the influence of the peripheral alkyl chains and the presence of the nucleotide "loop", on the catalytic activity.

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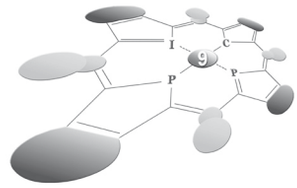

^{1}H HR-MAS NMR Based Metabolic Profiling of Cells in Response to Treatment with Chlorin-Polymer Systems

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[c]*University of Berne, Depts. Clinical Research and Radiology, Berne, Switzerland*

The application of polymer based nanoparticles has found great recognition as delivery systems for porphyrinic photosensitizers in photodynamic therapy (PDT). Polymer-based nanoparticles have the capability to enhance porphyrin solubility and stability under physiological conditions and ideally can improve their uptake and phototoxic efficiency in the tumour target tissue. Recently, we have shown by ^{1}H NMR spectroscopy that amino acid derivatives of chlorin e6 (xCE) are monomerized in aqueous solution by encapsulation into PVP [1] or Kolliphor P188 [2], a biodegradable triblock copolymer. While the cellular uptake of the porphyrinic compounds could be readily proved by fluorescence detection after cell incubation little is known about the metabolic response of the cells towards the porphyrin polymer systems and their single components in the dark. Therefore, the aim of this study was to directly monitor the metabolic response of cancer cells following incubation with the chlorin-polymer systems applying ^{1}H High Resolution Magic Angle Spinning (HR-MAS) NMR spectroscopy. HR-MAS NMR is a technique, which provides well resolved ^{1}H NMR spectra directly from semi-solid materials like living cells. Combined with multivariate statistical analysis it allows to monitor alterations in small metabolites following interventions like drug treatment. [3, 4]

In the present study, cultured HeLa cells were incubated with (i) serine-chlorin e6 (SerCE) encapsulated into a PVP-matrix (SerCE-PVP), as well as with (ii) SerCE and (iii) PVP alone and (iv) with pure buffer (PBS) serving as control. For each group, 8 samples were prepared leading to a total of 32 samples. After incubation the cells were washed, the pellets were taken up in D_2O-based PBS and the cell suspensions were directly submitted to HR-MAS NMR spectroscopy. Partial least squared discriminant analysis (PLS-DA) of the cell metabolite spectra lead to a complete separation between the SerCE-PVP versus PVP-treatment groups but also between SerCE and PVP each versus control. The load values revealed main alterations deriving from lipid components suggesting for higher lipid mobility in response to either SerCE-PVP or the single components. Specific to SerCE treatment in the presence or absence of PVP were alterations in choline containing compounds indicating interactions with phospholipids. Further studies are currently in progress to compare the effect of PVP and Kolliphor P188 as delivery system for SerCE on the metabolic response of HeLa cells.

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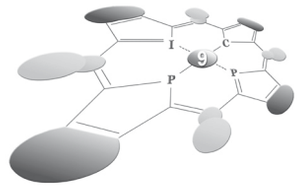

Energy transfers in donor-acceptor dyads built upon a truxene core

Claude P. Gros[a], Nicolas Desbois[a], Hai-Jun Xu[a], Adam Langlois[b], Paul-Ludovic Karsenti[b], Pierre D. Harvey[b]

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Several donor-acceptor dyads built upon a central truxene core are assembled and studied from a photophysical standpoint in order to examine their photo-induced energy transfer properties. These dyads are composed first of a Zn(II)-porphyrin donor and free-base porphyrin acceptor [Zn-Fb2], Figure 1. Second a BODIPY donor and Zn(II)-porphyrin acceptor [BOD-Zn2]. Third a Pd(II)-porphyrin donor and Zn(II)-porphyrin acceptor [Pd-Zn2]; and finally a Zn(II)-porphyrin donor and free-base corrole acceptor [Zn-COR2]. The findings of the photophysical analysis show that the Dexter double electron transfer plays an important role in the energy transfer process despite the long distance between chromophores. This conclusion indicated that the truxene core serves as a conjugated "wire" between chromophores providing a significant orbital overlap between the donor and acceptors. This overlap then allows for a double electron exchange to occur through the truxene bonds allowing us to conclude that truxene can in fact be used as a small scale, soluble model for graphene which is notoriously well known for its excellent conductivity properties.

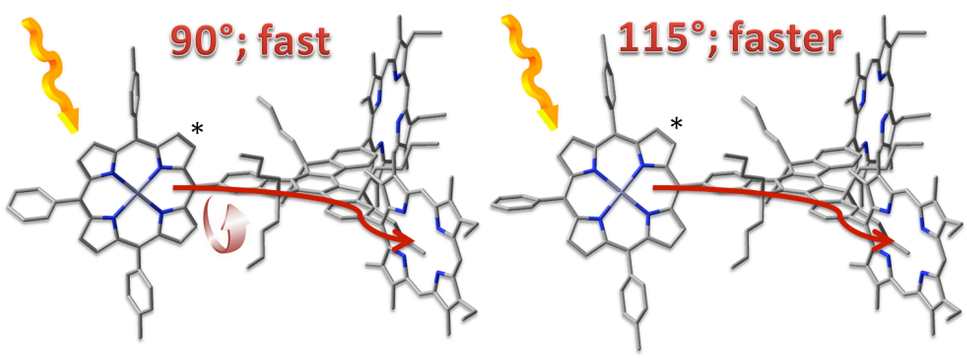

Figure 1

The "Consulat Général de France à Québec" and "Programme de Samuel de Champlain 2015/2016" are acknowledged for funding.

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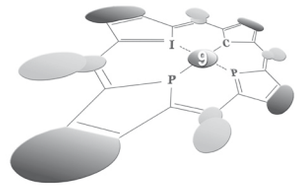

Low gap conjugated polymeric materials doped with porphyrins for organic solar cells

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Since the beginning of this century, organic photovoltaic cells (OPVs) have been the focus of many researches. Their main interest compared to traditional inorganic solar cells is their low-cost and fast production as well as their low weight and high flexibility opening a wide field of potential applications. Among OPVs, bulk heterojunction solar cells (BHJ)[1], that consist of a blend between electron donor and electron acceptor materials, are very promising devices and efforts have, so far, led to high Power Conversion Efficiencies (PCEs).[2]
One of the main parameters to investigate, in order to improve efficiencies, is the amount of photons absorbed by the active layer. Both porphyrins and BODIPY chromophores have been widely studied because of their impressive optical properties[3], such as very high absorption coefficients, leading to materials in BHJ devices reaching by now PCE of 8.5 %.[4]
In this work, we have designed several low bandgap conjugated copolymers made of alternated units of thiophene and BODIPY randomly branched with porphyrin units, the whole acting as light antennas.[5] We expect to harvest light from the whole solar spectrum and make it to converge by energy transfer (EnT) mechanisms to the unit responsible for the electron transfer (ET) toward the fullerene derivative acceptor. We will also report systematic modifications of the side chains on the polymer backbone to study the impact on solubility and so far the morphology of resulting films.

The "Consulat Général de France à Québec" and "Programme de Samuel de Champlain 2015/2016" are acknowledged for funding.

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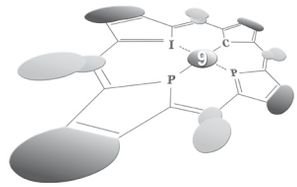

Synthesis, Photophysical, Spectroelctrochemical and Redox Properties of "Push−Pull" Octaphenylporphyrins

Nitika Grover[a], **Yang Song**[b], **Muniappan Sankar**[a] **and Karl M. Kadish**[b]

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β-substituted push-pull porphyrins are of broad interest due to their unique photophysical and electrochemical redox properties. They are widely utilized in the areas of NLO[1a], PDT[1b] and DSSC.[1c,1d] However, their potentials have been less explored due to the lack of facile synthetic methodologies for regioselective β-functionalization. Herein, we present a new series of β-substituted octaphenylporphyrins and the influence of unsymmetrical substitution on the photophysical and electrochemical properties of the compounds.[2] Notably, we could detect the unusual metal-centered oxidations of Ni^{II} to Ni^{III} and Cu^{II} to Cu^{III} dication radical in NiOPP(R)X_2 (X = H, CHO and CH_2OH) and CuOPP(NO_2)$(CN)_2$, respectively (Figures 1b and 1c) due to modulated HOMOs by asymmetric β-substitution. The metal centered oxidation of Ni^{II} to Ni^{III} is strongly influenced by nature of β-substituents (Figure 1b).

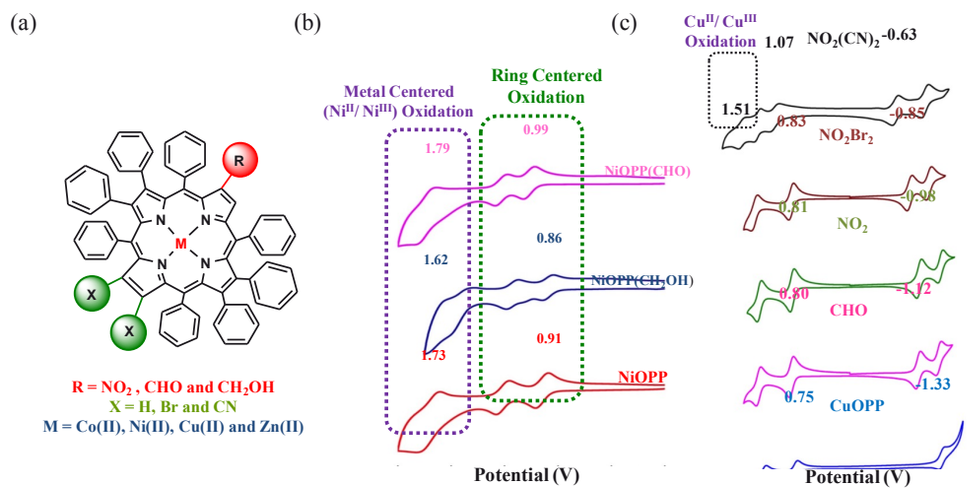

Figure1. (a) Schematic representation of synthesized β- Substituted porphyrins and their metal derivatives. (b) CVs of NiOPP(R) (R = CHO and CH_2OH) and (c) Cu(II) complexes of OPP derivatives.

In summary, these porphyrins exhibited high dipole moments, tunable redox properties, and red-shifted electronic spectral features due to push-pull β-substituents and the extent of nonplanarity of the porphyrin core.

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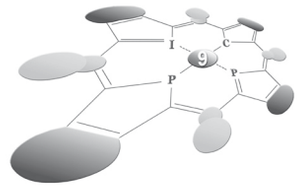

N-Confused Porphyrin- A Unique "turn on" and "turn off" Anion Sensor

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The development of colorimetric chemosensors for the selective detection of toxic anions based on supramolecular concepts is an active area of research.[1] N-H containing molecules, such as pyrrole and amide derivatives, are largely used for anion recognition, as N-H group serve as hydrogen bond donor towards anions.[2] Calixpyrroles, phlorins, corroles, sapphyrins, N-confused porphyrins, oxoporphyrinogens, and nonplanar porphyrins are of outstanding candidates for an immense variety of anion sensor applications *via* NH group of the pyrrole unit. In contrast to porphyrins, the confused structure of NCP displaying an outward-pointing N-H group, which can act as potential site for anions.[3] Herein, we have studied the anion sensing properties of free base and Ni(II) complex of *meso*-tetrakis(4'-carbomethoxyphenyl)-N-confused porphyrin (**1** and **1-Ni**) and the results were compared with *meso*-tetraphenyl-N-Confused porphyrin (NCP). **1** and **1-Ni** were able to detect $CN^{\square}$, $F^{\square}$ and $ClO_4^{\square}$ over the tested set of anions and found 10 times higher binding constant as compared to NCP. Interestingly, $ClO_4^{\square}$ addition caused fluorescence quenching (*turn off*) whereas $F^{\square}$ and $CN^{\square}$ addition resulted into fluorescence enhancement (*turn on*). The electron deficient porphyrin framework, large polarisable π-system and anion binding through outer NH or combination of above factors serve as foundation for N-confused porphyrin to act as anion sensor.[4]

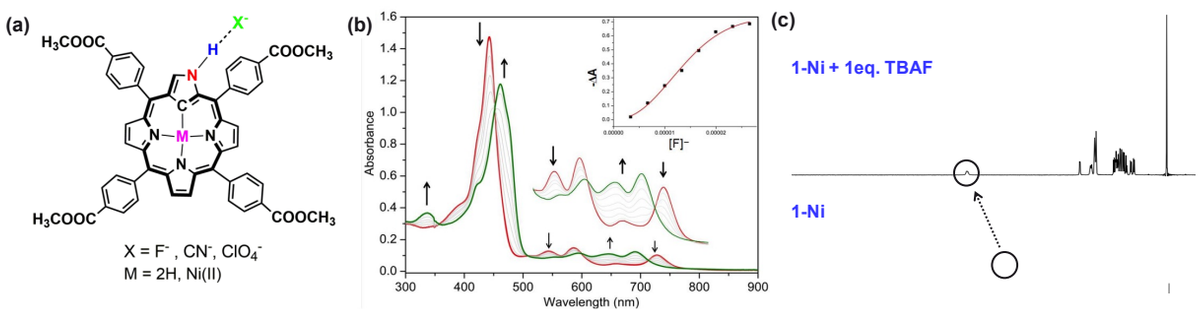

Figure 1. (a) Schematic representation of **1** and **1-Ni** binding with anions; (b) UV-Vis spectral titration of **1** with F^- ions in CH_2Cl_2 at 298 K; (c) ^1H NMR spectral changes of **1-Ni** in presence and absence of F^- ions in $CDCl_3$.

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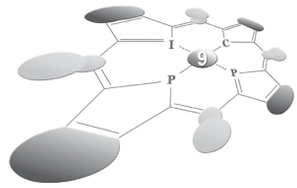

Industrial-scale syntheses of porphines & metalloporphyrins

Guo Cancheng[a], Luo Weiping[a], Liu Qiang[a], Guo Xin[b]

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Porphines and metalloporphyrins were widely be used in the field of catalysis, luminescent materials, medicine, etc. However,the high cost of the preparation of porphyrin compounds is restricting their large scale application. In order to improve the synthetic yield of porphyrins and reduce their cost, the new synthetic method of porphyrins and the corresponding industrial equipment were reported in this paper.
In the new methods, porphines (TRPPH2), metalloporphyrins (TRPPMX) and bismetalloporphyrins ([TRPPM]2O) were synthesized from the one-pot reaction of the pyrrole, benzyl aldehyde and metal salt (Fig 1). The corresponding industrial equipment with the 30 t/a output used to synthesize porphines and metalloporphyrins. The set consisted of the reactor, separator and solvent cycle units (Fig 2). Various porphyrins showed in Fig 1 has been synthesized successfully by the sets in Fig 2. The results show that the industuial-scale synthetic yields of porphyrins were better than that of in the laboratory. The purities of all products were over 97% by HPLC analysis.

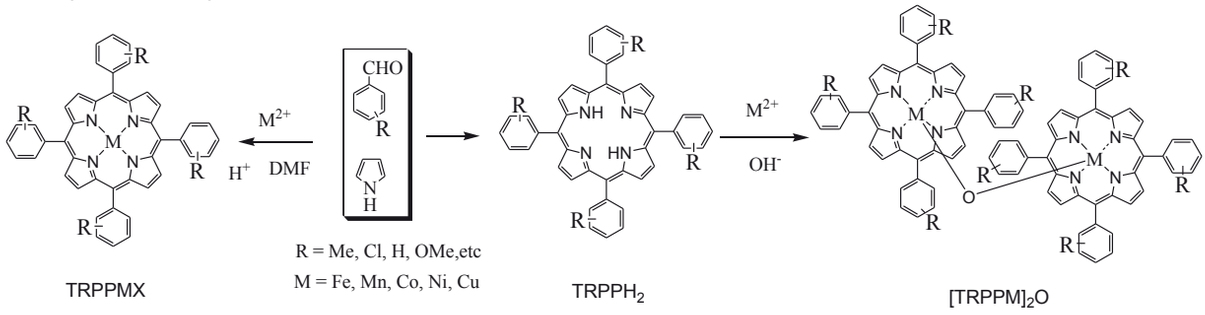

Fig 1 Synthesis route for porphines(TRPPH2) and metalloporphyrins(TRPPMX, [TRPPM]2O)

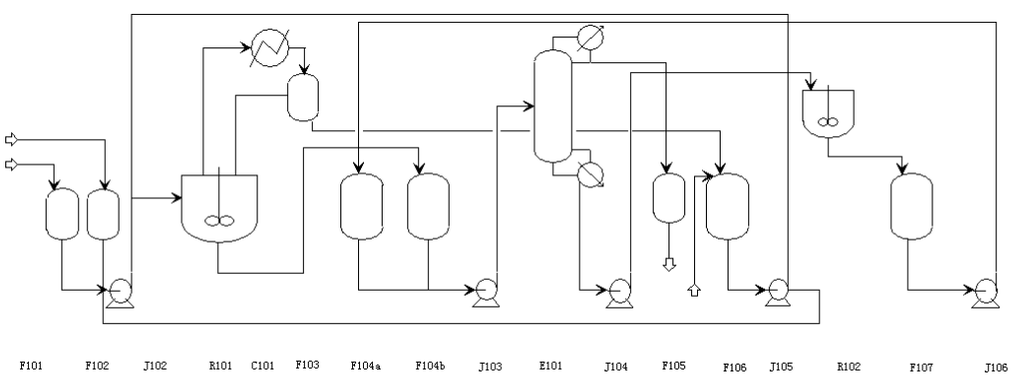

Fig 2 Industrial sets used to synthesize porphines(TRPPH2) and metalloporphyrins(TRPPMX, [TRPPM]2O)

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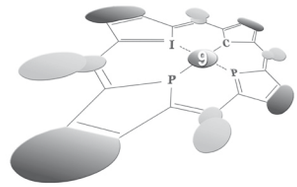
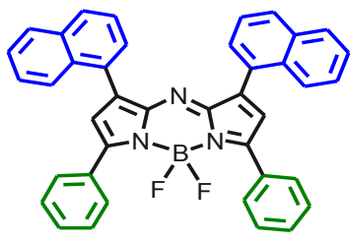


Donor-Acceptor Type Aza-BODIPYs

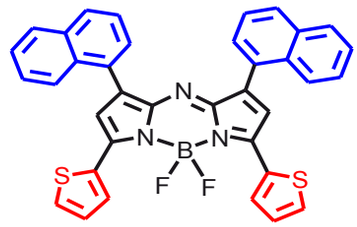
Naresh Balsukuri,[a] Iti Gupta[a]

[a]*Indian Institute of Technology Gandhinagar, VGEC Campus, Chandkheda, Ahmedabad- 382424, India.*

Aza-BODIPYs are sub-class of BODIPYs and very promising candidates as NIR dyes due to their strong absorption and emission properties around 600-800 nm range and versatile structure.[1] The aza-BODIPYs have found applications in optoelectronics, bio-imaging, sensing and PDT.[2] Due to their strong absorption and emission in red region aza-BODIPYs are more suitable as photosensitizer for biological and organic solar cells. The donor-acceptor (D-A) type aza-BODIPYs are of particular interest because facile substitution by energy donor moieties allows easy synthesis of variety of compounds,[3] where selective excitation of donor group can be achieved. Our group at IIT Gandhinagar is involved in the chemistry of BODIPY derivatives, D-π-A type corroles[4] and aza-BODIPYs. Here we present the synthesis and studies of aza-BODIPYs containing energy donor moieties (naphthalene, carbazole) at their 1,7-positions and either two phenyl or two thienyl groups at their 3,5 positions. The energy transfer properties and DFT studies will also be presented.



λabs = 653 nm
λem = 685 nm



λabs = 716 nm
λem = 730 nm

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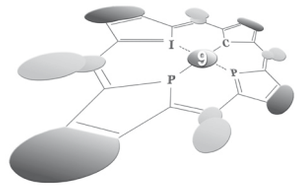

A novel bioelectrochemical sensing platform based on LBL assembly of cobalt phthalocyanines with amine modified MWCNT.

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Metal phthalocyanines (MPcs) (e.g.,Co and Fe), as excellent electrocatalysts , have been extensively employed to electrochemical oxidation of many important analytes based on their macrocyclic nature including extended π-systems. Indeed, the rich and reversible redox chemistry of MPcs is the key factor that allows them to serve as mediators in many electron transfer reactions[1,2].
Besides, hydrogen peroxide (H_2O_2) is a byproduct of several highly selective oxidases, and essential mediator in environmental analysis, medicine, food and biology. Detection of biomolecules at low concentrations is critically important to the early diagnosis and successful treatment of diseases[3,4].
In this work, asymmetric Cobalt Phthalocyanines(CoPcs) containing different substituted groups in peripheral positions were synthesized and characterized. After that, novel CoPcs were retained both the surface of modified nanomaterials and amine modified Multiwall Carbon Nanotubes (MWCNT) with spin coater or Layer by Layer (LbL) assembling method. In this way, it will be investigated electrochemical activity of these sensors towards H_2O_2.

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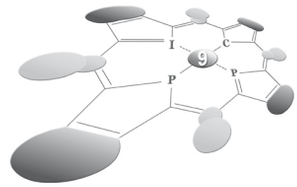

Preparation of New Extended-Conjugated Systems by Peripheral Modification on Subporphyrazines

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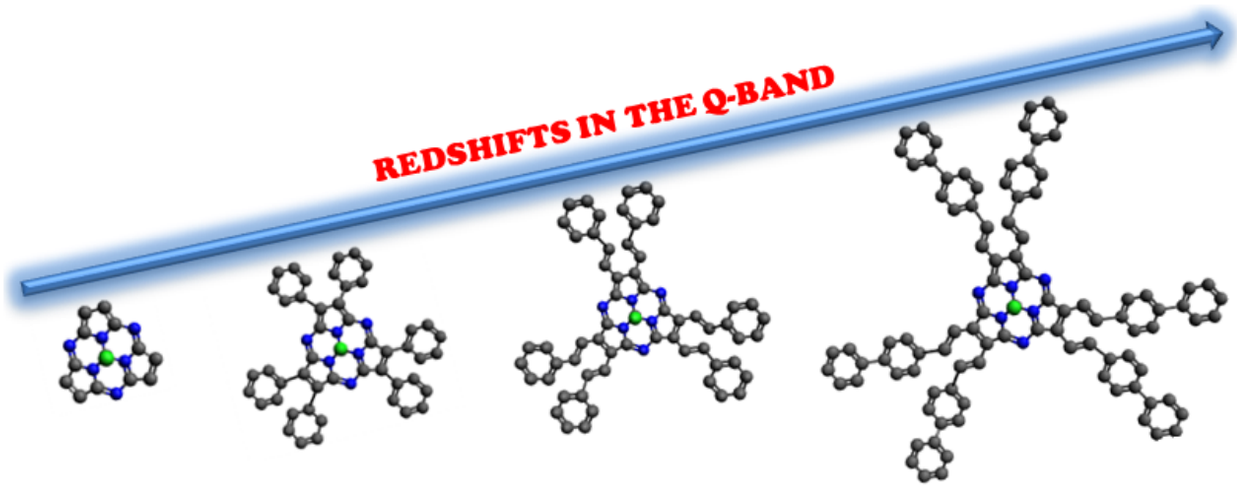
Subporphyrazine (SubPz) are aromatic porphyrinoids consisting of three pyrrole subunits with a 14 π-electron aromatic core and nonplanar cone-shaped conformation, giving these compounds outstanding physicochemical properties useful in the field of organic photovoltaics.[1] Peripherally hexaarylated SubPzs have been prepared recently through a palladium-catalyzed cross-coupling reactions.[2] This useful synthetic methodology has allowed to develop novel Subporphyrazine-based compound, expanding the orbital conjugation by incorporating of vinyl-aryl substituents, strongly influence on the optical and electronic properties of the SubPz core by means of effective conjugative interactions resulting significant redshifts of the charge-transfer and Q-bands.



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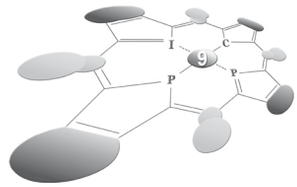

Hexafluoro isopropyl substituted phthalocyanines for selective detection of VOCs with chemical sensors

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Phthalocyanines and their metal complexes have found application in many different areas and they are among the most widely used chemically sensitive coating materials for chemical sensors and suitable for detecting volatile organic compounds (VOCs) and other analytes of interest in the gas and liquid phase [1,2].
In the past decade, new phthalocyanines containing electron withdrawing substituents such as fluorine have been developed [3,4]. These Pcs are of much interest due to their high solubility in polar solvents such as acetone or THF. The electronic properties are also widely affected by introducing electron donor or acceptor groups [5].
In this work, we have prepared and characterized metal phthalocyanine complexes which are octa substituted with 2-(4-aminophenyl)-1,1,1,3,3,3-hexafluoro-2-propanol containing moieties. These new compounds have been investigated in their chemical sensing properties against VOCs using the QCM (Quartz Crystal Microbalance). The responses to 12 different VOCs in dry and humid air have been studied. The compounds were found to exhibit excellent sensing properties. High responses have been observed for amines and polar compounds like ethyl acetate capable of interaction with the H donor group of the substituent. The sensing properties and the influence of the metal ion center will be discussed in detail.

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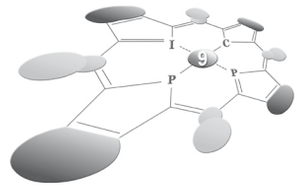
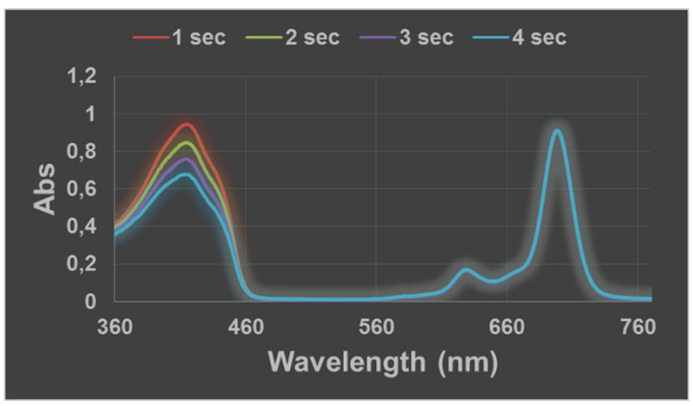


Synthesis and Photophysical Properties of alpha or betha Substituted Water–Soluble Zinc Phthalocyanines

Armağan Günsel, **Ahmet T. Bilgiçli, Meryem N. Yaraşır, Mehmet Kandaz**

Department of Chemistry, Sakarya University, 54140, Esentepe, Sakarya, Turkey

In this study, the synthesis, characterization and photophysical properties of water soluble phthalocyanines (Pcs) bearing 8-hydroxyquinoline-5-sulfonicacid conjugates and their cationic quaternized counterpart that play important roles their application in photodynamic therapy (PDT) were given. The periphery and non-periphery substituted phthalocyanines show high solubility and low aggregation tendency due to bulky 8-hydroxyquinoline-5-sulfonicacid steric hindrance moieties and axially bound counter chlorine anion. Singlet oxygen quantum yields, photodegradation quantum yields, photophysical properties and also the nature of the substituent and solvent effect on the photophysical and photochemical parameters of α-ZnPc and β-ZnPc are reported.



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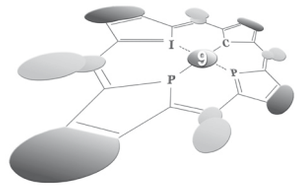

Development of Activatable Nano Photosensitizers Based on Phthalocyanines and Cubic Polyhedral Oligomeric Silsesquioxanes

Shenghua Han, Fang He, and Dennis K. P. Ng*

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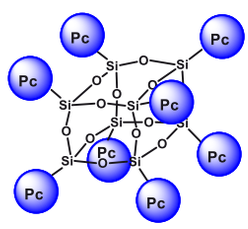
Photodynamic therapy (PDT) is an innovative therapeutic modality for a range of superficial and localized cancers. The photosensitizers involved are excited with light to generate reactive oxygen species (ROS) through the interactions with oxygen to promote cellular damages.[1] Among the various classes of photosensitizers, phthalocyanines have attracted much attention owing to their strong absorption in the tissue-penetrating red visible region, high singlet oxygen generation efficiency, high photostability, and ease of chemical and physical modifications.[2] As a promising approach to improve the efficacy of PDT, activatable photosensitizers have been developed. They can be activated by some cancer-related stimuli, such as the extracellular acidic environment[3] and higher tumoral glutathione (GSH) level[4] to achieve site-specific activation.

For the delivery of photosensitizers, nanoscale carriers exhibit many advantages. They can have high loading of photosensitizers, show an enhanced permeability and retention effect in tumor tissues, and serve as multifunctional platforms to impart additional theranostic components. However, the preparation of these materials sometime is tedious and has low reproducibility, and their structures are usually ill-defined. Cubic polyhedral oligomeric silsesquioxanes (POSS), which have a siloxane cage and eight pendant arms, are potential molecular nanocarriers that can overcome these problems.[5] We have recently designed and prepared a POSS-based GSH-responsive photosensitizing agent in which eight phthalocyanine moieties are conjugated to the corners of POSS via disulfide linkages. Upon interaction with GSH, the self-quenched phthalocyanine units are detached from the core and are therefore activated. In this presentation, we will report the preparation, GSH-responsive behavior, and *in vitro* photodynamic activities of this nano photosensitizer.



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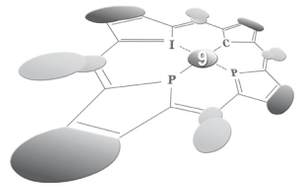


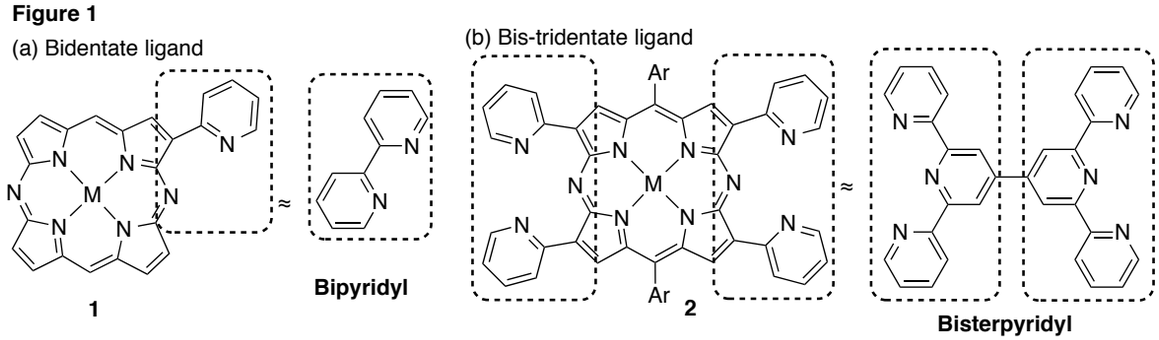
Synthesis and Properties of Tetrapyridyldiazaporphyrin

Yuya Hiraoka, Yoshihiro Miyake, Hiroshi Shinokubo

Graduate School of Engineering, Nagoya University, Japan

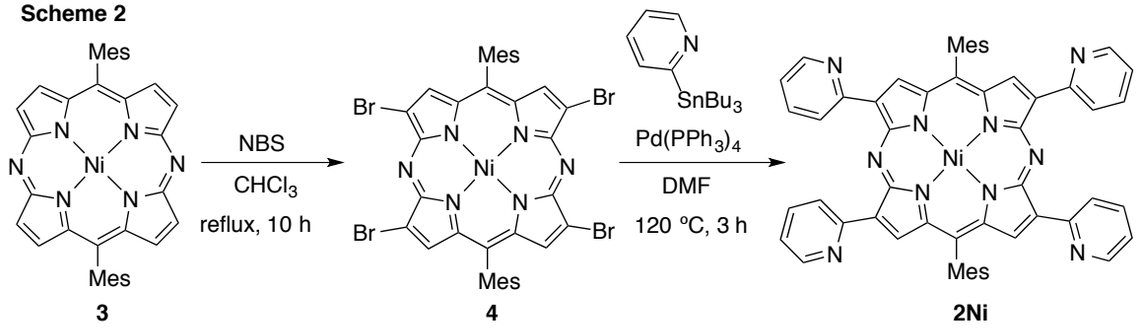
Diazaporphyrins are porphyrinoids having two sp^2-hybridized nitrogen atoms at *meso* positions. The nitrogen atoms at *meso* positions can coordinate to a variety of metal ions. We have already reported that pyridyldiazaporphyrin **1** works effectively as a bidentate ligand for several transition metals (Figure 1a).[1] In this study, we attempted to synthesize 3,7,13,17-tetra(2-pyridyl)-5,15-diazaporphyrin **2**. We expected that tetrapyridyldiazaporphyrin **2** would be a useful platform to investigate novel types of trinuclear complexes because of two terpyridine-like tridentate coordination sites (Figure 1b).

Figure 1



As illustrated in Scheme 2, tetrapyridyldiazaporphyrin Ni(II) **2Ni** was prepared by the cross coupling reaction of tetrabromodiazaporphyrin **3** with tributyl(2-pyridyl)tin in the presence of a palladium catalyst. X-ray diffraction analysis of **2Ni** revealed its nearly planar structure, suggesting the effective extension of π-conjugation over four pyridyl groups. In the UV-vis absorption spectrum, **2Ni** exhibited red-shifted Soret- and Q-bands compared to those of **1** and **2**. These results also support the effective π conjugation. In this poster presentation, we will also discuss the structure and properties of metal-coordinated tetrapyridyldiazaporphyrins.

Scheme 2



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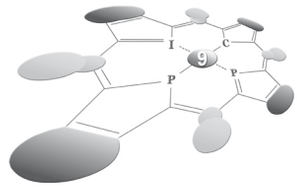
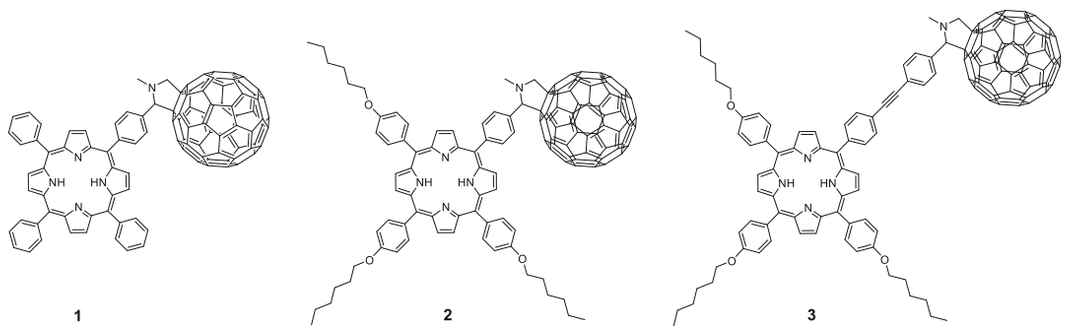


Novel Fullerene-Porphyrin Dyads for Investigation of Structure-Luminescence Properties Relationship

Emel Önal, Sevinc Zehra Topal, Ismail Fidan, Fabienne Dumoulin, Catherine Hirel

Gebze Technical University, Department of Chemistry, P.O B.ox 141, 41400 Gebze Kocaeli

A systematic structure-properties relationship study based on the determination of the fundamental properties of a set of three porphyrin-fullerene dyads(**1**-**3**) has been performed: their electrochemistry, molecular orbital levels and energy gaps, ground state absorption, fluorescence and singlet oxygen generation were determined. If several porphyrin-fullerene dyads are described, structure-properties relationship investigations are rather rare. The dyads were designed to benefit from a facilitated synthetic porphyrin-fullerene coupling thanks to an easy and novel access to formyl-functionalized porphyrins[1]. The effect of two structural parameters was investigated: the presence of electron-donating hexyloxy chains[2] at the para position of the meso-phenyl, and the presence of a phenylacetylene spacer. This latest appeared to have the most predominant effect on all these properties, which were interpreted with the final purpose to determine their suitability as oxygen sensors and photodynamic photosensitisers.



Scheme 1: Targeted fullerene-porphyrin dyads

Acknowledgement: This work has been funded in part by the **111M139** TÜBİTAK project.

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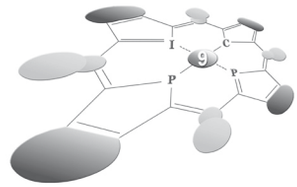

Palladium and Platinum Porphyrins Phosphorescence lifetime-based oxygen sensor response: influence of silver nanoparticles

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Optical sensors are commonly used for oxygen partial pressure determination. Over the past decades, the development of oxygen sensors in nanoscale are emerged as one of the most important research areas. The sensitivity of such sensors is roughly proportional to the luminescence decay of the dye, to be permeability of the employed matrix and size of the nanofibers. Luminescence lifetime-based oxygen sensors work on the principle of fluorescence/phosphorescence decay quenching of the dyes in the solid matrices. Especially, palladium (II) and platinum (II) porphyrins have been widely used in phosphorescence lifetime-based oxygen sensors owing to their strong long-lived NIR phosphorescence and also high sensitivity even at low oxygen concentrations [1].
In this study, the influence of phenylacetylide substituent and the role play by the metal center (Pd, Pt) were investigated *vs* phosphorescence lifetime-based O_2 sensitivity in toluene solution and in the nanofiber form. The O_2 sensing properties of phenylacetylide substituted palladium(II) and platinum(II) *meso*-tetraphenylporphyrins **(Pd-TPA)NF**; **(Pt-TPA)NF)** were compared to palladium(II) and platinum(II)*meso*-tetraphenylporphyrins-based nanofibers **(Pd-TPP)NF**; **(Pt-TPP)NF)** as reference probes. Moreover, phosphorescence lifetime-based O_2 sensing properties were improved by silver nanoparticles.

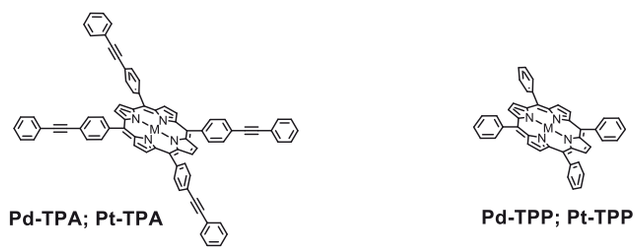

Figure 1. Oxygen sensing probes (M=Pd, Pt) investigated.

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Acknowledgement: This work has been funded by TÜBİTAK project No:**111M139**.

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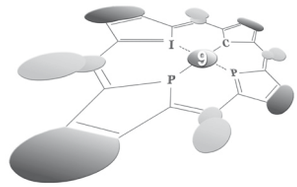

Synthesis and Properties of Corrorin-based Boron Difluoride Complex with a Helical Motif Skeleton

Yutaka Hisamune, Keiichi Nishimura, Kazuhisa Yamasumi, Masatoshi Ishida and Hiroyuki Furuta

Department of Chemistry and Biochemistry, Graduate School of Engineering, and Center for Molecular Systems (CMS), Kyushu University, Fukuoka 819-0395, Japan

4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY)-based dyes have been extensively studied for their singlet excited-state profile in most cases, and thereby utilized as labelling reagents, fluorescent switches, chemosensors, laser dyes and so-forth.[1] However, upon modifying the orientation of two simple BODIPY chromophores, being linked orthogonally, the resulting dimer shows the double substituted S_1 excited state, which leads to the enhanced population to the triplet manifold even without heavy atom effect.[2] On this basis, design and photochemical analysis of the dimeric BODIPY-based dyes should be of importance as potential candidate for materials in the photodynamic therapy, photocatalyst and triplet-triplet annihilation upconversion.[3]
In this study, we have synthesized a novel BODIPY-based dye (**2-BF$_2$**) based on the extended pyrrolyl methylene-substituted corrorin derivative and characterized the distinct helical twisted structure bridged with an extra freebase dipyrrin unit (Figure 1). The complex, **2-BF$_2$** exhibits two characteristic absorption band split in the visible region and the longer band is tailing up to 900 nm. Unlike monomeric BODIPYs, the complex **2-BF$_2$** gives no fluorescence, but emits in the presence of acid (e.g., trifluoroacetic acid). We will present the detailed structure and optical properties of **2-BF$_2$**.

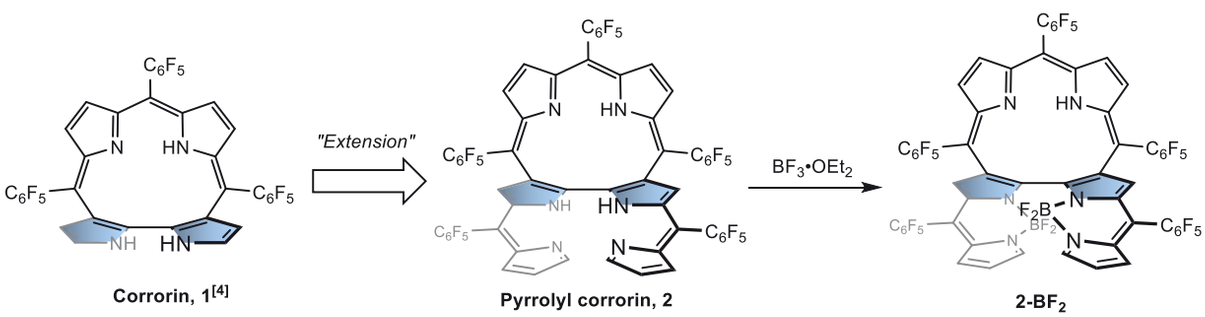

Figure 1. Structures of pyrrolyl methylene-subsituted corrorin **2** and its boron difluoride complex **2-BF$_2$**

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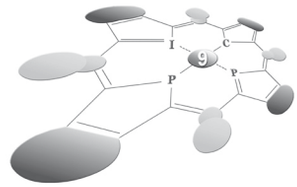

Synthesis and properties of expanded porphyrins composed of *β*-connected 2,2'-dipyrroles

Nobuhiro Hiura[a], Shigeki Mori[b], Masayoshi Takase[a], Hidemitsu Uno[a], Tetsuo Okujima[a]

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[b]*Advanced Research Support Center(ADRES), Ehime University, Matsuyama, 790-8577, Japan.*

Ring-expanded porphyrins belong to a class of larger porphyrinoids containing more than four pyrrolic (or other similar heteroaromatic) units. In recent years expanded porphyrins have emerged as a promising class of molecules in light of their optical, electrochemical, and coordination properties. Octaphyrin is one of expanded porphyrins in which eight pyrroles are linked via *meso* carbon bridges. Although Chandrashekar and co-workers reported a 34π aromatic octaphyrin(1.0.1.0.1.0.1.0) **1** with a planar core, generally it is observed that hexaphyrins and macrocycles which contain more than six pyrrolic units adopt a twisted nonplanar structure, resembling a figure-of-eight-type motif for octaphyrin.[1] First octaphyrin(1.0.1.0.1.0.1.0) **2** was reported by Vögel et al. in 1995, which showed no macrocyclic aromaticity due to its twisted porphyrin skeleton.[2,3] We herein report synthesis of octaphyrin(1.0.1.0.1.0.1.0) with planar structure by the use of *β*-connected 2,2'-dipyrrole as a building block. By linking the *β*-positions of dipyrrole, it is possible to fix the dihedral angle of the dipyrrole moiety leading to the enhanced planarity. Thus, thienodipyrrole **3** was designed and employed to synthesize a planar octaphyrin **4**. According to our synthetic protocol, *meso*-pentafluorophenyl-substituted octaphyrin **4** was obtained in 26% yield (Scheme 1). Crystal structure analysis of **4** revealed the slightly saddle-distorted structure.

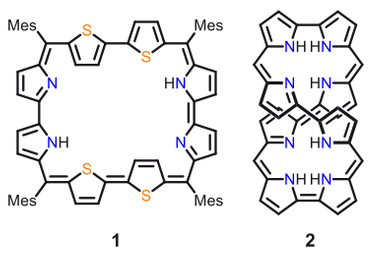
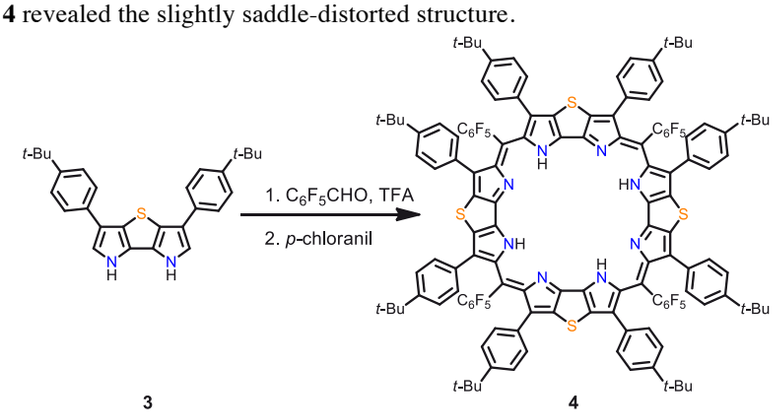


Figure 1. Octaphyrins **1** and **2** (Ethyl groups of the □-positions are omitted for clarity.).



Scheme 1. Synthesis of expanded porphyrin **4**.

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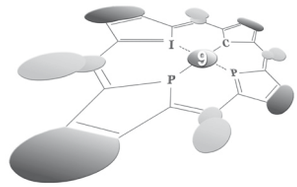

Photosensitizer-loaded Hollow Mesoporous Silica Nanoparticles for Fluorescence Imaging and Photodynamic Therapy of Cancer

Suk ho Hong[a], **Yongdoo Choi**[a]

[a]*Molecular Imaging and Therapy Branch, National Cancer Center, 323 Ilsan-ro, Goyang-si, Gyeonggi-do10408, Korea*

Photodynamic therapy (PDT) using combinations of chemical photosensitizers, light, and molecular oxygen has long been used successfully to treat cancers and other nonmalignant diseases. Despite many advantages over conventional chemotherapy, water-insolubility, limited tumor selectivity, and poor pharmacokinetics of PDT agents have been the major obstacles for their clinical applications. In particular, nonspecific activation of singlet oxygen generation in normal tissues causes prolonged skin photosensitivity, thereby limiting their utility as theranostic agents. Here we developed a system based on hollow mesoporous silica nanoparticles (HMSNP) that enables enhanced imaging and therapeutic efficacy of photosensitizers. Size of the synthesized HMSNP was about 120 nm. Talaporfin, a cholorophyll-based PDT agent in clinical use, was used as model photosensitizer. UV-Vis absorption and fluorescence spectra, drug-loading efficiency, and singlet oxygen generation were analysed. From the *in vitro* cell study, talaporfin-loaded HMSNP showed potential utility in near-infrared fluorescence imaging and PDT of lung cancer cells.

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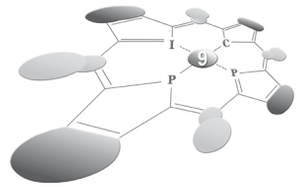


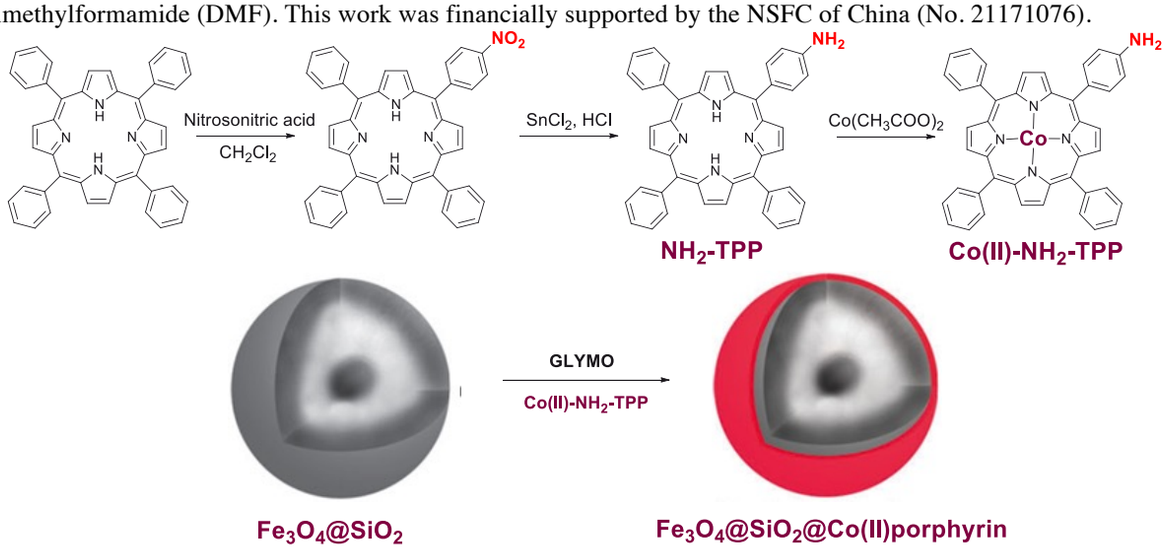
Recyclable Dechlorination of Toxic Lindane Electron Reductive Catalyzed by Fe_3O_4@SiO_2@Cobalt(II)Porphyrin

Tingting Huang[a], Xu Liang[a,*], Minzhi Li[a], Limin Zheng[b] and Weihua Zhu[a,*]

[a]*School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China*
[b]*State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China*

Lindane has been already listed as a new POP by the Stockholm Convention in 2009, is one of the toxic chemicals extensively used in most parts of our world. Two formulations of HCH, technical HCH and lindane, have been used widely to control agricultural and public health pests, and hence formed most γ-HCH in the environment. The persistence and organic phase solubility of HCH isomers cause signify cant biological accumulation and biomagnification in cells and tissues. Several porphyrins and phthalocyanines containing transition metal ions have been applied to catalyze the reductive dehalogenation of organohalides.

However the wide use of the catalyst will cause two pollution on the environment, since we study the recyclable catalyzed of Fe_3O_4@SiO_2@Cobalt(II)porphyrin magnetic materials, which can be recycle used through magnetic separation. Additionally, this catalyst has unique optical and electrochemical properties. GC-MS analysis indicate it has hign electroreductive dechlorinationreduction performance, and can be stable presence in N,N'-dimethylformamide (DMF). This work was financially supported by the NSFC of China (No. 21171076).



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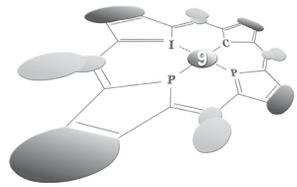


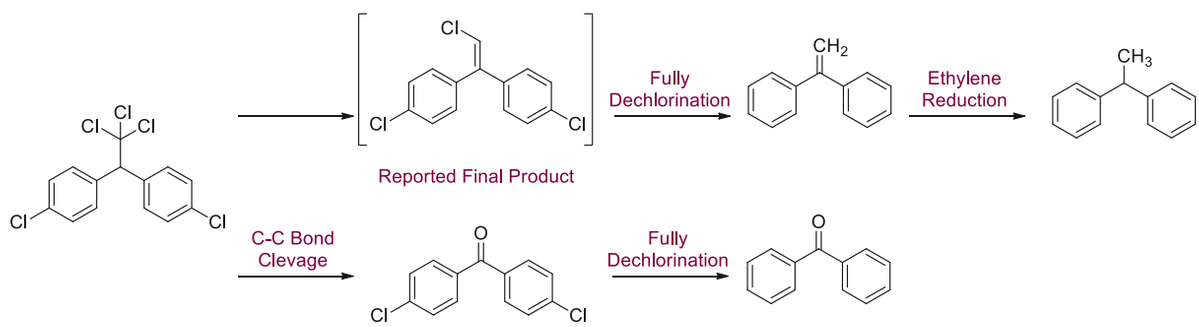
The First Example of Electrocatalyzed Full Dechlorination of DDT electrocatalyzed by Lipophilic Co(II)Pc

Tingting Huang, Xu Liang[a,*], Minzhi Li[a], John Mack[b], and Weihua Zhu[a,*]

[a]*School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China*
[b]*Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa*

DDT (1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane) was widely used for three decades as a potent pesticide for controlling malaria, typhus and other insect borne diseases but its use in agriculture has been banned in many countries since the mid-1970s because its exposure to human and wildlife can result in severe health problems [1–4]. Unfortunately, DDT is resistant to degradation in the environment and is still present in significant quantities in soil and water at numerous locations around the world. For this reason, research and development into new techniques for the degradation of DDT by various methods of dechlorination have attracted a great deal of interest in recent years. It has long been known that macrocycles containing transition-metal ions can be used as catalysts for the reductive dehalogenation of organohalides. One example is vitamin B_{12} which has been examined as a catalyst for the biomimetic reductive dechlorination of chlorinated pollutants such as DDT.

We hereby synthesized and isolated a new lipophilic Co(II)phthalocyanine. Electronic structure was studied by spectroscopy, electrochemistry and spectroelectrochemistry. Additionally, the controlled potential electrolysis measurements and GC-MS analysis indicate that this lipophilic Co(II)phthalocyanine has ultra-high catalytic ability which DDT can be converted to the full dechlorination product, 1,1'-diphenylethane, in a high yield. More interestingly, an unprecedented C-C bond cleavage dechlorination product was also formed. This work was financially supported by the NSFC of China (No. 21171076).



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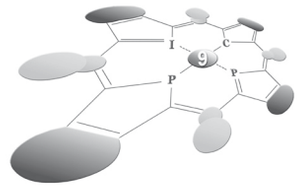

Transformations of rhodium(III) 21-carbaporphyrin. The intramolecular reversible C-C cleavage.

Karolina Hurej, Miłosz Pawlicki, Ludmiła Szterenberg, Lechosław Latos-Grażyński[a]

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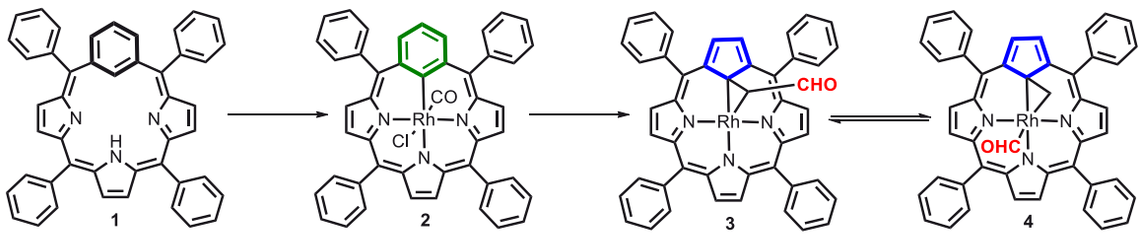
Macrocyclic environment allows for exploration of coordination variants less possible for monodendate or pincer ligands. Carbaporphyrins, belonging to this group, show a potential of being a suitable chemical background for observing unique features of a M-C bond reactivity. For instance palladium(II), gold(III) or rhodium(III) complexes of *p*-benziporphyrin gave a contraction of *p*-phenylene to a cyclopentadienyl unit.[1,2,3]



Surprisingly rhodium(III) *m*-benziporphyrin (**2**) undergoes the unprecedented transformation of the built in *m*-phenylene allowing an extrusion of a perimeter carbon atom to form rhodium(III) 21-carbaporphyrin (**3**), which stabilizes a rhodacyclopropane motif substituted by a formyl unit.[4]. Moreover the unique **3**–**4** conversion can be considered as an intriguing example of selective and reversible C-C bond activation controlled by acid-base conditions. The peculiar transformation encountered at the 21-carbaporphyrin cavity can be considered as a stimulating example of selectivity and C-C bond activation involving the transient η^3-allyl interaction.

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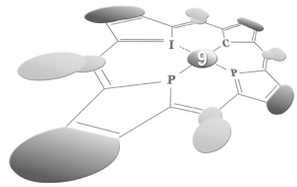

Uncommon Hexaarylbenzenes as Platform for Porphyrin-Fullerene Systems

H. Hölzel, D. Reger, D. Lungerich and N. Jux*

Friedrich-Alexander-University Erlangen-Nürnberg, Institute of Organic Chemistry II, Henkestr. 42, 91054 Erlangen, Germany (helen.hoelzel@fau.de)

Hexaarylbenzenes (HABs) show interesting properties that play an important role in materials chemistry. They have demonstrated intriguing characteristics as e.g., backbones in light-harvesting materials [1], as highly luminescent chromophores in organic light emitting diodes [2] and in the field of non-linear optics [3]. Further, HABs can be converted into hexa-*peri*-hexabenzocoronenes (HBCs) that contain a rather large π-system. The properties can be tuned by variation of their substitution pattern and substituents. Recently, K. Itami and co-workers published an advanced and highly sophisticated, but low-yielding synthetic route, towards uncommonly substituted HABs with up to six different substituents.[4]

Herein, we present the concept of donor-acceptor systems spaced by HABs or HBCs. Therefore we want to study the communication between porphyrins and fullerenes that are linked in various spacial arrangements (figure 1). The obtained insights from these push-pull architectures are crucial for the understanding of communication behavior in organic opto-electronic materials.

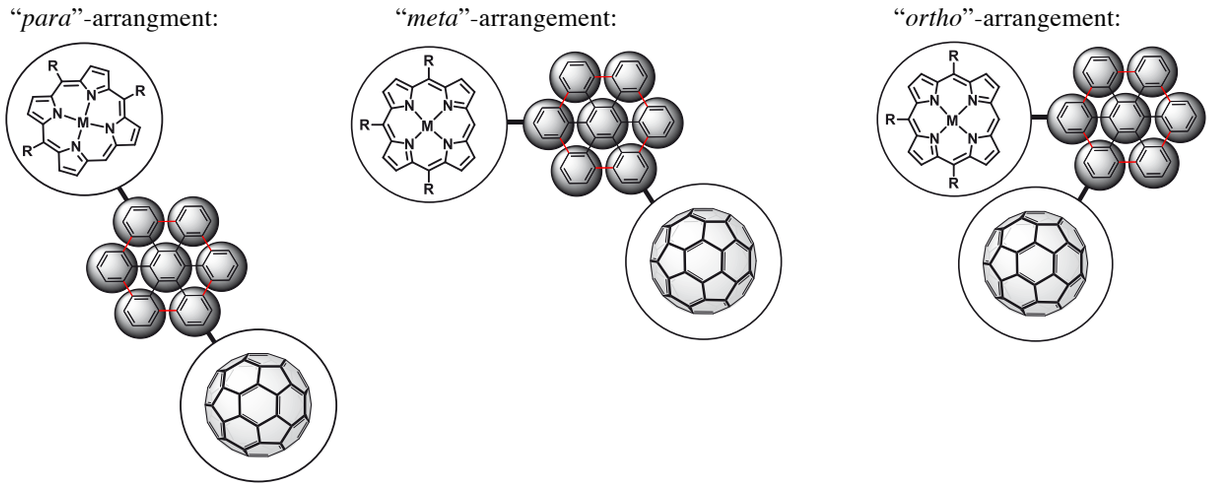

Figure 1: Different arrangements of porphyrins and fullerenes over the HAB- or HBC-system.

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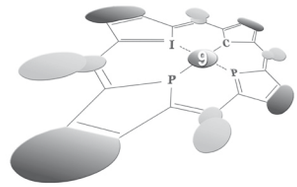

Synthesis and characterizations of polyamide-porphyrin hybrids

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α,ω-dicarboxylic acids (DCAs) are linear organic compounds with carboxylic acid groups capping both ends. Recently, industrial applications of DCAs are an important issue, which can be obtained from biomass such as vegetable oils and animal fats. In this study, a series of aliphatic polyamides were synthesized from C9-DCA, 4,4'-methylene-bis(cyclohexylamine) and small quantity of tris(2-aminoethyl)amine, followed by incorporation of porphyrin photosensitizer by chemical condensation with free amine moiety of polyamide. Characteristics of polyamide/porphyrin covalent hybrid was investigated by UV-Vis absorption, FT-IR, and ^{1}H NMR. We discuss the photophysical properties of polyamide/porphyrin hybrids.

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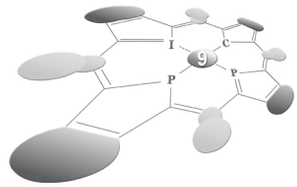

Structural features and coordination bonding in hemihexaphyrazine complexes with Y, La and Lu: a theoretical study

Yuriy A. Zhabanov[a], Alexander V. Zakharov[a], Nina I. Giricheva[b], Mikhail K. Islyaikin[a]

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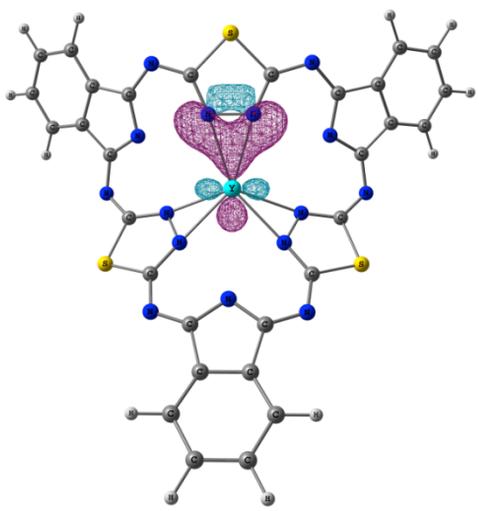
Metallocomplexes of an ABABAB-type macroheterocyclic compound (trithiadiazoletri(4-*tert*-butylisoindole)macrocycle) with trivalent metals (La, Lu, Tm) were synthesised for the first time in 2008 [1, 2]. The obtained substances were characterised by infrared and UV-vis spectroscopy, but their structure remains unknown. Since a signal corresponding to 1:1 composition was detected in MALDI TOF spectrum of La-complex, we have studied the structures of the macroheterocycle complexes with Y, La and Lu by DFT computations (B3LYP hybrid functional, the cc-pVTZ basis sets for C, N, S and H, and ECPs and triple-ζ valence basis sets for Y, La and Lu). The $YC_{30}N_{15}H_{12}S_3$, $LaC_{30}N_{15}H_{12}S_3$ and $LuC_{30}N_{15}H_{12}S_3$ complexes have equilibrium structures of C_s symmetry with non-planar macrocycles (see figure for the structure of the Y complex). The metal-nitrogen bond lengths are 2.370-2.409 Å (Y), 2.559-2.578 Å (La) and 2.334-2.380 (Lu). Planar structures of D_{3h} symmetry with the metal atom located in the centre of the macrocycle correspond to transition states. The barriers of the macrocycle inversion are 41 kJ/mol (Y), 5 kJ/mol (La) and 52 5 kJ/mol (Lu).



The electron density distribution NBO-analysis was performed and the nature of metal-ligand bonding was examined in the studied complexes. It is shown that lone electron pairs of the two nitrogen atoms of N-N bond in thiadiazole ligand fragments should be considered as the single unit donor, and macrocycle as a three-dentate ligand, despite the fact that the metal atom forms a bonds with six nitrogen atoms of the ligand.

Lanthanide contraction value is determined in the studied molecules. And it was close to the value in the groups of the compounds of the lanthanide halides with three monovalent ligands and lanthanide series of compounds with three bidentate ligands.

Acknowledgment: this work was supported by grant of the President of the Russian Federation (project MK-6073.2016.3).

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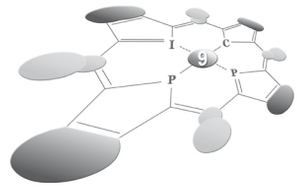

Photophysical property and cytotoxicity of porphyrin photosensitizers having hydrophilic and/or hydrophobic substituents

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Photodynamic therapy (PDT) is a promising cancer treatment that uses a photosensitizer. Among various photosensitizers, porphyrin has great potential as efficient PDT agent. To probe the effect of substituent number and type on the intracellular penetration and accumulation of photosensitizers, a new series of porphyrin derivatives having hydrophilic triethylene glycol and/or hydrophobic alkyl units were synthesized and characterized by UV-Vis absorption, fluorescence emission, MALDI-TOF-MS and ^{1}H NMR. Photophysical properties associated with singlet oxygen generation are studied and *in vitro* photocytotoxicity with MCF-7 human breast cancer cells are also investigated to determine their PDT potentiality

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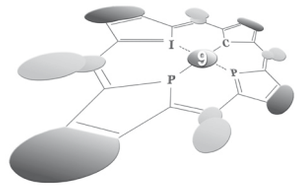

Porphyrin Nanorings for Quantum Interference

Cécile Roche,[a] Hua-Wei Jiang,[a] Qianfu Luo,[a] Guzmán Gil-Ramírez,[a] Sarah L. Chappell,[b] David Costa-Milan,[b] Oday A. Al-Owaedi,[c] Colin J. Lambert,[c] Richard J. Nichols,[b] Simon J. Higgins[b] and Harry L. Anderson[a]

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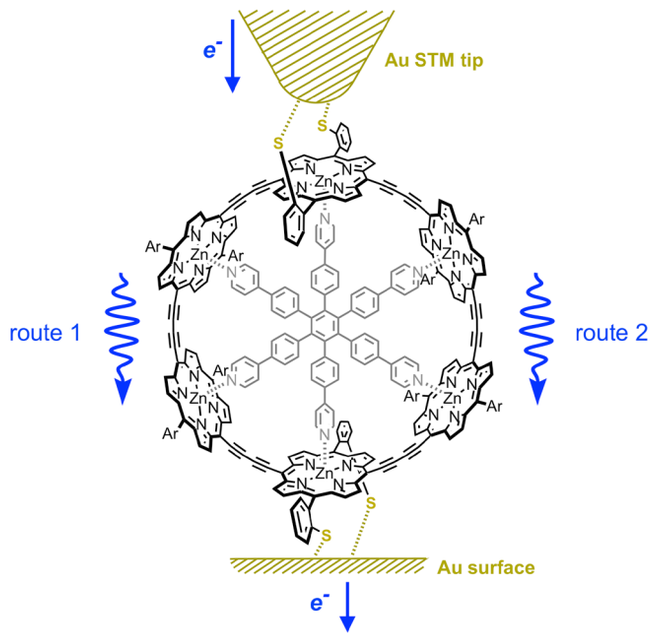
[c] *Lancaster University, Department of Physics, Lancaster LA1 4YB, UK*

The aim of this project is to design a molecular interferometer, which can mediate charge transport between two points by two different pathways, and to investigate quantum interference effects in the conductance of this single-molecule device by scanning tunneling microscopy (STM). The molecular design is based on sulfur-functionalized π-conjugated porphyrin nanorings, synthesized *via* a template-directed strategy.[1-4] The synthesis of the ring and model compounds will be presented, as well as conductance results and computational simulations.



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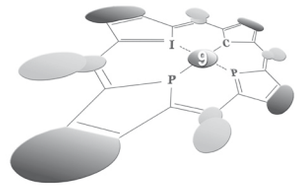

Sandwich-type tetrapyrrole-based OFETs and SMMs

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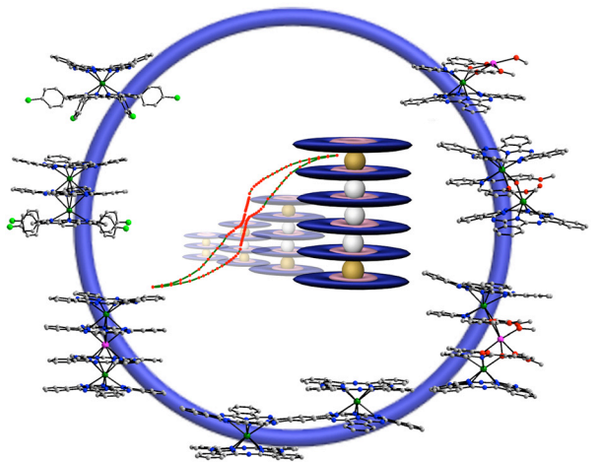
A series of sandwich-type phthalocyaninato and porphyrinato metal complexes have been designed and synthesized. The semiconducting and single molecule magnetic properties have been studied.



Sandwich-type tetrapyrrole-based SMMs

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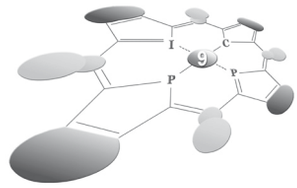

Electrochemistry and Spectroelectrochemistry of π-Extended Porphyrins

Xiaoqin Jiang * [a], Wenqian Shan [a], Yuanyuan Fang [a,b], R. G. Waruna Jinadasa[c], Siddhartha Kumar[c], Karl M. Kadish [a], Hong Wang[c]

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In the present paper, we report the electrochemistry and spectroectrochemistry of several series of π-extended porphyrins in nonaqueous media. Selected structures of the examined compounds include dibenzoporphyrins, A_2B_2 tetrabenzoporphyrins and a bisporphyrin with a linked 6, 13-pentacene-quinone group (See Chart 1). The spectral properties of each π-extended porphyrin in its oxidized and/or reduced forms was also measured using thin layer UV-vis spectroelectrochemistry. The effect of the number and type of fused π-ring system on the electrochemical and spectral properties of the compounds is described. (Support from Natural Science Foundation of China (21501070) and Foundation of Jiangsu University (15JDG131, 05JDG051).

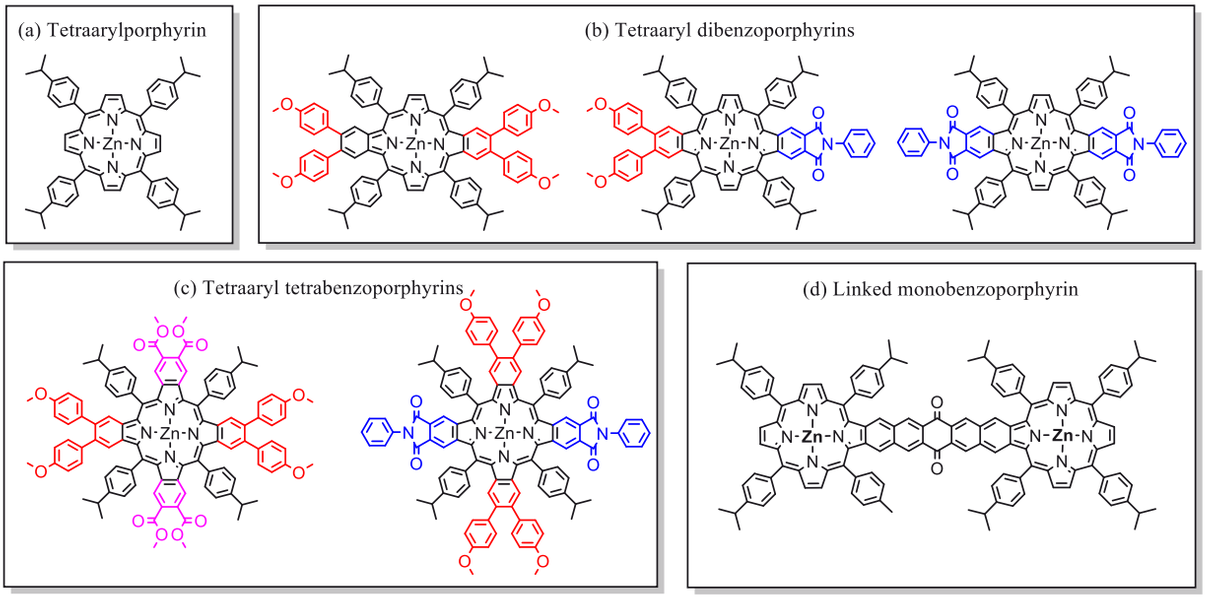

Chart. 1 Structures of investigated benzoprophyrins.

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Electrochemistry and Spectroelectrochemistry of Triple Decker Complexes Containing Phthalocyanines and Porphyrin or Corrole Macrocycles

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The present paper will describe the electrochemical and spectroscopic properties of triple-decker complexes containing phthalocyanine, porphyrin and/or corrole macrocycles in nonaqueous media. Selected examples of the examined compounds are shown in Chart 1. Each triple decker species undergoes 4-5 reversible one-electron oxidations and 3 one-electron reductions in PhCN or CH_2Cl_2 containing 0.1 M TBAP. The spectral changes obtained during controled potential oxidation or reduction were measured by thin-layer UV-vis spectroelectrochemistry and are used to assign the possible electron transfer sites. The effect of the third macrocycle (Pc, Cor or Por) and the metal ions on the electrochemical and spectpscopic properties will be described.

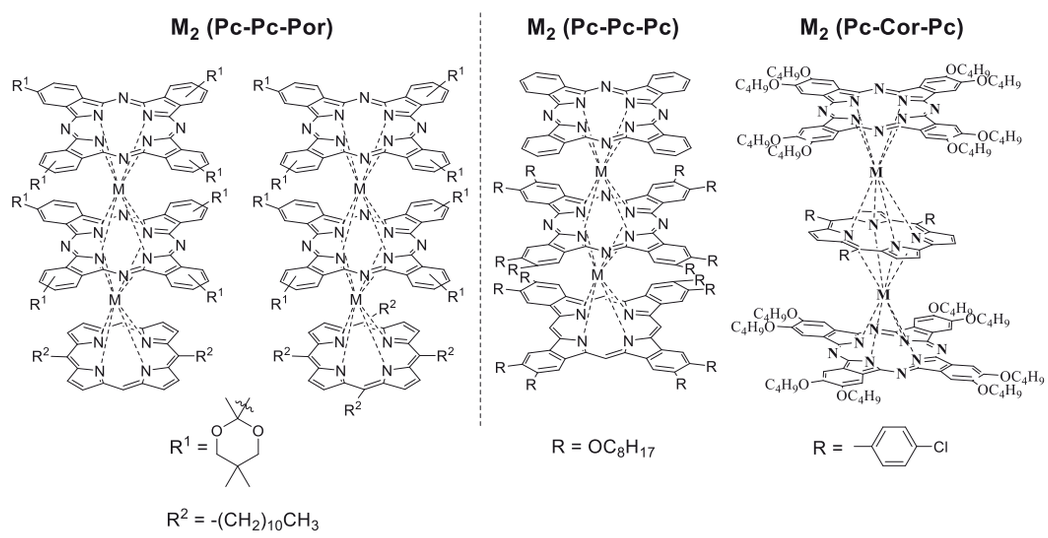

Chart 1. Structures of investigated triple decker compounds.

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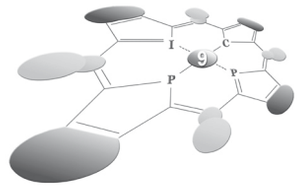

Biomimetic Self-assembling Acylphthalocyanines

Hong-Guang Jin, Mihaela Carmen Balaban, Sabine Chevallier-Michaud, Michel Righezza and Teodor Silviu Balaban*

Aix-Marseille Université, CNRS UMR 7313, Centrale Marseille, Chirosciences, Service 442, Avenue Escadrille Normandie-Niemen, F-13013 Marseille, France. E-mail: jesonjin08@gmail.com/ts.balaban@univ-amu.fr

Highly ordered self-assembling functional dyes with efficient energy utilization are desirable for materials science.[1] Compared to traditional covalent bonds, the supramolecular self-assembly based on noncovalent interactions is a powerful approach to reach this goal. Green photosynthetic bacteria can capture light efficiently even at 100 m under water surface[2] thanks to their special organelles, called chlorosomes, which agglomerate homologues of bacteriochlorophylls (BChl's) *c*, *d*, *e*. Our group has mimicked[3] and extended[4] the self-assembly algorithm by employing different recognition motifs as well as various solubilizing groups grafted onto porphyrins or chlorins which self-assemble in the same way as the natural BChl's. Here, we synthesized a series of biomimetic self-assembling phthalocyanines (Pc's)[5] equipped with carbonyl groups as recognition motifs, a central zinc atom and diverse solubilizing alkyl chains mimicking the natural BChl's. Upon self-assembly a very broad and red-shifted Q-band absorption extending to over 900 nm was put into evidence.

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Synthesis of A3B azaphthalocyanine covalently functionalized reduced graphene

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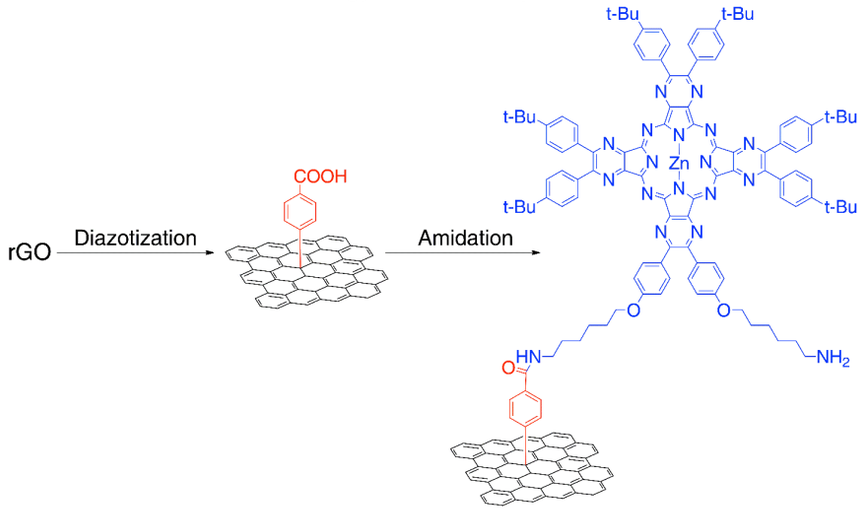
To enhance the processibility and performance of graphene material, the introduction of functnional groups to the graphene sheet. Recently, photoactive components such as phthalocyanines, porphyrins and diketopyrrolopyrroles were covalently attached to graphene yielding unique optoelectronic properties. [1-2]
The attachment of phthalocyanine to graphene has been explored through many strategies. [3-4]
In this paper, novel strategy was applied to the preparation of tetrapyrazinoporphyrazine-reduced graphene oxide hybrid material. Reduced graphene oxide was functionalized with carboxylic acid groups via diazotization with 4-amino benzoic acid and subsequent amidation with the synthesized aminoalkyl-tetrapyrazinoporphyrazine. FT-IR, Raman, TGA, UV-vis and fluorescence spectrophotometry methods were utilized for characterization of the hybrid material, which exhibited an electron/energy transfer ability.



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Synthesis of Novel Porphyrin-Phthalocyanine Dyads Photosensitizer

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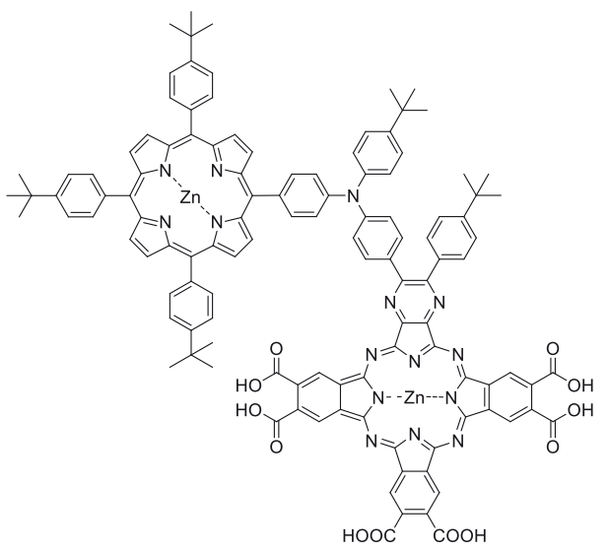
Conjugates of porphyrins and phthalocyanines are very interesting structures because of these macrocycles have complementary absorptions in the visible region and the emission spectra of phthalocyanines do not show significant overlap with those of the porphyrins. Furthermore, with the advantage of their fine stability, these conjugates are good choices for usage in molecular photonics, catalysis and light harvesting architectures with a good spectral coverage in the blue and red wavelengths.
Different synthetic strategies have been used to prepare multiporphyrin-phthalocyanine arrays. In this work, a new porphyrin-phthalocyanine dyads are synthesized and fully characterized by elemental analysis, ^{1}H NMR and MALDI-TOF mass. Their photophysical properties are detected by UV-visble and Fluoroscence spectrum.



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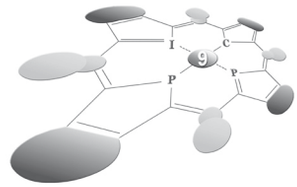
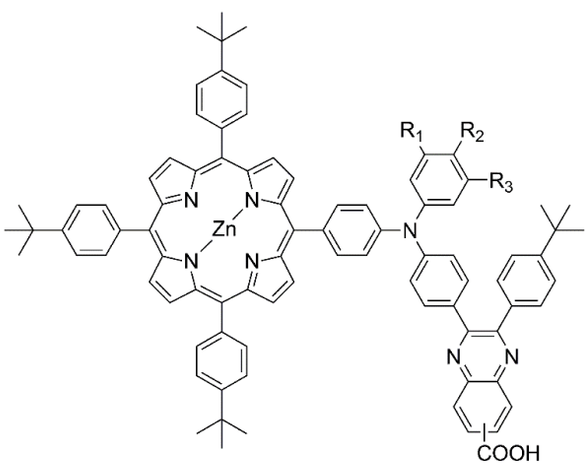


Synthesis of A_3B-Type Quinoxaline-substituted Porphyrin Photosensitizer

Chang Young Jung, Jong Min Park, Wang Yao, Joong Hyun Cho, Dae Hyun Kim, Jae Yun Jaung*

Department of Organic and Nano engineering, Hanyang University, 222 Wangsimni-ro, Seongdong-gu, Seoul 133-791, Korea
Tel : +82 2 2220 0492, E-mail : jjy1004@hanyang.ac.kr

A series of A_3B porphyrin photosensitizers containing a triphenylamine structure linked with quinoxaline, which is terminated with a carboxyl group was synthesized through an A_3+B pathway. No scrambling phenomena were observed, and purification of the products was convenient. The triphenylamine structure was selected due to its potentially strong absorption and electron-donating capabilities, while the carboxyl group was intended to enhance compound solubility in a polyethylene glycol/ water mixture as a hydrophilic pharmaceutical carrier. These novel A_3B zinc porphyrin derivatives exhibited longer wavelength in the Q band due to introduction of the quinoxaline appended triphenylamine unit compared to the A_4 porphyrin. The structures were characterized by ^{1}H NMR, elemental analysis, and MALDI-TOF-MS, and the photophysical and photochemical properties of the complexes were investigated.



a : R_1&R_3= -H, R_2= -CH_3
b : R_1&R_3= -H, R_2= -*tert*-butyl
c : R_1&R_3= -*tert*-butyl, R_2= -H

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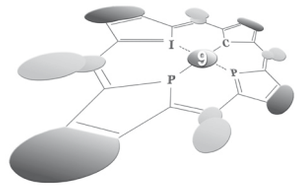

Fluorescent chemosensor for copper(II) based on new A_3B zinc phthalocyanine

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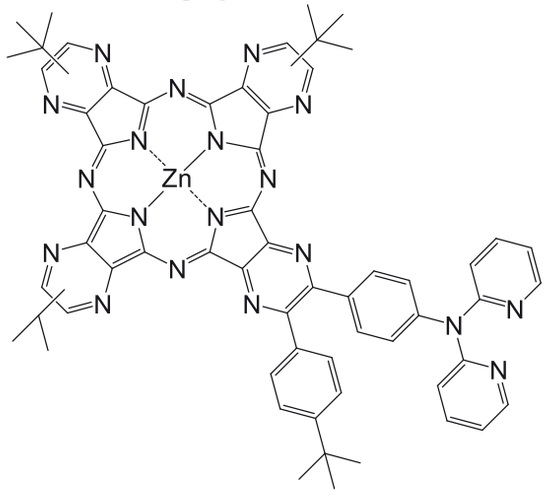
A new copper(II) fluorescent sensor A_3B zinc phthalocyanine consisted with 2,2'-dipyridylamine (2,2'-dpa) has been designed and synthesized. It is made up of two separately functional groups: the zinc phthalocyanine works as a fluorophore while the dpa part performs as a selected binding site for metal ions. These compounds are fully characterized by elemental analysis, ^{1}H NMR and Maldi-TOF mass. Furthermore, they display a high selectivity for Cu^{2+} ion among the metal ions detected (Hg^{2+}, Mn^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+}, Ag^{+}, Cu^{2+}, Sn^{2+}, Mg^{2+}) while both absorbance and fluorescence spectra indicate changes in visible region as treated with Cu^{2+} in methanol solution. Moreover, its fluorescence can be revived by addition of EDTA disodium solution and the synthetic strategy for phthalocyanines consisted with 2,2'- dipyridylamine is conveniently with good yield and notable photophysical properties of sensor can be contributed to developing new fluorescent sensors for metal ions.



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Pyrrolopyrrole Aza-BODIPY Monomers and Dimers: Control of Absorption in the Far-red and NIR Regions

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Chromophores, which can cover a wide range of visible and near infrared (NIR) regions, have been attracting a great deal of attention due to their possible application in organic photovoltaics so that molecular designs towards this goal have been intensively investigated. Recently we have reported that novel aza-BODIPY-based compounds, pyrrolopyrrole aza-BODIPYs (PPABs, **Figure 1**), which were synthesized by a Schiff base forming reaction of diketopyrrolopyrroles and heteroaromatic amines and subsequent boron coordination, exhibited intense absorption and fluorescence in the far-red and NIR regions depending on the types of the heteroaromatic ring units in the structure of PPABs and the substituents on the pyrrolopyrrole moiety.[1,2] During the synthesis of a series of PPABs, we observed a drastic change of the sharp absorption of the PPABs to panchromatic absorption in the visible and NIR regions upon dimerization of PPABs. In addition, the emission profiles of the PPAB dimers were dependent on the excitation wavelengths.

In the present study, in order to get an in-depth insight into the optical properties of the dimer species, we synthesized a series of PPAB dimers bearing different types of heteroaromatic ring units such as benzothiazole (**1**), pyridine (**2**), and further π-extended dimethylfluorene substituents (**3**). Moreover, we investigated how the linker units, phenyl and thienyl groups (**4** and **5**), affected on the optical properties in the monomers.

In the poser presentation, control of absorption of PPABs by aryl substituents and dimerization, and molecular designs of chromophores in the far-red and NIR regions based on the current system will be discussed.

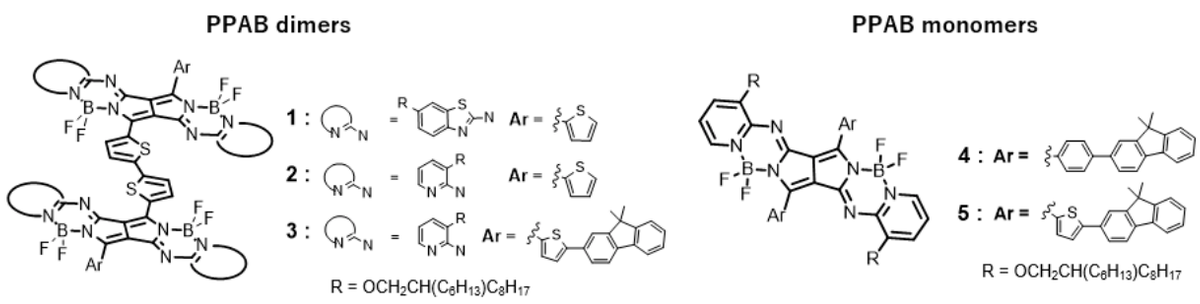

Figure 1. Structures of PPAB dimers (**1**,**2**, and **3**) and PPAB monomers (**4** and **5**) in this study.

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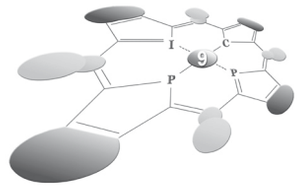

Strapped porphyrins functionalized MWNTs for photoconversion and electrocatalysis

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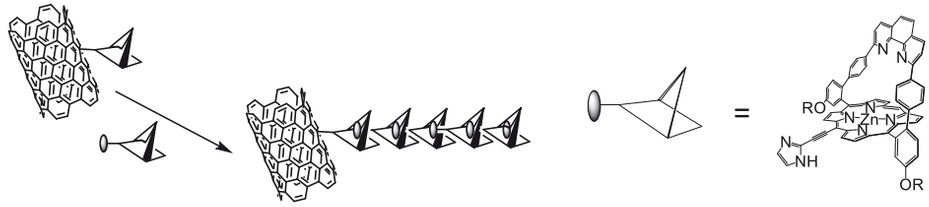
In the race for miniaturization, molecular materials allow us to downsize measurable physical changes to the nanoscale. The design and synthesis of molecular materials possessing tailor-made redox and/or photochemical properties is thus a major challenge in the field of molecular electronics. In this field, porphyrins are an extensively studied electro-active chromophore due to the abundance of naturally occurring porphyrin-based architectures that inspire chemists. One of the actual trends in the use of molecular materials in devices is based on assemblies of molecules (π-stacks in organic field effect transistors, self-assembled monolayers, light emitting diodes, …) that take advantage of the low-cost of self-assembly and organization. Our project consists in the development of functional molecular nano-objects that combine self-assemblable porphyrinic building blocks with carbon nanotubes that hold great promise in the development of nanotechnologies and nanodevices. Nanobrushes will then be prepared using the selective recognition of imidazoles in the strapped zinc porphyrin receptor as the driving force for self-assembly.[1] Functionalities will be introduced to target catalysis, especially oxygen reduction,[2] and light–harvesting properties for solar energy conversion. In this poster, we wish to report the synthesis of a phenanthroline-strapped zinc porphyrin, its grafting on MWNTs and early results concerning the growth of self-assembled porphyrin nanobrushes.



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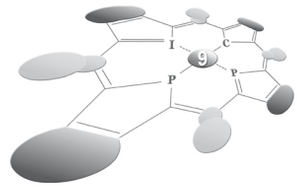


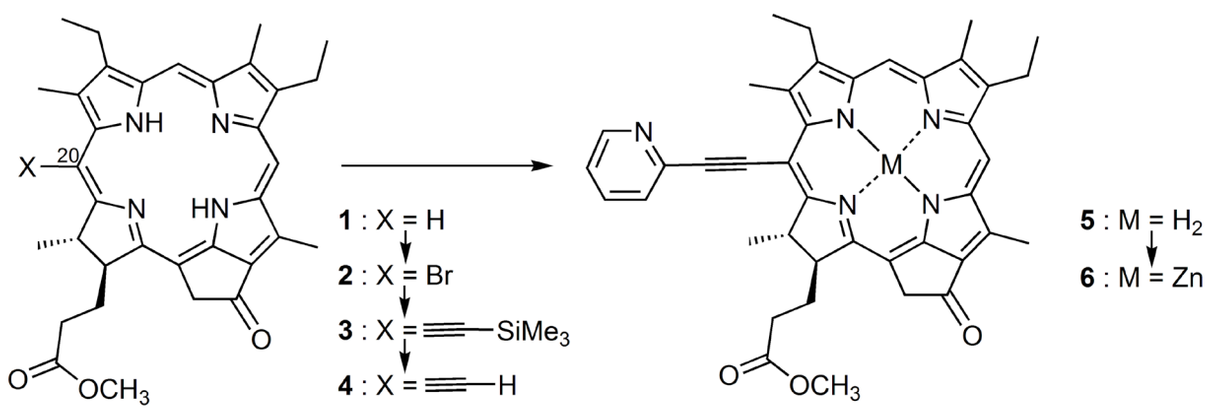
Acid and Base Sensitivities of Synthetic Zinc Chlorophyll Derivatives Bearing a Pyridyl Group

Yusuke Kamatani, Ayaka Wada and Hitoshi Tamiaki

Graduate School of Life Sciences, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan

Chlorophylls are known as light-harvesting, energy-transfering and charge-separating pigments in natural photosynthesis. In photosynthetic apparatus, chlorophylls are usually fixed on peptides through coordination of peptidyl residues including an imidazolyl group to their central Mg atom and hydrogen bond of acidic residues with their peripheral carbonyl groups. Here, we report on the synthesis of zinc chlorophyll-*a* derivatives bearing a pyridyl group and their responce to additional acids and bases in a solution.

First, a 2-pyridyl group had been examined to be directly introduced to methyl mesopyropheophorbide-*a* (**1**), one of the chlorophyll-*a* derivatives, at the 20 position, but in vain. So an ethynylene spacer was inserted between the chromophores. Methyl 20-ethynyl-mesopyropheophorbide-*a* (**4**) was prepared according to reported precedures [1] via 20-bromination of **1**, Stille coupling of **2** with tributyl(trimethylsilylethynyl)tin, and deprotection of trimethylsilyl group in **3** to **4**. Sonogashira coupling of **4** with 2-bromopyridine gave **5**, followed by zinc metalation to afford a desired conjugate of zinc chlorin with pyridine **6**. The synthetic conjugate **6** was dissolved in chloroform and the solution was titrated with carboxylic acids. UV-Vis-NIR absorption spectral changes showed that the longest absorption (Qy) band was shifted to a shorter wavelength due to the protonation of a pyridyl group. The same solution was also titrated with primary amines and imidazole, giving bathochromic shifts of the Qy maximum because of coordination of the additional bases to the central zinc atom. Moreover, ^{1}H-NMR spectral analysis proved both the interaction in deuterated chloroform.



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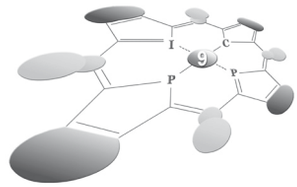

A Push–Pull Unsymmetrical Porphyrazine/Phthalocyanine Hybrids for Solar Cells

[a]Emre Güzel[a], Armağan Günsel[a], Mehmet Kandaz[a*], M. Salome Rodriguez Morgade[b*], Thomas Torres[b**]

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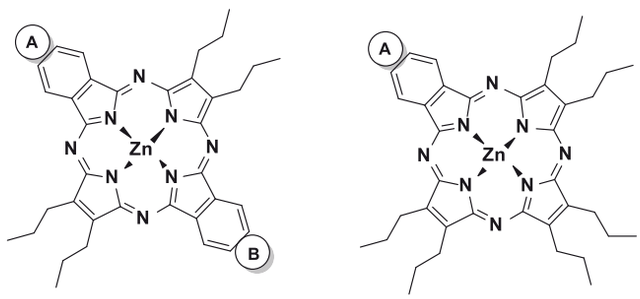
[b]*Department of Organic Chemistry Facultad de Ciencias, Universidad Autónoma de Madrid Cantoblanco,*

Population and economic growth mean constantly increasing energy needs, mirrored primarily in electricity demand, which outpaces all other energy carriers. In addition, the levels of greenhouse gases being emitted in the atmosphere are alarming, confirming that the existing energy trends are problematic, not only from an economic, but also from an environmental point of view. Utilization of renewable sources and particularly solar energy provides, by far, the most solid answer to these questions and the most viable long-term solution. There is no doubt that there is a growing awareness of the urgency for solar energy systems to forge ahead[1,2].



A=B= NO_2; A=B=NH_2;A=B=I
A=DPA, B=I; A=DPA, B=COOH

A=NO_2; A=NH_2;A=I

In this work, in particular, electron-donating propyl, amino, diphenylamino and electron withdrawing nitro, iodo and carboxylic acid groups have been introduced into trans porphyrazine hybrids[3].

We thank to research funds of Sakarya University (BAP-2015,02-04-001), and TUBİTAK (114Z448).

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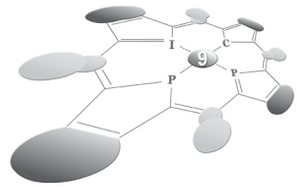

Elucidation of Selectivity for Silver Ion by "Turn off" Fluorescence of Pc Bearing Thioalcohol Groups

Merve Umutlu[a], Orhan Güney[a] and Mehmet Kandaz[b]

[a]*Istanbul Technical University, Department of Chemistry, 34469 Maslak, Istanbul, Turkey*
[b]*Sakarya University, Department of Chemistry, 54140 Esentepe, Sakarya, Turkey*

Fluorescent chemosensors capable of selectively detecting metal ions in environment or biological systems were of current interest in supermolecular chemistry because of their high selectivity, sensitivity, and simplicity [1]. In this regard, numerous literature reports have appeared that explored fluorescence chemosensor in the detection and discrimination of transition metal ions owing to their extremely toxic impact on our environment or biological systems [2]. The fluorescent sensor absorbs and emits in the spectral range of visible light, exhibits a reversible response, is widely variable concerning receptor groups, and its optical properties also allow a miniaturization including LED's and photodiodes. The detection of the analyte, metal ions is based on a static quenchnig of fluorescence upon binding to metal ions [3]. Phthalocyanines (Pcs) are highly versatile and stable chromophores with unique physicochemical properties that make them, alone or in combination with many other functional structures for the construction of molecular materials or electro and photoactive moieties. Therefore, the synthesis of precursors bearing one/or more functionality is vital in the preparation of new photoactive phthalocyanines and the design of Pcs linked to strong fluoroprobe moieties appears particularly promising.
In present work, we have synthesized a thiol sunstituted as a fluorescent chemosensor for the purpose of quantitative detecting of Ag(I) ion based on fluorescence quenching. A comparative study on silver ion and mercury recognition property of Pc has been carried out to elucidate the effect of the solution parameters on sensing ability of fluoroprobe. The photophysical properties and pH-dependent fluorescence and absorbance behavior of Pcs were elucidated in the absence and presence of both Ag(I) and Hg(II). Complex stoichiometry and interference effect of foreign metal ions were evaluated by spectrofluorometric titration based on quenching and excimer emission data obtained upon Ag(I) ion concentration.

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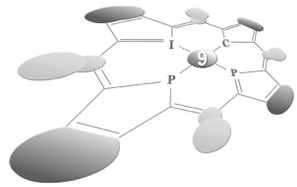

Covalent and Non-covalent Bonded Chlorin Derivatives on Graphene Oxide Nanosheets for Photodynamic Therapy

Eun Seon Kang*, Il Yoon*, Woo Kyoung Lee and Young Key Shim*

Photodynamic Therapy Institute and School of Nanoscience and Engineering, Inje University, 197 Injero, Gimhae, Gyeongnam 50834, Republic of Korea

Photodynamic therapy (PDT) is a relatively new cancer modality that uses light, photosensitizer (PS), and oxygen for the treatment of various forms of cancer using photodynamic action.[1] The PDT treatment derives great promise from the dual selectivity that is produced by both a preferential uptake of the drug by the diseased tissue and the restriction of carefully regulated light absorption onto the specific tumor sites.[2]

Graphene, a very recent rising star material, having an atomically thin, 2D honeycomb lattice that consists of sp^2-hybridized carbons, exhibits remarkable electronic, thermal, optical, and mechanical properties.[3] Particularly, graphene oxide (GO), graphene's hydrophilic derivative, has been found important potential applications in drug delivery due to their large specific surface area and abundant functional groups (epoxide, hydroxyl, and carboxyl groups).[4]

GO nanosheets (GONs) were prepared by a modified Hummers' method.[5] Chlorin derivatives having versatile functional groups (carboxyl, hydroxyl, aldehyde, amine) were synthesized from chlorophyll-a paste followed by extraction, oxidation, and imide formation.[6] The chlorin derivatives were covalent bonded on the GONs through various synthetic methods contain coupling reactions (□COO□ bond), click reaction (triazole ring formation), and *N*-alkylation (N□C bond) reaction.[7] In addition, non-covalent bonded chlorin derivatives on the GONs were prepared for a comparative study with the covalent bonded chlorin derivatives on the GONs. Finally, the covalent and non-covalent bonded chlorin derivatives on the GONs were characterized using a combination analysis by FT-IR, NMR, UV-vis, Raman spectroscopies, XPS and TGA analyses, and TEM images.

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When loop becomes tail - base-off cobalamin

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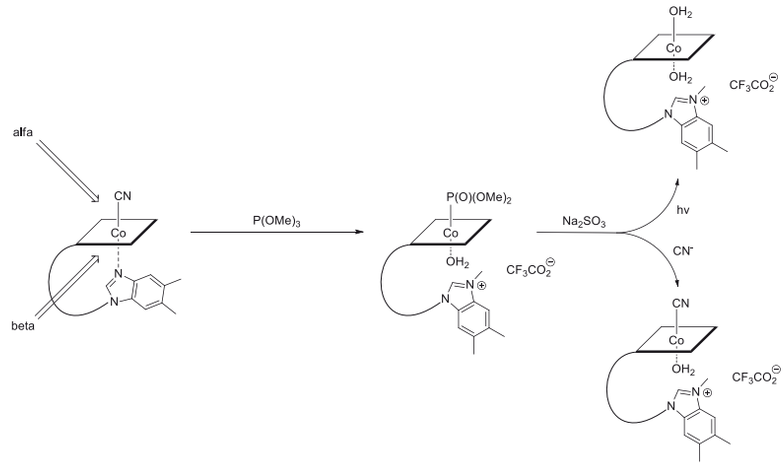
Vitamin B_{12} is an organocobalt compound, in which the central Co ion is bound by two axial ligands and four corrin nitrogen atoms, known to be essential for human beings.[1] The α-ligand is not only coordinated to cobalmin via nitrogen atom of dimenthylbenzimidazole group (DMBZ), but also bounded covalently through the riboso-phosphate bridge. When the Co-N bond is cleaved, vitamin B_{12} exists in the base-off form, favoured by a great variety of factors (pH, competing ligand *etc*.).[2,3]
However, at room temperature the base-on form predominates due to thermodynamic factors. Enzymes, on the other hand, prefer to bind B_{12}-cofactor in the base-off form, since additional site capable of noncovalnet interaction is exposed.[4] Derivatization of vitamin B_{12} to produce a permanent base-off form, by quaternization of N_{DMBZ}, would allow determination if modification of a "loop" affects catalytic activity of this corrinoid compound.

Herein, we present a method of N_{DMBZ} atom methylation employing microwave irradiation and subsequent axial-ligand exchange. Final products were subjected to a series of both physicochemical, biological, and catalytic testes.



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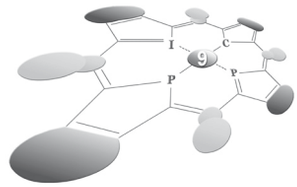

Porphyrin Analogues of Trityl Cation and Anion

Kenichi Kato, Hideki Yorimitsu, And Atsuhiro Osuka

Department of Chemistry, Graduate School of Science, Kyoto University

Since the discovery as the first identified carbocation in 1901, triphenylmethyl cation and its derivatives have provided rich information about many reaction mechanisms and π-electronic delocalization, and found widespread usage as protecting groups, Lewis acids, and chromophores and fluorophores. On the other hand, carbocations adjacent to porphyrin have been scarcely studied so far. In these studies,[1,2] strong absorptions were observed in near infrared (NIR) region for the porphyrin-stabilized cations as a consequence of effective charge delocalization. It is desirable to develop more general synthetic ways to generate such cations. In addition, porphyrin-stabilized carboanions have not been characterized, to the best of our knowledge. Here, we disclose the effective generation of porphyrin analogues of trityl cation from the corresponding carbinols prepared by the reactions of carbonyl compounds with porphyrinyllithium reagents.[3] We also report on the generation of a porphyrin analogue of trityl anion.

Bis(4-*tert*-butylphenyl)porphyrinylcarbinols were prepared via highly nucleophilic porphyrinyllithium reagents, and treated with trifluoroacetic acid to generate the corresponding carbocations stabilized by *meso*- or *β*-porphyrinyl groups. Their UV/vis/NIR absorption and ^{1}H NMR spectra revealed the more effective charge delocalization to the *meso*-porphyrinyl group with decreasing the aromatic nature of the porphyrin macrocycle than that to the *β*-porphyrinyl group. A propeller-like porphyrin trimer, tris(*β*-porphyrinyl)carbinol, was also synthesized and converted to the corresponding cation that displayed a more intensified absorption reaching over NIR region. Although *β*-porphyrinylmethyl carboanions were highly unstable, a *meso*-porphyrinylmethyl carboanion was successfully generated as a stable species upon deprotonation of bis(4-*tert*-butylphenyl)(*meso*-porphyrinyl)methane with potassium bis(trimethylsilyl)amide and 18-crown-6. This anion was characterized to hold apparent Soret- and Q-like bands, which indicates stronger porphyrinic nature compared with the corresponding cation.

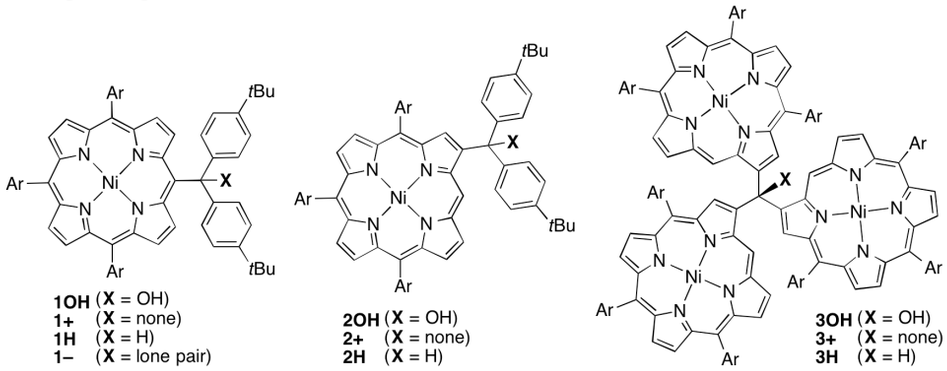

Figure 1. Chemical formulas of porphyrin analogues of trityl cation and anion. Ar = 3,5-di-*tert*-butylphenyl.

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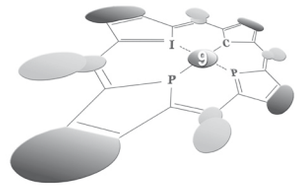

meso-Aryl Substituted Amethyrin Analogs with Pyridine Subunits

Xian-Sheng Ke, James T. Brewster II and Jonathan L. Sessler*,[a]

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Expanded porphyrins are attractive not only in the context of aromaticity and metal-coordination chemistry, but also as nonlinear optical materials, functional dyes, and photodynamic therapy agents.[1] Amethyrin, which represents one kind of hexapyrrolic expanded porphyrin, has been shown to possess interesting electronic properties (Figure 1a), as well as an ability to coordinate a number of metal ions.[2] Initial work done by Corriu showed that modifications to the amethyrin core, including replacement of two pyrroles by pyridine subunits, would allow for the stabilization of new bimetallic transition metal complexes.[3] However, to our knowledge the non-transition metal coordination chemistry of these systems was never explored. Recently, Setsune and co-workers reported the condensation between 2,6-bis(3,4-diethyl-2-pyrryl)-pyridine and formaldehyde to yield a *meso*-free dipyrihexaphyrin. The resulting species proved to be highly reactive and unstable in the presence of nucleophiles (e.g. alcohols and amines) at mild conditions.[4] We envisioned that the incorporation of appropriately modified aryl groups in the *meso*-position would greatly improve the stability of the overall macrocyclic system. Herein, we report the synthesis and photophysical properties of amethyrin analogs (**1**-**3**, Figure 1b), as well as preliminary exploration of **1**-**3** in actinide complexation.

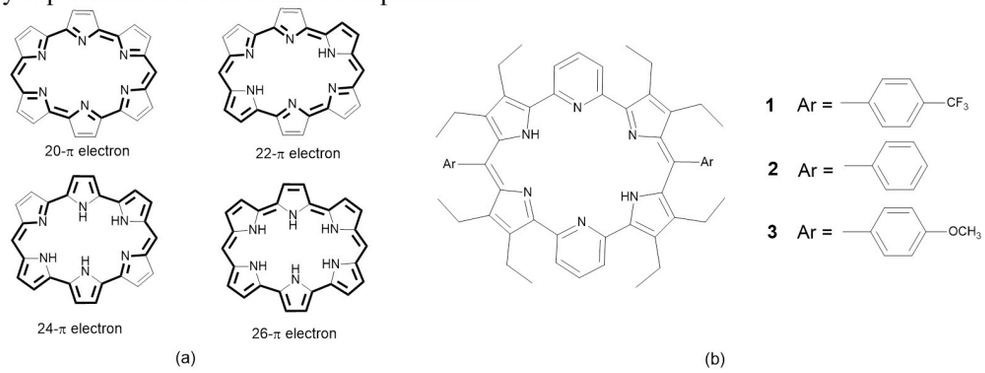

Figure 1. (a) Possible oxidation states of amethyrin; (b) chemical structures of the amethyrin analogs (**1**-**3**).

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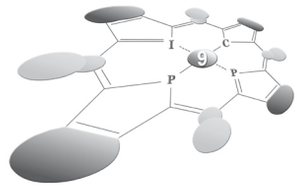

Electrogeneration and electrochemistry of σ-bonded cobalt porphyrins with π-extended systems and/or highly electron-withdrawing pyrrole substituents

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A series of electrochemical correlated cobalt(II) β-substituted nitroporphyrins with π-extended systems and highly electron-withdrawing β-substituents were investigated as to their electrochemistry, spectroelectrochemistry and highly reactivity of the electroreduced compounds with alkyl halides. Structures of the investigated compounds are shown in Chart 1. Each porphyrin is characterized by several redox reactions involving the conjugated π -ring system or the central metal ion which could convert to its Co(III) or Co(I) forms under the application of an applied oxidizing or reducing potential. The measured $E_{1/2}$ values were shown to vary with the electron–donating or electron-withdrawing properties of the substituents. A linear relationship exists between half-wave potential and sum of Hammett substituents constants for these two series of porphyrins which suggests a similar oxidizing/reducing mechanism throughout the series. The reduced Co(I) porphyrin is highly reactive with alkyl halides and give a product which was assigned as a σ-bonded Co(III) methyl derivative and was also characterized electrochemically and spectroelectrochemically.

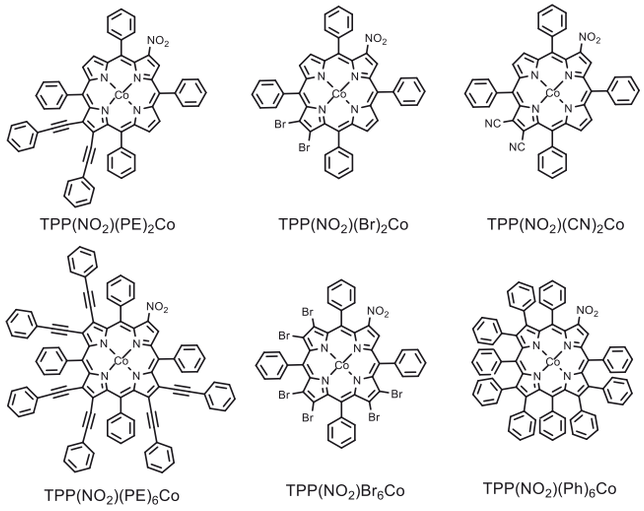

Chart 1. Selected structures of investigated Co(II) porphyrins

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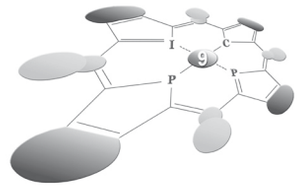

Unleashing the Metal Chelation Capability of the Texaphyrins through the Synthesis and Nanoassembly of Texaphyrin-Phospholipid Building Blocks

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The discovery and synthesis of novel, inherently multifunctional building blocks for nanoparticles, particularly those made of organic molecules, is of significant difficulty. The limited number of reported organic, multifunctional building blocks underscores the need of new, synthetically attainable constructs. A macrocycle of interest, texaphyrins, pentaaza Schiff base macrocycles, share a strong, but 'expanded', similarity to porphyrins, where they possess a 5-coordination state in comparison to the 4-coordination state in porphyrins. With demonstrated capabilities of forming 24 different stable 1:1 complexes with metal cations, applications of texaphyrins have been demonstrated in cancer therapy and imaging.[1] Despite the chelation capability and multifunctionality of texaphyrins, the use as a building block for nanoparticles has been unattainable, due to the synthetic difficulty of texaphyrin constructs capable of self-assembly. The discovery and synthesis of a texaphyrin-based building block would offer a new dimension in nanomedicine, enabling the use of dozens of medically relevant metal ions in a single building block nanoparticle, which will redefine how we develop future building blocks in nanomedicine.

Herein, we introduce "nanotexaphyrin"; the first all-texaphyrin based organic nanoparticle self-assembled from a novel texaphyrin-phospholipid conjugate. Nanotexaphyrin exhibits a liposome-like structure, strong absorption of near-infrared photons, high-density packing of macrocyclic monomers, and structure-dependent fluorescence quenching. A library of 18 different metal-coordinated texaphyrin-phospholipid conjugates were synthesized, effectively creating a nanotexaphyrin library, each with a particular application through exchange of metal ions, while still possessing the exact same building block. Gadolinium-nanotexaphyrin (Gd-nanotexaphyrin) was evaluated for MRI capabilities, demonstrating a relaxivity of $r_1 = 0.58\ mM^{-1}s^{-1}$ at 7 *T*, in a concentration dependent manner. We further demonstrate the capabilities of another nanotexaphyrin, Lutetium-nanotexaphyrin (Lu-nanotexaphyrin), which was shown to have potent singlet oxygen generation with small doses of light. The field of texaphyrins has renewed interest and a sense of unlimited potential with the advent of nanotexaphyrins, where exciting preliminary results will propagate further research into this field.

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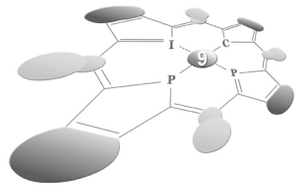

Resonance Raman investigations on cobalt hangman porphyrins during electrocatalytic hydrogen formation

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Hydrogen formation is one of the key electrochemical reactions for hydrogen based clean power generation. Enzymes can perform this reaction efficiently, however, their redundant instability in aerobic conditions make them less applicable in industrial applications[1]. Therefore, biomimetic compounds with a copied active site structure are highly attractive. Hangman porphyrins with cobalt as metal center and an acid as hanging group provide a rational design of such a compound, facilitating proton coupled electron transfer reactions like the hydrogen evolution reaction (HER). Electrochemical investigations of these compounds confirmed their high electrocatalytic activity towards HER[2].
In our study we focused on spectroelectrochemical probing of intermediates during HER catalysis. We used resonance Raman (RR) spectroscopy to assign the vibrational pattern of Co hangman porphyrins with an acidic hanging group to a certain redox state and reaction intermediate. Furthermore, we immobilized the compound on a roughened silver electrode for in situ analysis during electrocatalysis. Here, we combined surface-enhanced resonance Raman (SERR) spectroscopy with electrochemistry to directly refer structural changes of the active site to its electrocatalytical activity during HER. We were able to detect catalytically relevant spectroscopic changes of the complexes in solution that were similar to the ones observed for the surface bound hangman complexes during turnover conditions.

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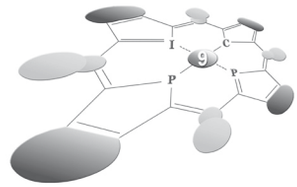

Distinct Photophysics in Two Linkage Types of β-β′ Linked Zn(Ⅱ) Porphyrin Linear Arrays

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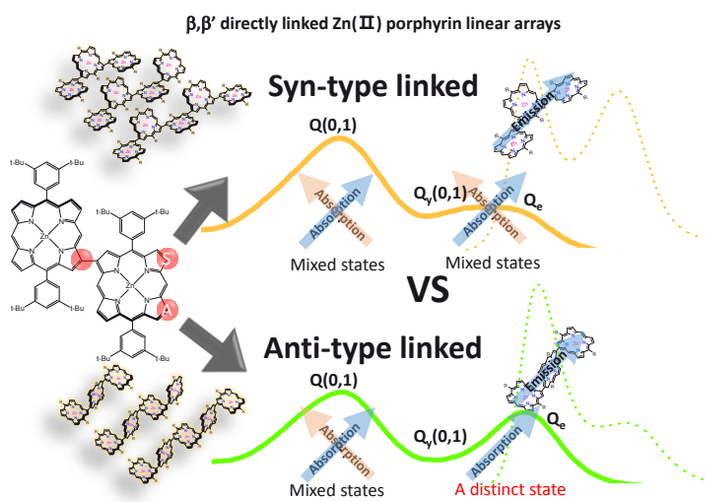
Photophysical properties and the excited state dynamics of molecular arrays are strongly dependent on many structural factors; chromophore group, dihedral angle, linkage length, linkage position, center to center distance between chromophores, and linkers. Here, we have investigated the linkage position-dependent photophysical properties of two types of β-β directly linked Zn porphyrin linear arrays (syn- and anti-types). Especially, we have focused to elucidate the relationship between the origin of the lowest state and the linkage position by steady-state and time resolved anisotropy experiments including femtosecond transient absorption (fs-TA) anisotropy and temperature-dependent absorption measurements. Also calculations on time-dependent density functional theory (TD-DFT) and exciton strength have been conducted to compare the two series having two different linkage positions. Based on these experiments and calculations, we propose that linkage position-dependent exciton strength have resulted their different origin in the lowest state. This work is limited to the directly linked linear arrays, a simple set of syn- and anti-type compounds would take a part as a guideline to understand more complicated system. Thereby, we expect that the controlling the molecular arrays for desired photophysical properties would be advanced for many applications.



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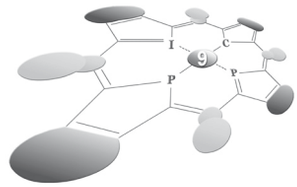

Synthesis and photophysical property of π-extended porphyrins modified with hetero thiophene units

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Semiconducting π-extended porphyrin is a promising candidate as p-channel materials for OFET. In particular, strong intermolecular interactions of porphyrin is expected to have a significant influence on the OFET performance.[1] We report on the synthesis of semiconducting π-extended porphyrin where mono- and di-thiophene units are directly attached at the 5, 15-meso-positions, respectively. It was prepared by acid-catalyzed condensation of 2-thiophenecarboxaldeyde, 2,2□:5□,2□-terthiophene-5-carbaldehyde and diypyrromethane with 1:1:2 molar ratio, respectively followed by oxidation. All porphyrin derivatives are fully characterized by using 1H NMR, MALDI-TOF MS, UV-Vis absorption and fluorescence spectroscopy. This work presents the photophysical property of hetero-substituted π-extended porphyrin derivatives and ther OFET devices porformances.

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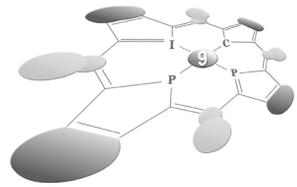

Corrole Based Donor-Acceptor Systems

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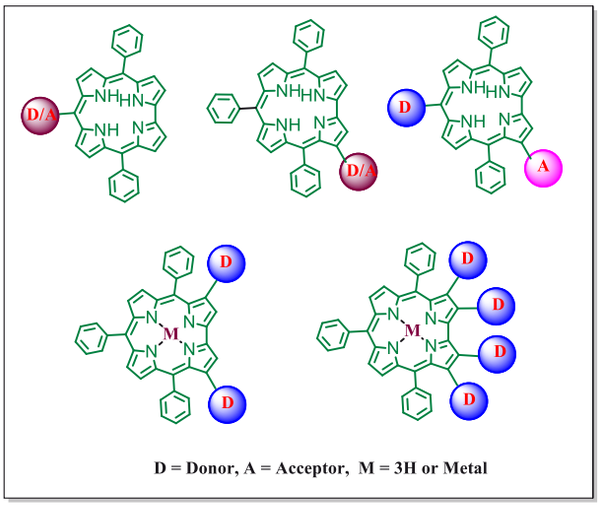
During the new century, corrole and its metal derivatives have been introduced into many applications that include catalytic oxidation, reduction and as group transfer reactions, as sensors and sensitizers for photodynamic therapy and sensitizers in Dye Sensitized Solar Cells (DSSC). The goal of this research is to design Donor-Acceptor (D-A) systems based on corroles as to gain better understanding of the initial events of natural photosynthesis.[1]
The theme of the research work is the design of donor-acceptor systems based on corroles to better understand the initial events of natural photosynthesis. In addition to this, the information available on photoinduced reactions of these D-A systems applied for the design of sensitizers for DSSC applications[2]. All these D-A systems were analysed their properties by spectroscopic techniques like, structural (^{1}H NMR, MALDI-MS, IR analysis), photophysical [UV-visible, fluorescence (steady-state and life-time)], electrochemical measurements and theoretical calculations (DFT & TDFT).[3-4] We now present our newest results on design and synthesis of corroles, substituted at their peripheral positions with either energy/electron donors or acceptors subunits.



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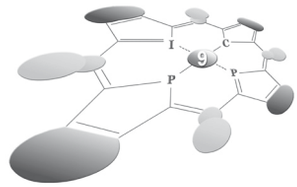

Synthesis of Novel Asymmetrical Cobalt Monobenzo-Thioporphyrazines and their Bio-inspired Catalytic Property

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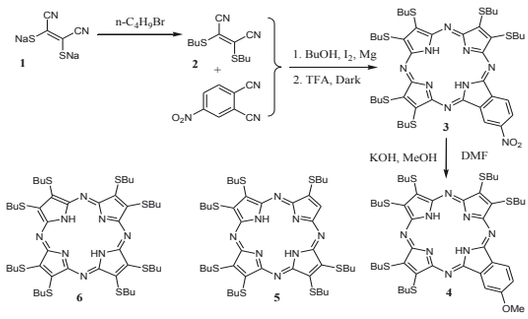
Recent developed approaches involved the application of green oxidants such as O_2 or H_2O_2 and highly effective catalysts[1], among which the bio-inspired catalysis may be one of the best approaches[2]. Two novel monobenzoporhyrazines bearing nitro and methoxyl respectively on fused benzene ring were successfully synthesized. Also, an asymmetrical porphyrazine 5 with one butylthio branch at the pyrrolic β-positions substituted by hydrogen atom was successfully isolated in the course of synthesis of symmetric octakis(butylthio) porphyrazine 6. Their corresponding cobalt complexes **7**, **8**, **9** and **10** were subsequently obtained and characterized. Their catalytic ability was assessed by aerobic oxidation of benzoin, showing and the highest benzil yield of 95.6% at room temperature through 2mol% CoPz **8** in THF in presence of 10mol% DBU.



Scheme 1 Synthesis of metal-free poly(butylthio) porphyrazine and substitutented monobenzoporhyrazines

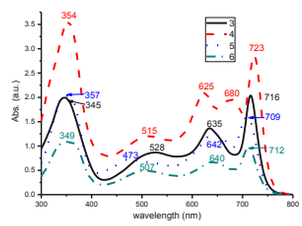


Figure 2. UV-Vis for freebase Pz 3, 4 ,5, 6.

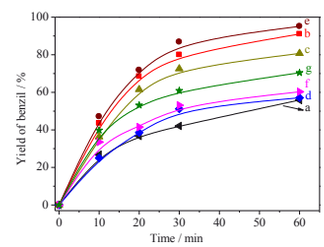


Figure 3 Aerobic oxidation of benzoin catalyzed by CoPzs* in presence of 10 mol% DBU in THF.

* a: in the absence of CoPz; b: 10mol% complex **7**; c: 2mol% complex **7**; d: 1mol% complex **7**; e: 2mol% complex **8**; f: 2mol% complex **9** ; g: 2mol% complex **10**.

Both catalytic experiments and DFT calculations demonstrated that the catalytic activity of the cobalt thioporphyrazine was affected mainly from extended π-system of peripheral fused benzo ring and secondarily from electron-donating substitutents. A possible mechanism was also presented from the in situ UV-Vis spectra, in which a novel and characteristic absorption peak of metal-oxo was observed. And the detailed characterization of reactive kinetics and expansion of oxidation of alcohols needs to be further studied.

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Direct Fabrication of the Graphene-Based Composite for Cancer Phototherapy through Graphite Exfoliation with a Photosensitizer

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Phototherapy (PT) including photodynamic therapy (PDT) and photothermal therapy (PTT) is a promising noninvasive treatment for cancer. To increase the efficacy of the therapy, a photosensitizer should be delivered to the lesion as selectively as possible, most likely with aid of a carrier. It would be better if the loading capacity of the carrier is higher, as long as the composite has enough dispersibility in a physiological environment. Herein, we report application of pristine graphene as a drug carrier for phototherapy (PT) [1]. The loading of photosensitizer, chlorin e6 (Ce6), was achieved simply by sonication of the Ce6 and graphite in aqueous solution followed by centrifugation. During the loading process, graphite was gradually exfoliated to graphene to give its composite with Ce6 (G-Ce6). This one-step approach is considered to be superior to the graphene oxide (GO) based composites, which required pretreatment of graphite by strong oxidation and/or addition of surfactant. Additionally, the directly exfoliated graphene ensured high drug loading capacity, 160 wt%, which is ten times larger than that of the functionalized GO. In the cell experiment, almost all the cells were killed in the presence of G-Ce6 (more than 0.10 μg/mL) under light irradiation (Fig. 1b), while Ce6 without graphene exhibited almost no toxicity. Neither G-Ce6 nor Ce6 showed cytotoxicity without light irradiation as shown in Fig. 1a. We have fabricated a promising composite for PT through direct exfoliation of graphene from graphite with a photosensitizer, Ce6.

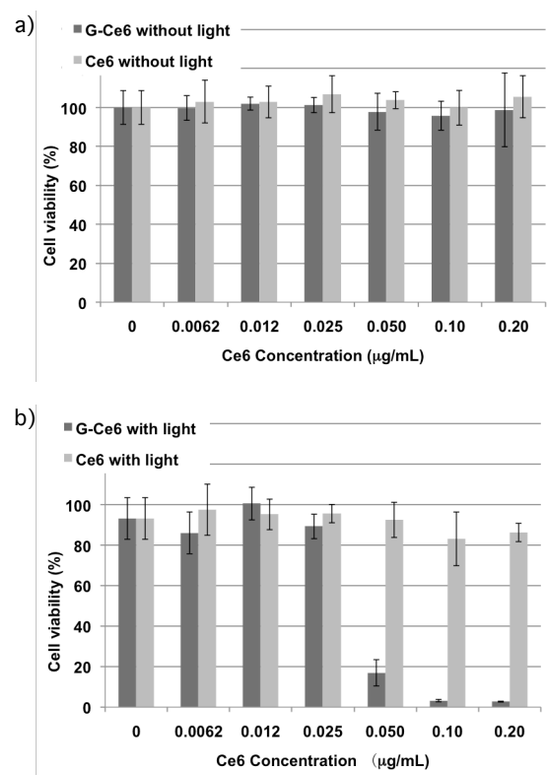

Fig. 1 Cell viability of HeLa cells treated with G-Ce6 or Ce6 at various concentration without (a) or with (b) irradiation of 660 nm laser for 2 min. Error bars were based on four parallel measurements.

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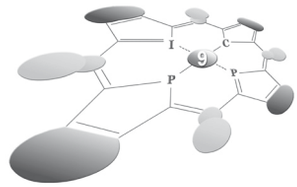

Tris(phthalocyaninato) Europium-based Ambipolar OFET: Temperature Effect of Solvent Vapor Annealing on the Morphology and Performance

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A new homoleptic tris(phthalocyaninato) europium complex $Eu_2[Pc(ONh)_8]_3$ was designed and synthesized. The temperature effect of the solvent vapor annealing on the morphology and ambipolar organic field effect transistor (OFET) performance of $Eu_2[Pc(ONh)_8]_3$ was investigated. Depending on an increased temperature from 60℃, 80 ℃to 100℃, the *o*-dichlorobenzene vapor annealing over the $Eu_2[Pc(ONh)_8]_3$ film, prepared by using the quasi-Langmuir-Shäfer (QLS) method, led to the effective improvement for both the general molecular order (morphology) and film-crystallinity, and thus the carriers mobilities for both hole and electron (Fig.1). Remarkably, balanced carrier mobilities of 0.08 $cm^2V^{-1}s^{-1}$ for holes and 0.04 $cm^2V^{-1}s^{-1}$ for electrons were obtained at 100℃, which was four orders higher than that of the pristine solution-based quasi-Langmuir-Shäfer (QLS) film. This result will be helpful for the development of small molecule-based organic electronics with potential application in nano-electronic complementary integrated circuits through the combination of molecular design and film fabrication techniques.

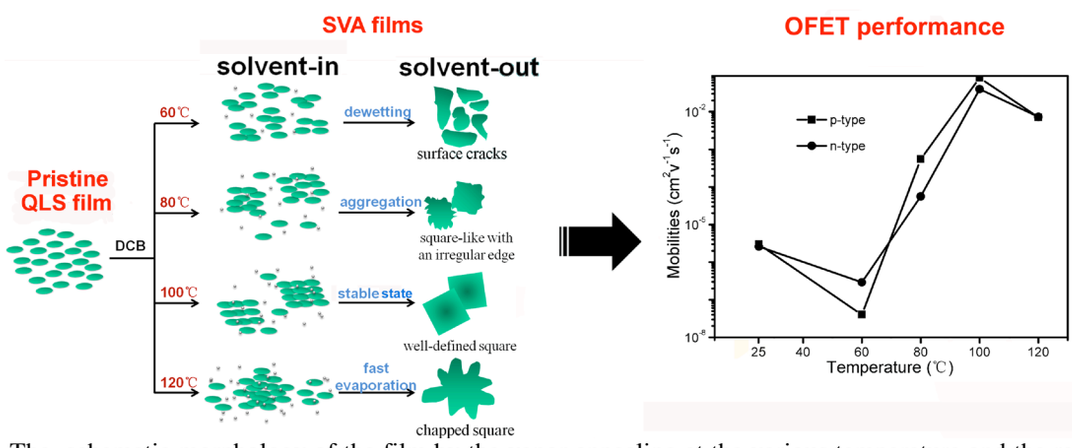

Fig. 1 The schematic morphology of the film by the vapor annealing at the various temperature and the resulting carrier mobilities of $Eu_2[Pc(ONh)_8]_3$

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Acknowledgement: This work was financially supported by the National Natural Science Foundation of China (No. 21371073).

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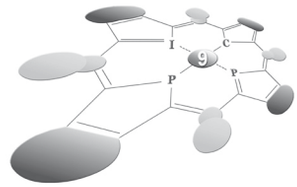

Excitation energy deactivation funnel in 3-Substituted BODIPY-Zn-porphyrin conjugate

Mikalai Kruk[a], **Nguyen Tran Nguyen**[b], **Bram Verbelen**[c], **Volker Leen**[c], **Wim Dehaen**[c]

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The boron-dipyrromethene dye (BODIPY) was combined at the 3-position with a Zn-porphyrin to afford a conjugate. A strong spectral overlap between the porphyrin Q-bands absorption and BODIPY absorption was shown to be achieved in the visible region [1]. The photophysical properties of the ZnP-BODIPY conjugate have been studied with steady state and time-resolved absorption and fluorescence spectroscopy in toluene and tetrahydrofuran solutions. The fluorescence of the ZnP-BODIPY conjugate was found to originate from the BODIPY moiety independent of the excitation wavelength. This prominent feature is due to the very efficient (up to $\sim 10^{10}$ s^{-1}) energy transfer from the excited Zn-porphyrin moiety to BODIPY, leading to complete quenching of the Zn-porphyrin fluorescence. The energy transfer in the opposite direction, namely from the excited BODIPY moiety to the Zn-porphyrin in the ground state, also takes place, but its rate constant is smaller. This difference in the rate constants of the energy transfer is rationalized in terms of the difference in the Förster overlap integrals *J* for the resonance energy transfer. The efficiency of the energy transfer from the BODIPY moiety to the Zn-porphyrin was found to be solvent dependent. The Förster overlap integral is different in non-coordinating solvent toluene and coordinating solvent THF due to noticeable spectral changes in the Zn-porphyrin absorbance. Formation of 5-coordinated (ligated) species leads to a red shift and an increase in the absorptivity of the long-wavelength 0-0 transition band of the Zn-porphyrin. These spectral changes promote an increase in the Förster overlap integral. As a result, a high fluorescence quantum yield $\Phi_f = 0.75$ has been measured for the ZnP-BODIPY conjugate in toluene, whereas the value $\Phi_f = 0.05$ has been obtained for the ZnP-BODIPY conjugate in THF. This finding opens the possibility to design supramolecular systems, where the luminescent response can be continuously adjustable. Indeed, when a pair of solvents such as toluene/THF is taken, the luminescence response can be assigned as that of an "on-off" type. However, the red shift and the absorptivity of the 0-0 band in Zn-porphyrins is known to vary almost continuously according to the choice of the coordination solvent, since the strength of Zn-L coordination bond depends on the nature of ligand. Thus, the ZnP-BODIPY conjugate represents a supramolecular system with unique luminescent response, whose intensity can be easily tuned in the wide range by external action. External action implies the axial coordination of the chelated metal ion in Zn-porphyrin moiety of conjugate mediated by solvent (solvent composition) changes. This feature makes the studied BODIPY-porphyrin conjugate a promising compound for the design of new photochromic devices.

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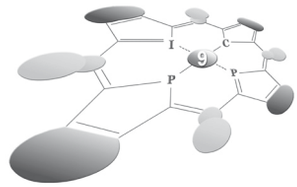

Fluorescence of mixed phenyl-mesityl 5,10,15,20-tetraarylporphyrin series: role of macrocycle conformation

Mikalai M. Kruk[a], Irina V. Vershilovskaya[a], Stefano Stefani[b], Pieter Verstappen[c], Thien Huynh Ngo[d], Ivan G. Scheblykin[e], Wim Dehaen[f] and Wouter Maes[c]

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The 5,10,15,20-tetraphenylporphyrin (H_2TPP) and 5,10,15,20-tetramesitylporphyrin (H_2TMesP) are the prototype representatives of unhindered and hindered *meso*-aryl-substituted porphyrins. Being almost indistinguishable in their free base forms, no similarity remains upon the macrocycle protonation. Whereas the sequential formation of mono- and diprotonated species is documented for the H_2TMesP, the diprotonated form of H_2TPP appears in a single step involving the simultaneous attachment of two protons. The mechanism of porphyrin basicity control by the *meso*-aryl-substituents has recently been understood with the help of by DFT quantum-chemical calculations and *ab initio* molecular dynamics simulations [1].
We report on the UV-Vis absorption and fluorescence spectra for a series of mixed phenyl-mesityl 5,10,15,20-tetraarylporphyrins – with B_4, AB_3, *trans*-A_2B_2, *cis*-A_2B_2, A_3B and A_4 type architecture (A = phenyl, B = mesityl) – in their free base, mono- and diprotonated form. Substitution of a single *meso*-phenyl group with a sterically more demanding mesityl group is found to be sufficient to provide stabilization of the monoprotonated porphyrin species. An increase in the number of mesityl substituents barely influences the free base fluorescence quantum yield (ca. 0.09), but leads to a substantial and progressive rise of the fluorescence quantum yield for both the mono- and diprotonated species, reaching maximum values of 0.21 and 0.30 for the mono- and diprotonated forms of 5,10,15,20-tetramesitylporphyrin, respectively. The progressive replacement of ortho,ortho'-substituted mesityl groups with unhindered phenyls results in an additive pattern of spectral changes for the free base porphyrins, whereas for both mono- and diprotonated species a specific jump at a certain substitution level is observed, along with a gradual additive pattern before and afterwards. This feature is interpreted as a signature of the transition between the hindered-like and unhindered-like conformations of the tetrapyrrolic macrocycles in the protonated forms. First type of macrocycle conformation is found for B_4, AB_3, *trans*-A_2B_2 compounds, while the second one for *cis*-A_2B_2, A_3B and A_4 molecules. Within both of these subgroups, the spectral changes follow an additive mode, whereas the structural transition of tetrapyrrolic macrocycle (conformation switching) occurs in going from *trans*-A_2B_2 to *cis*-A_2B_2. These two macrocycle conformations provide a different interaction of the two one-electron ((a_{1u},e_g) and (a_{2u},e_g)) configurations, which leads to changes of the configuration weights A^2 of the a_{2u} and a_{1u} orbitals.

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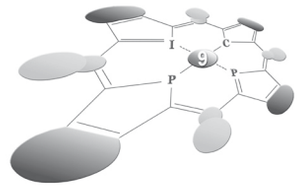

Dibenzoporphyrin(2.1.2.1): Highly Bent *o*-Phenylene Bridged Bisdipyrrin

Daiki Kuzuhara,[a] Wataru Furukawa,[a] Naoki Aratani,[a] Hiroko Yamada[a,b]

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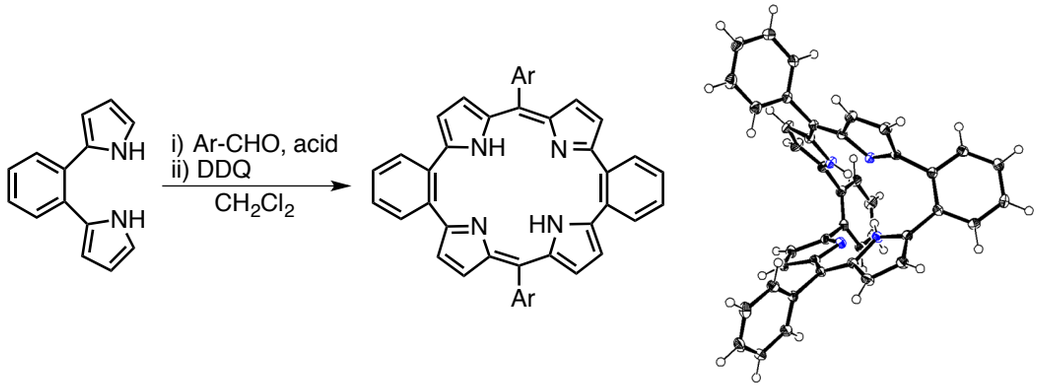
Curved and bent molecules have great attractive attentions with a unique reactivity, opt- and electrochemical properties, and applications for the host-guest chemistry. However, it is still challenging issue to make bent or curved porphyrin derivatives because most of porphyrin derivatives have a highly planar and a robust structure with an 18π aromatic structure. It is known that when pyrroles or methine carbons of porphyrin are replaced to the other aromatic rings or *o*-phenylene linkages, the different macrocyclic geometries and electronic properties are induced. Here, we present that we have succeeded in the synthesis of dibenzoporpyrin(2.1.2.1) with a highly bent structure by simple condensation reactions. Dibenzoporpyrin(2.1.2.1) derivatives were obtained from *o*-dipyrrolylbenzene with various aldehydes in the presence of acid. This cyclization reaction proceeded with electron–donation and –withdrawing substituents on *p*-position of phenyl group, five-membered heterocycles and ethynyl groups. In addition, dibenzoporpyrin(2.1.2.1) behaves as a dianionic tetradentate ligand which leads to porphyrin–like coordination property. We will report the details of synthesis of dibenzoporpyrin(2.1.2.1) and its metal complexes. Also optical and electrochemical properties, and crystal structures of them will be discussed.



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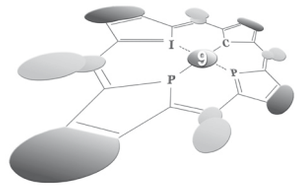

Simulating Wide-Range Absorption of Porphyrins using Real-Time Time-Dependent Density Functional Theory

Daniel LaMaster, Adam Bruner, and Kenneth Lopata

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA

Porphyrin excited states play a vital role in photodynamic therapy (PDT) as well as a variety of photochemical transformations. Computing wide range absorption spectra is difficult in practical application due to the large size of practical systems and the large number of excitations (roots) that have to be calculated to capture the entire spectrum. Here, time-dependent density functional theory (TDDFT) is a promising tool, as it offers a good trade-off between accuracy and efficiency, but traditional frequency-domain (linear-response) TDDFT requires computing a large number of roots to resolve the full spectra. A real-time TDDFT approach, on the other hand, based on a time-resolved solution, can capture the full spectrum from a single simulation. In this work, the spectra of a variety of porphyrins are computed over a wide range of photon energies spanning the visible and X-ray, both to illustrate the utility of a real-time TDDFT approach for excited states in these systems and to elucidate the origins of spectral features due to systematic functionalization.

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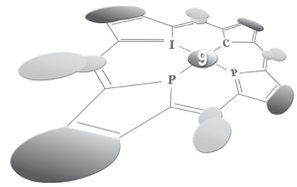

Correlation Between Structure of Zn Phthalocyanine and Redox Stability for Solar Water Splitting Cell

Jae Moon Lee[a], Sang-a Choi [a], Sim Bum Yuk[a], Jae Pil Kim*[a]

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Over the last 30 years, Solar energy conversion technology has been considered as attractive alternatives to fossil fuels and coal. Dye-sensitized photoelectrochemical cells (DS-PECs) based on mesoporous TiO_2 film which can produce clean hydrogen molecules from water is one of the most promising area of the solar energy conversion technology. Recently, some research groups reported that the decrease of the efficiency is caused by separated sensitizer molecules suffering from repeated redox cycle. But there have been few studies that have attempted to research the stability, it is extremely important though. Therefore the present study aimed to find optimal structure of phthalocyanines binding with titania and to provide chemical basis for the stability. A few Zn phthalocyanine sensitizers were synthesized, characterized with nuclear magnetic resonance (NMR), elemental analyzer (EA), and matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF). The redox stability was confirmed by fourier transformed Infrared spectroscopy (FT-IR), ultraviolet-visible spectroscopy (UV-VIS). Solar to hydrogen(STH) efficiency was measured by solar simulator.

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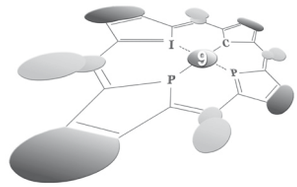

Synthesis of highly dispersed cationic phthalocyanine dyes for improving transmittance of LCD green color filter

Sim Bum Yuk, Sang-a Choi, Jae Moon Lee, Jin Woong Namgoong, Jae Pil Kim*

Department of Materials Science and Engineering, Seoul National University, 08826, Seoul, Republic of Korea

LCD color filter containing soluble organic dyes have an aggregation issue in baking process which induces low transmittance of the color filter. Therefore, strategy to keep dispersed state of the dyes during this process is required [1].

In this study, we enhanced affinity between dye and binder that are major components of millbase by their electrostatic attraction. Cationic phthlalocyanine dyes and anionic binders were synthesized for this purpose. Solubility of the dyes were improved by alternating their counterions from iodine to bulky anionic compound. Structure analysis of the synthesized dyes and binders were confirmed by elemental analysis, mass, gel permeation chromatography and IR-spectroscopy. Optical and thermal properties of the dyes were investigated by UV-visible spectrometer and TGA in comparison with iodo-phthlaocyanines. Dispersibility of the dyes in solution state were confirmed by dynamic light scattering.

Dye-based color filters were fabricated using the synthesized dyes and binders. As a result, electrostatic attraction between them was given an effect for reducing size of the dyes in millbase and prevented aggregation in film state.

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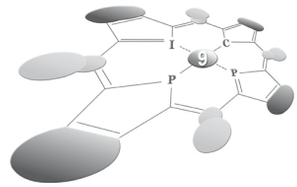


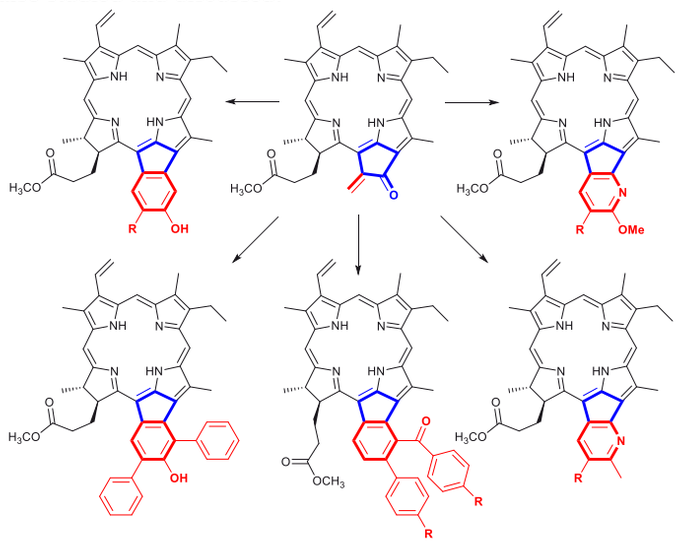
Aromatic Ring Fused Chlorophylls: Efficient Synthesis and Unique Optical Properties

Jiazhu Li, Yan-Long Li, Nailiang He, Jun-Gang Yin, Jin-Jun Wang

College of Chemistry and Chemical Engineering, Yantai University, Yantai 264005, China

Aromatic ring fused porphyrins have recently attracted considerable attentions due to their potential applications in NIR electroluminescence displays, nonlinear optical materials, photodynamic therapy, and molecular electronics[1, 2]. In comparison with porphyrin, chlorophyll a derivatives have highly asymmetric structures with various functional groups surrounding their periphery, which make it difficult to construct aromatic ring systems fused with the chromophore of chlorophylls[3, 4].

In this study, a series of chlorophyll a derivatives fused with aromatic rings have been synthesized based on the enone possessing chlorin we reported previously[5]. The structures of all these compounds were identified by using UV-Vis, 1D and 2D NMR, MS and elemental analysis. The unique optical properties of these aromatic ring fused chlorophylls were also studied and discussed.



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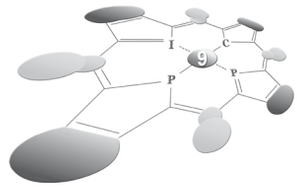


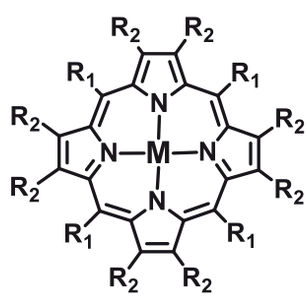
Rational Molecular Design of Metallo-Porphyrin towards Enhanced Removal of Toxic Organochlorides

Minzhi Li, Xu Liang*, Lili Liang, Cui Ni and Weihua Zhu*

School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China

Organochlorides, the organic compounds containing at least one covalently bonded atom of chlorine, have a broad range of applications due to their divergent chemical properties. Under this point of view, facile and highly efficient removal of environmental toxic organochlorides become social challenges. Right now, macrocyclic compounds containing transitionmetal ions can be used as the efficient catalysts for chemical and electrochemical dechlorination of environmental harmful organochlorides. Compared with chemical dechlorination, electrochemical dechlorination of environmental harmful organochlorides catalyzed by metal-porphyrinoids can be more easily achieved. Generally, metallo-porphyrin electrocatalyzed dechlorination reaction produce a σ-bond between organochloride and electrogenerated metallo-porphyrin anion (described as $[(Por)M(I)]^-$ + RX □ $(Por)M(III)(R) + X^-$) as a key intermediate. Thus, studies on the relationship between the electronic structure of metallo-porphyrins and electrocatalyzed dechlorination reactivity is a meaningful work for future rational molecular design enhanced removal of toxic organochlorides. In this study, we confirm the decrease electron density of metalloporphyrinods by introduction of both strong electron-withdrawing pentafluorophenyl-units at *meso*-positions, and high-valence metal center like Fe(III) will more easily produce $[(TF_5PP)Fe(I)]^-$ anions, and the newly formed $[(TF_5PP)Fe(I)]^-$ can then further easily react with the original organohalide compound in solution or it can react with its dechlorinated product if it also contains a halogen group.

Acknowledgments: This work was supported by the Natural Science Foundation of China (No. 21171076).



R_1 = H, phenyl, F_5-phenyl

R_2 = H or Ethyl

M = Fe(III)Cl, Co(II), Mn(II)

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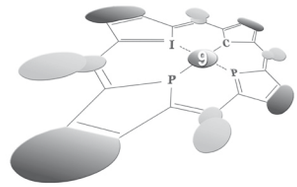


Tuning the Cobalt(III)corroles Electroreductive Catalyzed Lindane Dehalogenation through *meso*-Substituents

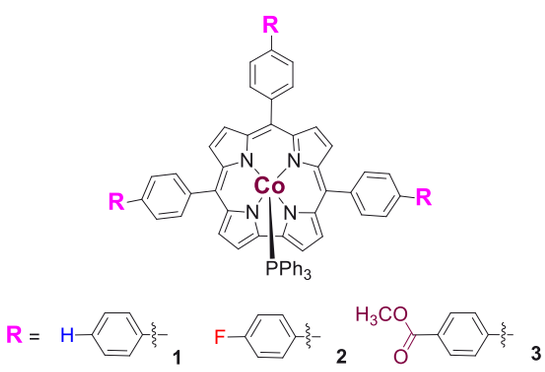
Minzhi Li, Xu Liang*, Tingting Huang, Mingfeng Qin and Weihua Zhu*

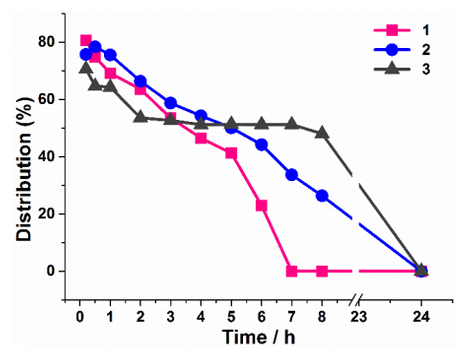
School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China

Organic pollutants (POPs) are hardly damaged in the environment, and the presence of POPs are not only near their source region but also in pristine areas far from the sources. Even low concentration of POPs can pose a considerable threat to human health and the ecosystem because they tend to be accumulated in lipid-rich tissues of biota quite easily and biomagnified through terrestrial and aquatic food chains. One of most well-known POPs, lindane, γ-type technical hexachlorocyclohexane (HCH) that has been used both as an agricultural insecticide and as a pharmaceutical treatment for lice and scabies. Unfortunately, the time of lindane has been gone. Till the end of 2006, the use of lindane had been banned in 52 countries and restricted in 33 others. In 2009, an international ban on the use of lindane in agriculture was implemented under the Stockholm Convention on Persistent Organic Pollutants[1-4].

In this study, we produce a facile and mild electrocatalyzed dechlorination by using a series synthetic Co(III)corroles containing different meso-substituents. Electronic structure of Co(III)corroles was characterized by spectroscopy, electrochemistry, and spectroelectrochemistry. The controlled potential dechlorination products analysed by GC-MS indicate that meso-substituents of these synthetic cobalt(III)corroles have a large influence on the dechlorination efficiency. Also, these Co(III)corroles exhibit satisfied dechlorination results and lindane was dechlorinated to chlorobenzene under electron reductive catalysis for the first time.

Acknowledgments: This work was supported by the Natural Science Foundation of China (No. 21171076).





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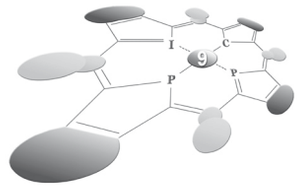

Surprising Outcomes of Classic Ring Expansion Reactions When Applied to Octaethyloxochlorin

Ruoshi Li,[a] Eileen Meehan,[a] Matthias Zeller,[b] and Christian Brückner*,[a]

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[b]*Department of Chemistry, Purdue University*
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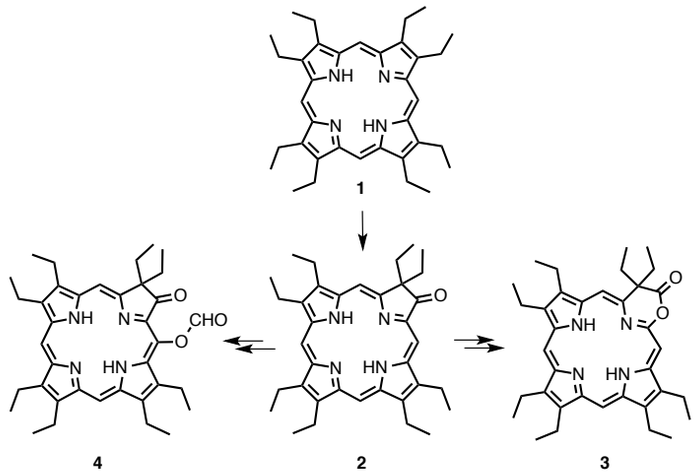
Few methods are available to convert octaethylporphyrin **1** to analogues containing non-pyrrolic building blocks.[1] Many of these analogues promise to possess altered optical properties compared to regular porphyrins or chlorins. By virtue of the presence of functional groups at their chromophore periphery, porphyrinoids containing non-pyrrolic building blocks also demonstrated their potential in a number of sensing applications. A three-step conversion of a pyrrole in octaethylporphyrin **1** to a 1,3-oxazinochlorin **3** along a surprising abnormal Beckmann pathway, followed by intramolecular ring closure and hydrolysis, was recently reported.[2] Thus, a lactone was formed instead of a lactam, the expected Beckmann rearrangement product of the intermediate oxime. We detail this reaction and a number of other ring-expansion reactions that take unexpected turns. For instance, oxochlorin **2** treated under Schmidt reaction conditions provided a product with an oxidized β-position. Oxochlorin **2** treated under a wide range of Baeyer-Villiger oxidation conditions never formed any of the expected lactones but an oxochlorin *N*-oxide or *meso*-oxidized product **4**. The surprising outcomes indicate that the steric barriers of these classic ring expansion reactions are too high when performed within the steric constraints of the porphyrin macrocycle.



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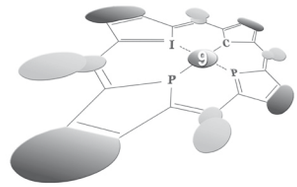
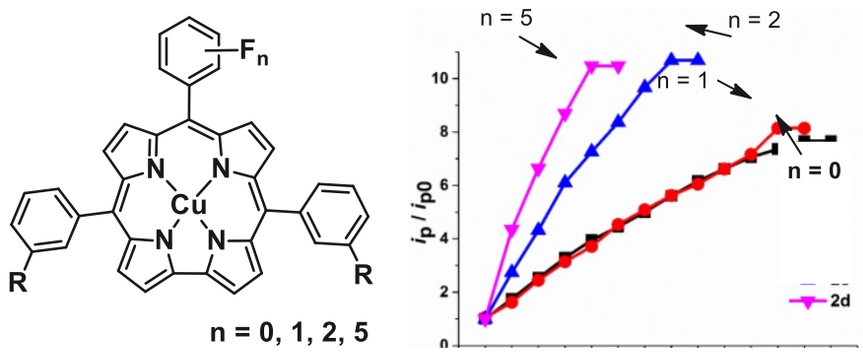


Facile Modulation the Hydrogen Evolutions by A_2B Type Cu(III)Corroles Containing Different Fluoro-Atoms

Xu Liang*, Yu Jiang, Minzhi Li, and Weihua Zhu*

School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China

During the past decades, globally increasing energy demand and environmental concerns related to the use of fossil fuels have made energy research the paramount task for our society. H_2 has emerged as an ideal energy source because it is carbon-free, renewable, and produces only water as a combustion product. Electrochemical reduction of protons is an effective and convenient process to convert electrical energy to chemical energy through generating H_2.[1] On the other hand, the porphyrinoid complexes of nonmetals have received a considerable amount of attention in recent years, since their optical and biological properties could lead to applications as functional dyes in a number of different high-technology fields, such as organic solar cells, photodynamic therapy, heat absorbers, and organic catalysis. Corroles are porphyrin analogues with a direct pyrrole-pyrrole bond and an extra N-H proton on the inner ligand perimeter, best known for forming the basic structure in vitamin B_{12}. Right now, there has been a strong research focus on the use of corroles as functional ligands, largely due to their ability to stabilize higher oxidation states of the coordinated metal such as Cr(V), Fe(IV), Co(IV), and even Mn(V) or Co(V).[2-3] To design and synthesize new metallo-corroles with natural abundant elements and effectively modulate the hydrogen evolutions in simple manners are interesting, but still challenging. Thus, we design and synthesize a new series of A_2B type Cu(III) corroles containing different fluoro-atoms. Structure of these corroles were confirmed by various techniques and electronic structure was characterized by spectroscopy, electrochemistry and spectroelectrochemistry. Further measurements of hydrogen evolutions electrocatalyzed by these metallo- corroles indicate that the catalytic abilities can be facile modulated by one substituent. Financially supported by Financial support was provided by the NSFC of China (no.21171076).



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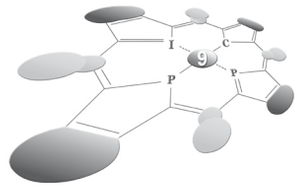
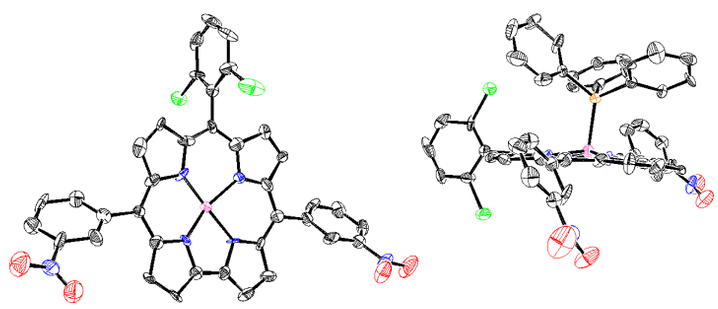


Halogenated A_2B type Co(III)corroles: Synthesis, Properties and Modulation Hydrogen Evolution Reactions

Xu Liang[a,*], Minzhi Li[a], Yu Jiang and Weihua Zhu*

[a]*School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China*

Corroles are porphyrin analogues with a direct pyrrole-pyrrole bond and an extra N-H proton on the inner ligand perimeter, best known for forming the basic structure in vitamin B_{12}. Right now, there has been a strong research focus on the use of corroles as functional ligands, largely due to their ability to stabilize higher oxidation states of the coordinated metal such as Cr(V), Fe(IV), Co(IV), and even Mn(V) or Co(V).[1-3] To design and synthesize new metallo-corroles with natural abundant elements and effectively modulate the hydrogen evolutions in simple manners are interesting, but still challenging. Thus, we design and synthesize a new series of A_2B type Co(III) corroles containing different halogenation substituents. tructure of these corroles were confirmed by MS, HNMR and single crystal analysis, and electronic structure was characterized by spectroscopy, electrochemistry and spectroelectrochemistry. Further measurements of hydrogen evolutions electrocatalyzed by these metallo-corroles indicate that the catalytic abilities can be facile modulated by one substituent. Financially supported by Financial support was provided by the NSFC of China (No. 21171076).



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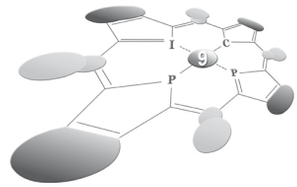

Optical Carbon Dioxide Sensors Based on Azaphthalocyanine Indicators

Lukas Lochman[a], Veronika Novakova[b], Petr Zimcik[a], Sergey Borisov[c]

[a]*Faculty of Pharmacy in Hradec Kralove, Charles University in Prague, Heyrovskeho 1203, Hradec Kralove, 50005, Czech Republic, lochmanl@faf.cuni.cz, http://portal.faf.cuni.cz/Groups/Azaphthalocyanine-group/*
[b]*Graz University of Technology, Stremayrgasse 9, 8010, Graz, Austria*

Azaphthalocyanines (AzaPcs) are aromatic compounds with extensive system of double bonds. They are intensively studied due to unique fluorescence properties like absorption and emission over 650 nm, high extinction coefficient (approximately 200 000 $Lmol^{-1}.cm^{-1}$) and high fluorescence quantum yields. Recently, AzaPcs have been shown as promising indicators for metal cations[1, 2] or pH sensitive indicators.[3] Principle of sensing is based on intramolecular charge transfer (ICT) which is responsible for effective quenching of excited states. ICT occurs between donor (e.g. phenolate) and acceptor (macrocyclic core). Switching between ON/OFF states is driven by the blocking/enabling of ICT leading to significant increase/decrease of fluorescence intensity. The aim of this work is to study the possibility to use AzaPc indicators in CO_2 optical sensor devices. The pH sensitive AzaPc indicators[3] with one, two or four phenolate/phenol moieties were immobilized into several hydrogel matrices along with a quaternary ammonium base. A huge increase in fluorescence intensity is observed in presence of CO_2 (Fig. 1). The sensitivity of the optical sensors can be tuned over a wide range and strongly depends on type of hydrogel and the quaternary ammonium base.

The work was supported by Grant Agency of Charles University (494214) and scholarship Aktion Austria-Czech Republic.

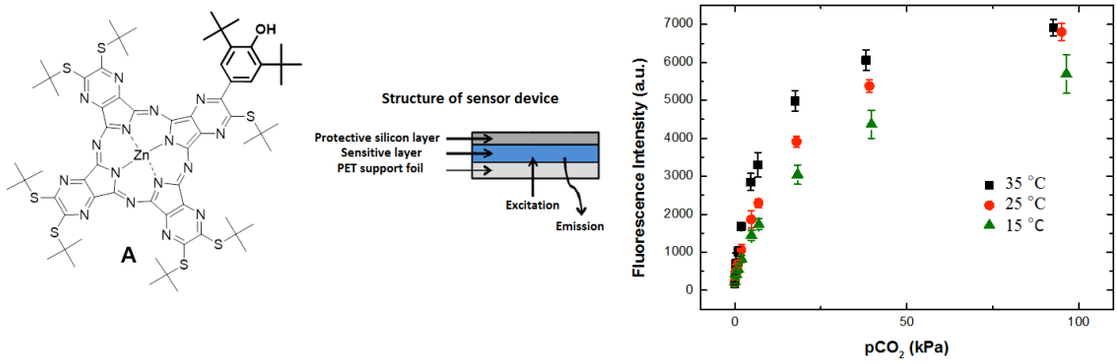

Fig. 1. Structure of sensor device and temperature dependency for compound **A** in Hydrothane 5 matrix

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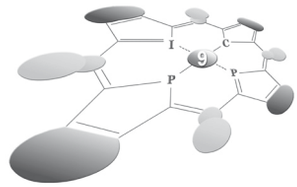

Water-Soluble Quinoline-Annulated Porphyrins as Contrast Agents for Photoacoustic Cancer Imaging

Michael Luciano[a], Mohsen Erfanzadeh[b], Feifei Zhou[b], Quing Zhu[b], and Christian Brückner[a,*]

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[b] Department of Electrical and Computer Engineering, University of Connecticut, Storrs, Connecticut 06269-3060, United States

The freely water-soluble PEGylated mono-quinoline-annulated porphyrin derivative **2** was prepared by deprotection/PEGylation of the corresponding *meso-tetrakis*(*p*-methoxyphenyl)porphyrin-derived mono-quinoline-annulated porphyrin **1**. Similar to the *meso*-phenylquinoline-annulated porphyrins,[1] the PEGylated derivative possess a red-shifted and broadened UV-vis absorption (λ_{max} > 800 nm) spectrum compared to that of the porphyrin starting material, exhibits little fluorescence, but a strong photoacoustic response. We previously reported the utility of the *meso*-phenyl derivatives as photoacoustic imaging (PAI) contrast agents *in vitro*.[2] We report here the *in vivo* evaluation of **2** as a PAI contrast agent in mice models bearing implanted tumors.

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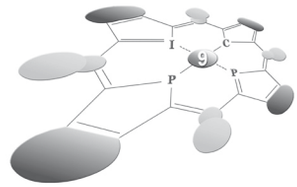

Design, synthesis and optical properties of novel tailed tripeptide porphyrin

Ming-hua Huang [a], Jun Xue[a], Ling Xiao [a], Guo-tian Luo [a,b*]

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[b] *Key Labroratory Organ-Pharmaceutical Chemistry of Jiangxi Provice, Ganzhou, 341000, China*
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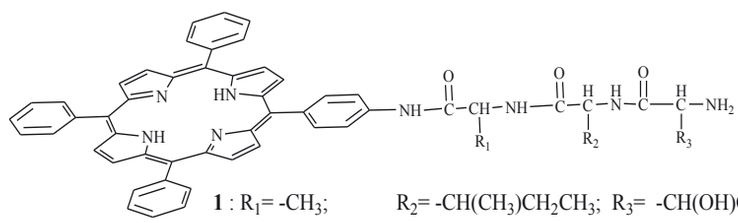
Photodynamic therapy (PDT) is an approved therapeutic procedureto treat cancers using combinations of chemical photosensitizers and light [1, 2]. Many novel photosensitizers have been researched in preclinical and in clinical settings [3–5]. Porphyrin derivatives have attracted considerable attention. Such as the porphyrin based photosensitizer, Photofrin is administered systemically for the clinical treatment of esophageal and bronchial carcinomas as well as for treating Barrett's esophagus. Porphyrins are naturally occurring organic compounds which are involved in a variety of important biological processes [6-7].A novel tailed tripeptide porphyrin was designed and synthesised by the reactions of pyrrole、benzaldehyde and BOC protected amino acid. The target compound and intermediates were characterized by MS,^{1}H-NMR, EA and UV-Vis spectrum. The research result shows that the fluorescence emission peak is at around 650nm, which conform to the requirements of optical photosensitizer.



1 : R_1= -CH_3; R_2= -$CH(CH_3)CH_2CH_3$; R_3= -$CH(OH)CH_3$

2 : R_1= -CH_2-C_6H_5; R_2= -$CH(CH_3)CH_2CH_3$; R_3= -$CH_2CH(CH_3)_2$

Fig 1. The structures of novel tailed tripeptide porphyrin

*This work was supported by a grant from the National Natural Science Foundation of China(21161001).

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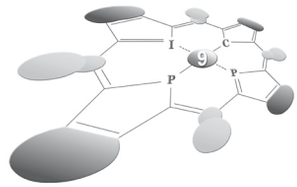

A New Electrochemical Molecular Transformation of Halogenated Pollutants Catalyzed by B_{12} Model Complex

Zhongli Luo, Hisashi Shimakoshi, Yoshio Hisaeda

Department of Chemistry and Biochemistry, Graduate School of Engineering Kyushu University, JAPAN

The electrochemical degradation of organic halides catalyzed by vitamin B_{12} derivatives have been extensively studied since the reaction proceed under mild reaction conditions without secondary pollutants[1]. Recently, we developed an electrochemical molecular transformation system catalyzed by hydrophobic B_{12} model complex, and used it in the degradation of DDT under anaerobic conditions[2]. Here we report the improvement of this system: esterification and amidation of benzotrichloride derivatives under aerobic conditions.

Firstly, we carried out the electrochemical dechlorination of benzotrichloride derivatives under anaerobic conditions to avoid the reaction between oxygen and Co^{I}, which decrease the efficiency of electrochemical catalysis. As a result, only simple dechlorinated products were formed. Under aerobic conditions, by contrast, esters were formed as main products from benzotrichloride derivatives in alcohols, in the presence of oxygen. The intermediates—oxygen centred radical and acyl chloride were detected by ESR and GC-MS analysis, respectively. Amidations were also proceeded in acetonitrile in the presence of amine. In our system, we can obtained different products from the same staring materials by controlling the reaction atmosphere.

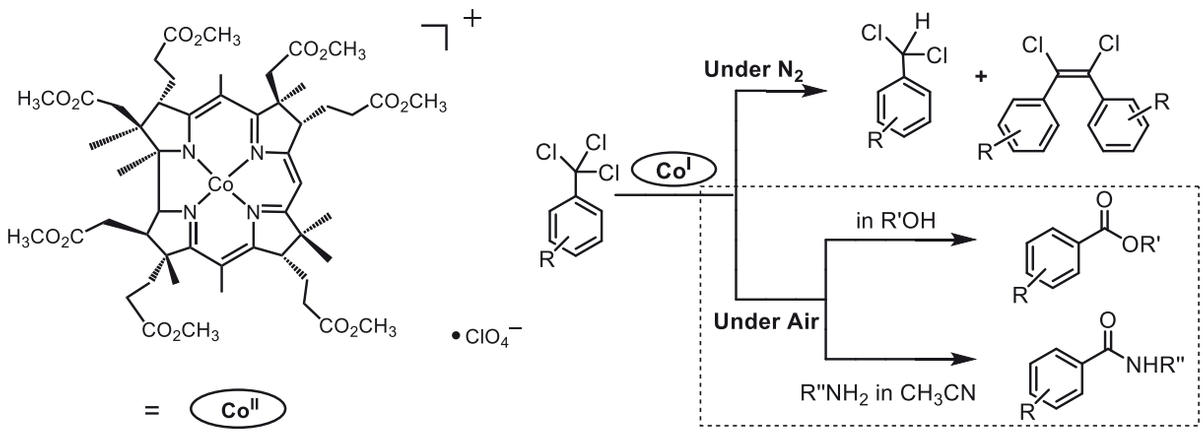

Fig.1 The electrochemical molecular transformation of halogenated pollutants catalyzed by B_{12} model

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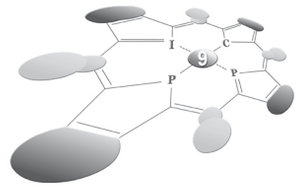
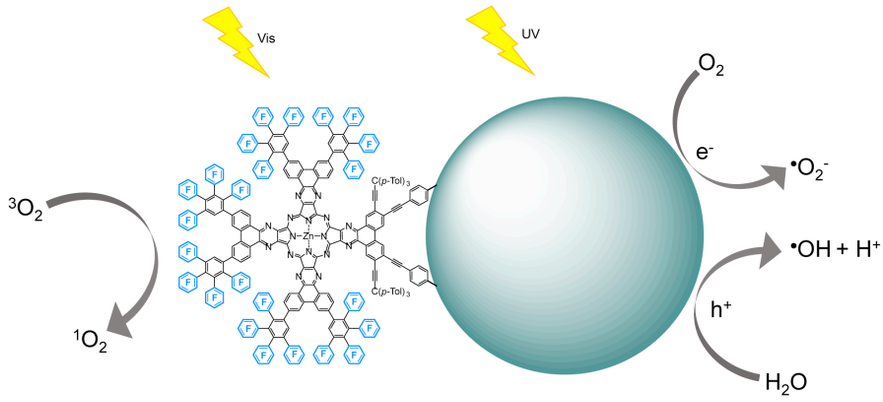


Fluorinated asymmetric porphyrazines for resistant photocatalytically active hybrid nanoparticles

Patricia Löser, Rüdiger Faust*

Prof. Dr. Rüdiger Faust, University of Kassel, Heinrich-Plett-Straße 40, D-34132 Kassel (Germany)

For passive air purification photocatalytically active titanium dioxide (TiO_2) has already become a prominent candidate.[1] The absorption of UV-radiation induces the production of reactive oxygen species like $\bullet O_2^-$ and •OH on the oxide surface, which effectively decompose certain organic and inorganic materials.[2] However, in low-light areas (on north facing façades or on interior surfaces) pure TiO_2-photocatalysis is ineffective, a fact that is unfortunate in light of numerous potential applications. Our approach to address this problem is to modify TiO_2 with porphyrazines (Pz) that act as antenna dyes. Because of their ability to generate singlet oxygen ($^1O_2$) upon excitation with visible light, these dyes in the above sense contribute to the photoinduced production of reactive oxygen species.[3] Through the formation of a Pz/TiO_2-hybrid material light from the UV to the red end of the visible can be used, leading to what we call **dual pathway photocatalysis**.
To this end, we have designed an asymmetric [3+1]-Zn-Pz featuring 120 fluorine-substituents in three of the four quadrants to ensure sufficient resistance of the Pz towards autophotooxidation. The fourth quadrant bears two hydroxyl-based anchoring groups that guarantee strong binding between the chromophores and the particle surface, and that assure an orthogonal arrangement between TiO_2 and Pz for electronic decoupling. In this contribution we present key-steps of the Pz-synthesis and the development of the Pz/TiO_2-hybrid nanoparticles. Furthermore, we will report pertinent characteristics of the new hybrids such as selected optical properties, particle-size distribution, and the zeta-potential. In addition, we will highlight their photocatalytic activity in the UV and the visible.



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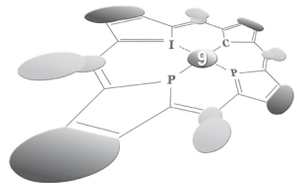

Tetrakis(phthalocyaninato) Terbium-cadmium Quadruple-decker Liquid Crystals with Good Semiconducting Properties

Qi Ma[a], Hailong Wang[a], Yanli Chen[b], and Jianzhuang Jiang*[a]

[a]*Beijing Key Laboratory for Science and Application of Functional Molecular and Crystalline Materials, Department of Chemistry, University of Science and Technology Beijing, Beijing 100083, China*
[b]*Shandong Provincial Key Laboratory of Fluorine Chemistry and Chemical Materials, School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China.*

Neutral and mono-oxidized states of novel sandwich-type tetrakis[2,3,9,10,16,17,23,24-octa(dodecanoyloxy)phthalocyaninato] terbium-cadmium quadruple-decker complex {[Pc(OC12H25)8]Tb[Pc(OC12H25)8]Cd[Pc(OC12H25)8]Tb[Pc(OC12H25)8]} (**1**) and {[Pc(OC12H25)8]Tb[Pc(OC12H25)8]Cd[Pc(OC12H25)8]Tb[Pc(OC12H25)8]}·SbCl6 (**2**) were synthesized and spectroscopically characterized. Polarized optical microscope (POM) together with differential scanning calorimeter (DSC) measurement revealed their similar two rectangular columnar mesophases over a relatively lower temperature range and higher temperature range, respectively, within their wide liquid crystal temperature range of 19-266°C for **1** and 4-249°C for **2**. Temperature-dependent X-ray diffraction (XRD) analysis result disclosed the very much slight difference in terms of the neighboring quadruple-decker-stacking between these two mesophases, which in turn accounts for their electric conducting behavior along with the change in temperature. In addition, due to the ionic conductive nature, the mono-oxidized liquid crystals of **2** display more than 2 order of magnitude higher electric conductivity than that for **1**, with the highest value 4.1 × 10-4 S cm^{-1} achieved at 140°C.

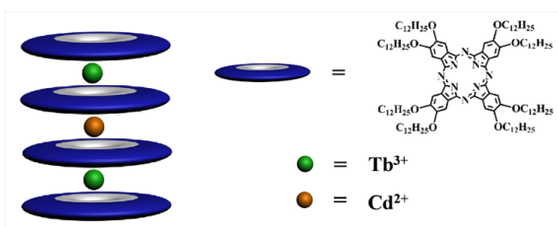

Figure 1. Schematic molecular structure of tetrakis(phthalocyaninato) Tb(III)-Cd(II) quadruple-decker complex.

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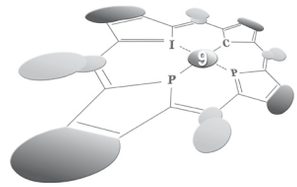


Photodynamic Activity of Non-aggregating cationic and anionic Phthalocyanines and Azaphthalocyanines.

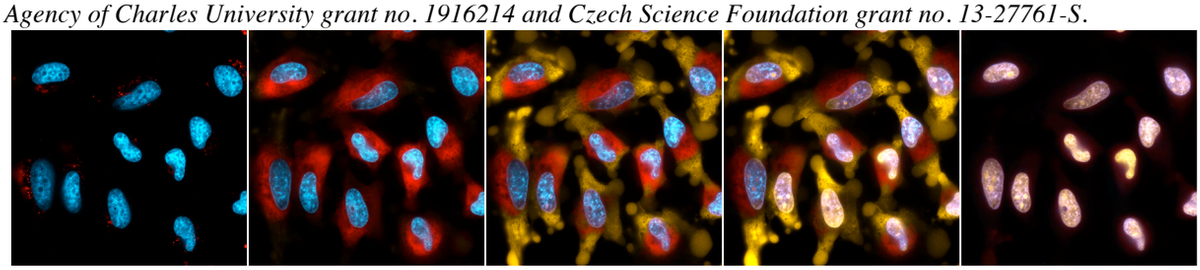
Miloslav Machacek, Veronika Novakova, Jan Kollar, Pavel Cermak, Petr Zimcik and Tomas Simunek

Faculty of Pharmacy in Hradec Kralove, Charles University in Prague, Czech Republic

In this study, *in vitro* photodynamic activity of water-soluble photosensitizers (PSs) from the group of phthalocyanines (Ps) and their aza-analogues – tetrapyrazinoporphyrazines (TPyzPz) and tetrapyridoporphyrazines (TPyPz) was evaluated. Experiments were performed in two approaches: classical Photodynamic Therapy (PDT) protocol with 12 h pre-incubation and Vascular-Targeted Photodynamic Therapy (VTP) protocol, where no pre-incubation took place. PSs involved in this study are mostly highly hydrophilic non-aggregating PSs bearing anionic or cationic substituents in rigid or flexible arrangement with high absorption in near infra-red area. Their photodynamic effect was studied on several cell lines – human cervical carcinoma (HeLa), melanoma (SK-MEL-28), breast adenocarcinoma (MCF-7), lung adenocarcinoma (A549) and mouse non-malignant fibroblast (3T3) in PDT protocol or human immortalized endothelial cell line (EA.Hy926), human primary endothelial cells (HUVEC), 3T3 and HeLa in VTP protocol. Dark toxicity (without the presence of activating light) was also established after 24 h of incubation with PSs.

Character of substituent (*i.e.* anionic or cationic) and especially the rigidity of its arrangement were found to be the key factors influencing photodynamic activity of studied PSs. Thus, all cationic compounds proved to be efficient PSs after irradiation with red light ($\lambda > 570$ nm, 12.4 mW/cm^2, 11.2 J/cm^2) reaching exceptionally high photodynamic activity (up to nanomolar concentrations observed at TPyPz bearing rigid peripheral substituents) while showing low inherent toxicity[1] in the absence of light to both malignant and non-malignant cells. Lower photodynamic activity of anionic PS was strongly affected by interaction with proteins and partially also by intralysosomal acidic pH. On the other hand, binding to proteins protected the PS from self-aggregation and preserved its activity of some extent even in low lysosomal pH.[2]

Studying the mode of cell death, activated PSs damaged lysosomal (PDT) or plasma (VTP) membranes and spread throughout the cell where they caused additional damage to other organelles. This led to quick and efficient cell demise – with several definite hallmarks as are membrane blebbing, mitochondrial fragmentation, nucleus condensation and fragmentation and cytoskeleton remodelling. *The study was supported by the Grant Agency of Charles University grant no. 1916214 and Czech Science Foundation grant no. 13-27761-S.*



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The effect of pluronic silica nanoparticles on the photophysical properties and photodynamic therapy activity of mono substituted metallated porphyrin.

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[b]*Biotechnology Innovation Centre, Rhodes University, Grahamstown 6140,South Africa*

Photodynamic therapy (PDT) is a minimally invasive treatment modality of tumor cells, which requires laser beam light of appropriate excitation wavelength, a viable photosensitizer (porphyrin) and molecular oxygen [1]. Porphyrins are well known photosensitizers for PDT. On the other hand, pluronic-Silica (PluS) nanoparticles (NPs) have low toxicity, photophysical inertness and a high surface to volume ratio and good water solubility [2]. Because of these properties PluS NPs are compatible with most formulations for medical applications such as PDT [3]. Furthermore these NPs have other glass properties, such as permeability and optical transparency, which are important for controlled release and photo-activation of the photosensitizer [4]. This work reports on the immobilization of three porphyrin complexes (containing Zn, ClGa and Si as central metals) onto the nanoparticles. The photophysical properties of the porphyrins are assessed when alone or when linked to PluS NPs, Fig. 1. The porphyrins in this work are asymmetrically substituted to allow for a more defined likening to PluS NPs. This work reports for the first time, on the grafting of porphyrins to PluS NPs and their PDT properties

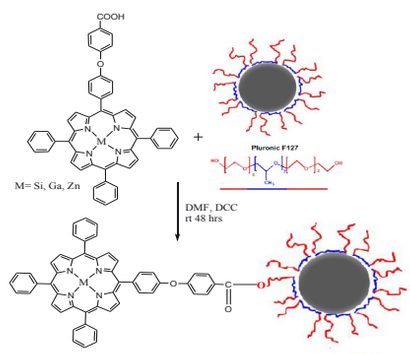

Fig. 1. Conjugation of PluS NPs to a porphyrin molecule

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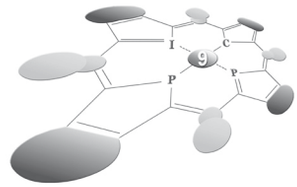

Structure and Physical Properties of Cyclo[8]pyrrole-Polyoxometalate Complex

Hiroki Matsumoto[a], Shigeki Mori[b], Masayoshi Takase[a], Hidemitsu Uno[a], Tetsuo Okujima[a]

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Cyclo[8]pyrrole is a ring-expanded porphyrin analogue with no *meso*-carbons which is expected to apply to functional dyes due to the strong near-infrared absorption. Cyclo[8]pyrrole exhibits highly dicationic character and is usually be isolated as diprotonated octaphyrin sulfate or dichloride salt. There are some researches of anion exchanging of cyclo[8]pyrrole. In 2008, Sessler has reported photoinduced charge separation in a complex of pyrene carboxylate anion and cyclo[8]pyrrole[1].

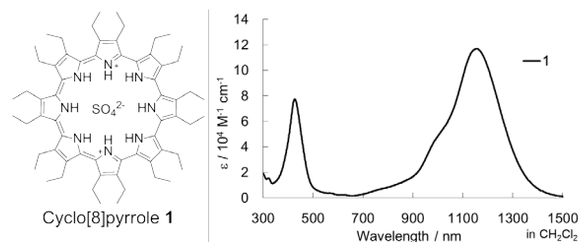

Figure 1. Absorption spectrum of cyclo[8]pyrrole **1**

On the other hand, the polyoxometalates (POMs) which have been known as the redox catalysts are utilized as many applications including photochemical response and optoelectronics. The combination of two photofunctional materials, porphyrinoids and POMs, has gained much attention as the functional materials. For instance, the complex of Mo(V)-porphyrin with a directly coordinated POM, named Porphyrin Hamburger, has been reported to show reversible multi-redox processes by Fukuzumi's group in 2007[2].

We successfully prepared different type of the complex of porphyrinoid and POM, which was formed by electrostatic interactions and hydrogenbonding, by anion exchanging of cyclo[8]pyrrole sulfate **1**. The obtained complex also exhibits hamburger-like shape in single crystal structure. The cyclic voltammogram of the obtained complex exhibits a reversible reduction process and three oxidation process similar to sulfate **1**. The redox process of POM moiety in the cyclo[8]pyrrole-POM complex was not observed although POM in the Porphyrin Hamburger showed specific redox process. We will report herein the structure and physical properties of cyclo[8]pyrrole-POM complex.

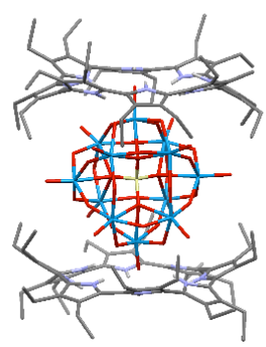

Figure 2. Crystal structure of cyclo[8]pyrrole-POM complex

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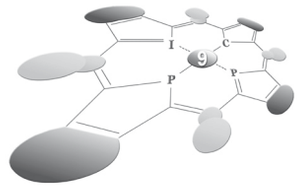

Synthesis and Properties of 1,5-Diazafulvalenes

Yuya Matsuzaki[a], **Yoichi Shida**[a], **Shigeki Mori**[b], **Masayoshi Takase**[a], **Hidemitsu Uno**[a], **Tetsuo Okujima**[a]

[a]*Graduate School of Science and Engineering, Ehime University, Matsuyama, 790-8577, Japan.*
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Fulvalene derivatives exhibit characteristic redox properties with both electron-donating and electron-accepting characters and they attract much attention as both p-type and n-type semiconducting materials. Tetrathiafulvalene (TTF) is well known due to its high electron-donating character.[1)] On the other hand, there have been a few reports on new structures of acceptor components. Recently, electron-accepting fulvalene derivatives have been reported by Wudl and his co-workers in 2010,[2)] and by Fukazawa and her co-workers in 2013.[3)] Herein, we report synthesis and properties of 1,5-diazafulvalene **1**–**4** as novel electron-acceptors (Figure 1).

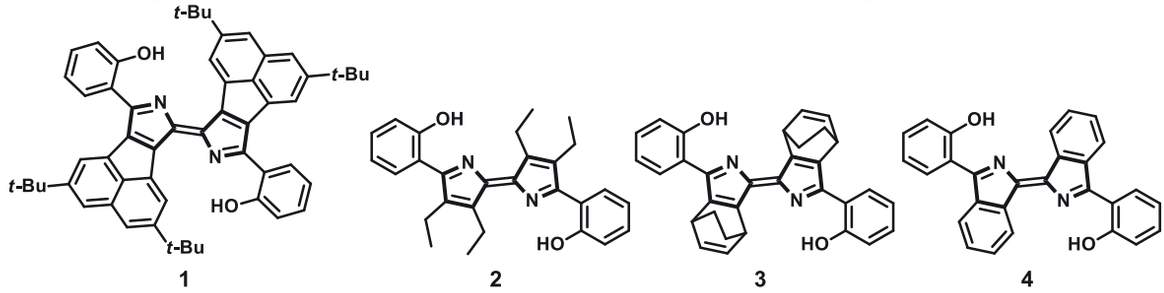

Figure 1

Oxidative coupling of α-*o*-hydroxyphenylpyrroles using iron(iii) chloride afforded **1**–**4**, which were stabilized by intramolecular hydrogen bond. They exhibited 2-step reversible reduction peaks in CV. This result suggests the reversible redox system based on Hückel 6π aromaticity of a radical anion and a dianion (Figure 2).

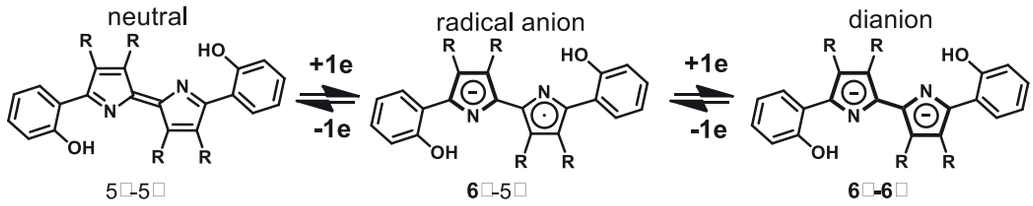

Figure 2

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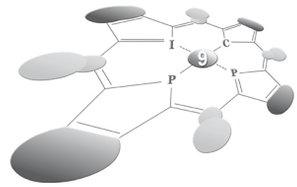

Synthesis of Near-IR BODIPYs via Functionalization of β,β'-Bicyclo-3,5-Diiodo-8-Aryl-BODIPYs

Qianli Meng, Frank R. Fronczek and M. Graça H. Vicente

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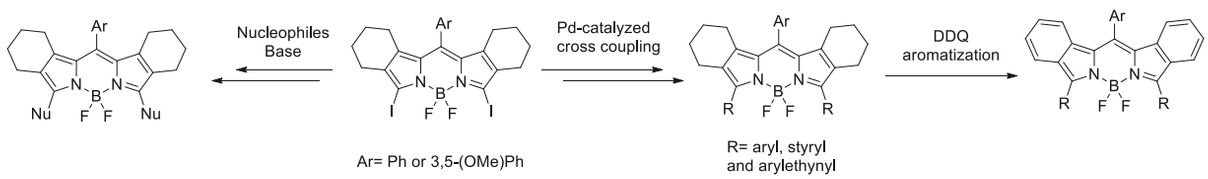
β,β'-Bicyclo-3,5-diiodo-8-aryl-BODIPYs were prepared from commercially available reagents, and their functionalization were investigated via Pd-catalyzed cross coupling reactions and substitution reactions at the 3,5-positions. [1,1□-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) has been studied as the most effective catalyst for symmetrical and unsymmetrical cross coupling reactions, including Suzuki, Stille and Heck reactions in relatively high yields. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone in refluxing toluene was applied to aromatize β,β'-bicyclo-3,5,8-triaryl-BODIPYs to give β,β'-dibenzo-3,5,8-triaryl-BODIPYs in 32-54% yields. Downfield NMR chemical shifts were observed in the ^{11}B- and ^{19}F-NMR spectra after each 3,5-cross couplings and aromatization. The highly reactive 3,5-diiodo-BODIPYs were substituted with various nucleophiles, including mono- and disubstitution with O-, N-, S- and C-nucleophiles. Photophysical studies show that DDQ aromatization provided BODIPYs with 77-89 nm red shifts of absorptions and fluorescence emissions, smaller Stokes' shifts and generally higher quantum yields. Among substitution reactions, O-, C- nucleophiles blue-shifted absorptions and fluorescence emissions compared with 3,5-diiodo-BODIPYs, while N- and S-nucleophiles red-shifted them.



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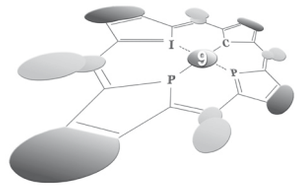


Conjugates of Photodynamic and Fluorescent Azaphthalocyanines With Oligonucleotides and their Behavior in Water Environment

Miletin M., Novakova V., Zimcik P[a]

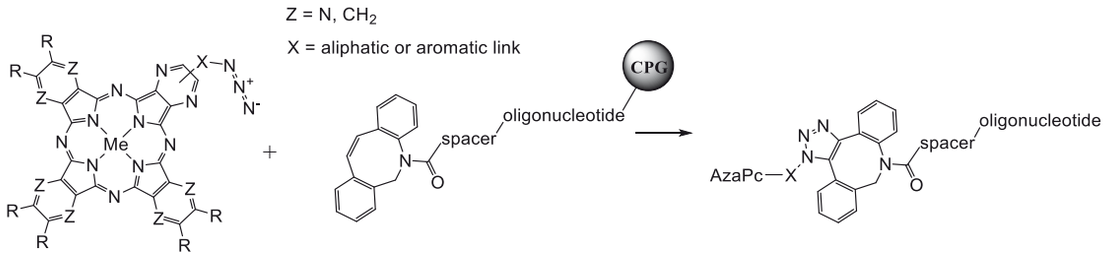
[a] *Department of Pharmaceutical Chemistry and Drug Control, Charles University in Prague, Faculty of Pharmacy Hradec Kralove, Heyrovskeho 1203, 500 05 Hradec Kralove, Czech Republic, miletin@faf.cuni.cz*

Functionalized synthetic short nucleic acids sequences (oligonucleotides) are among main tools of molecular biologic methods employed in research, as well as in many diagnostic and forensic approaches. Also their use in therapeutic area is subject of big scientific effort. Therefore, new functional molecules for of oligonucleotide derivatization are of continuing interest.

Fluorescence and/or its quenching are the main abilities required at oligonucleotide labeling molecules for diagnostic or forensic applications. Because of their excellent photochemical and photophysical properties, phthalocyanines (Pc) and their azo-analogues (AzaPc) are hot candidates for both fluorescent and fluorescence quenching functional moieties of oligonucleotide probes[1,2]. Even more, singlet oxygen producing Pc/AzaPc can be employed as photoactive subunits of photodynamic antisense and aptamer oligonucleotide therapeutics.

To attach the functional molecules to oligonucleotides, copper free azide-cyclooctyne Huisgen cycloaddition (click chemistry) belongs to the most efficient methods[3]. To employ it, we have synthesized several non-symmetrical (A_3B type) AzaPc molecules bearing one aliphatic or aromatic azido group for specific and equimolar attachment of one AzaPc to one oligonucleotide sequence.

Conjugates with various oligonucleotide sequences were prepared on solid phase, taking advantage of free choice of reaction solvent and easier purification of the labeled oligonucleotide. The conjugation efficiency was evaluated.



Photophysical properties of the prepared AzaPc-oligonucleotide conjugates were tested under various conditions in water solutions to examine their potential of use in biological environment.

The study was supported by Czech Science Foundation, project No. 13-27761S

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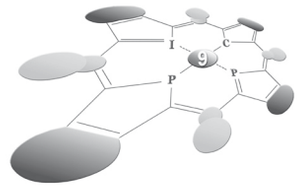


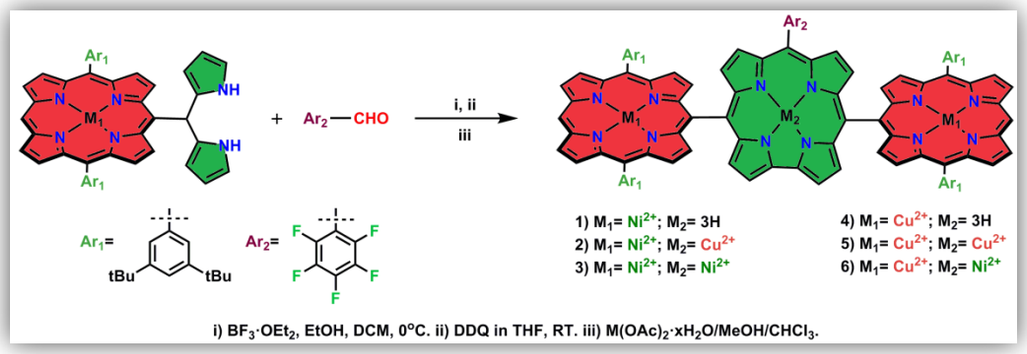
First Example of a Modular Porphyrinoid Assembly Capable of Stabilizing Different Metal Ions in a Single Molecular Scaffold

Muthuchamy Murugavel, R.V.Ramana Reddy, and Jeyaraman Sankar*[a]

[a]*Indian Institute of Science Education and Research Bhopal, Bhopal By-pass Road, Bhauri, Bhopal-462066, M.P., India.*

Covalently-interconnected multiporphyrinoids have attracted the attention of both chemists and physicists for understanding energy and electron transfer processes.[1] The electronic modulation of multiporphyrinoids can be fine-tuned by the type of spacers and the mode of linkage.[2] *meso–meso* directly linked porphyrin arrays, unique candidates favouring rapid energy and electron transfer, have been synthesized and highly explored. [3] These multiporphyrin arrays could stabilize homo-nuclear divalent metal ions.

A multiporphyrinoid system with the capability of stabilizing metal ions in different oxidation states in a single molecular frame work can be exploited in the fields of multi-site catalysis, single molecular magnets and photosynthetic mimics. Covalently connected porphyrin (dianionic)-corrole (trianionic) hybrids can be the first example for the same.[4] With this aim, we have envisioned and synthesized new *meso-meso* directly linked Porphyrin-Corrole hybrids (**P**$_{[5]}$•**C**$_{[5,15]}$•**P**$_{[5]}$) with different metal ions in a single molecular framework.[5]



The versatility of the hybrid has been demonstrated by successfully stabilizing homo and heterotrinuclear coordination motifs. In particular, it is worth noting that the **P**$_{[5]}$•**C**$_{[5,15]}$•**P**$_{[5]}$ hybrid can further be manipulated due to the presence of substituent-free *meso*-positions on both sides.

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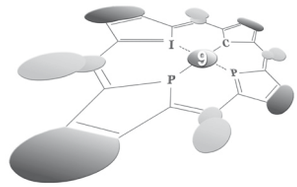


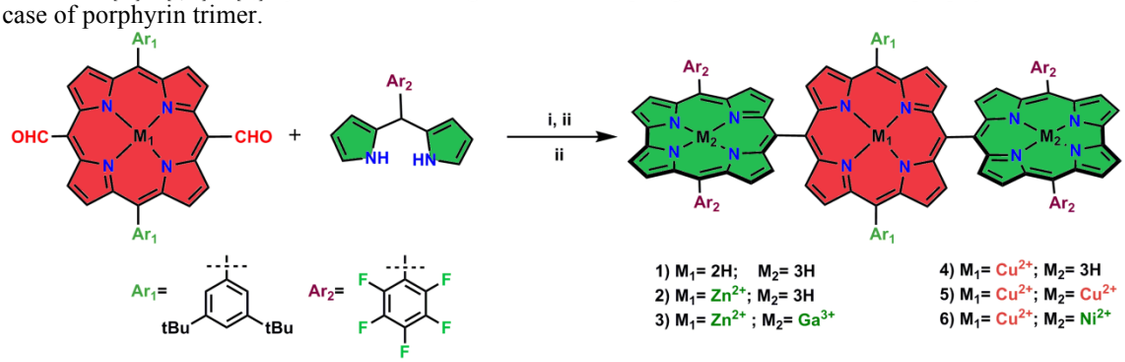
Corrole-Porphyrin-Corrole ($C_{[10]}$•$P_{[5,15]}$•$C_{[10]}$) Hybrids with Metal Ions in Multiple Oxidation States

Muthuchamy Murugavel, Jyoti Rai, R. V. Ramana Reddy, and Jeyaraman Sankar*[a]

[a]*Indian Institute of Science Education and Research Bhopal, Indore By-pass Road, Bhauri, Bhopal-462066, M.P., India.*

Corrole, a ring-contracted tetrapyrrolic trianionic ligand with a skeleton of corrin ring has quite interesting properties like stabilization of metal ions in their higher oxidation states, higher fluorescence quantum yields and larger Stokes shift.[1] Tailoring of multicorroles and incorporation of corroles into porphyrins which leads to corrole-porphyrin multi-hetero arrays has scarcely been reported,[2] though the metalated hybrids can be exploited for multisite catalysis, molecular magnets and biological mimics. These hybrid arrays devoid of spacers have effective transition dipole moment interactions along the long molecular axis which results in strong excitonic coupling.[3]

In this context, herein reported three discrete Corrole-Porphyrin-Corrole (**$C_{[10]}$•$P_{[5,15]}$•$C_{[10]}$**) hybrids with the capability of stabilizing metal ions in multiple oxidation states. The stability of the hybrid was enhanced by sequential metalation of porphyrin and corrole macrocycles with Zn^{II} and Cu^{II}/Ga^{III}. The solid state structure of **$GaC_{[10]}$•$ZnP_{[5,15]}$•$GaC_{[10]}$** hybrid is revealed for the first time by single crystal X-ray diffraction studies. All synthesized **$C_{[10]}$•$P_{[5,15]}$•$C_{[10]}$** hybrids have strong excitonic coupling between corrole and porphyrin moieties as in the case of porphyrin trimer.



i) $BF_3{\cdot}OEt_2$, EtOH, DCM, 0°C. ii) DDQ in THF, RT. iii) $M(OAc)_2{\cdot}xH_2O$/MeOH/$CHCl_3$.

It is noteworthy here to mention that **$GaC_{[10]}$•$ZnP_{[5,15]}$•$GaC_{[10]}$** hybrid exhibits dual emissions, falls on photodynamic therapeutic window and multiple redox potentials which could make the hybrid as a potential candidate for photodynamic therapy and molecular memory devices.

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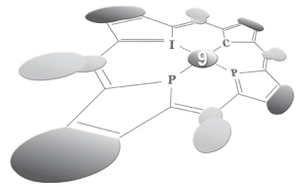


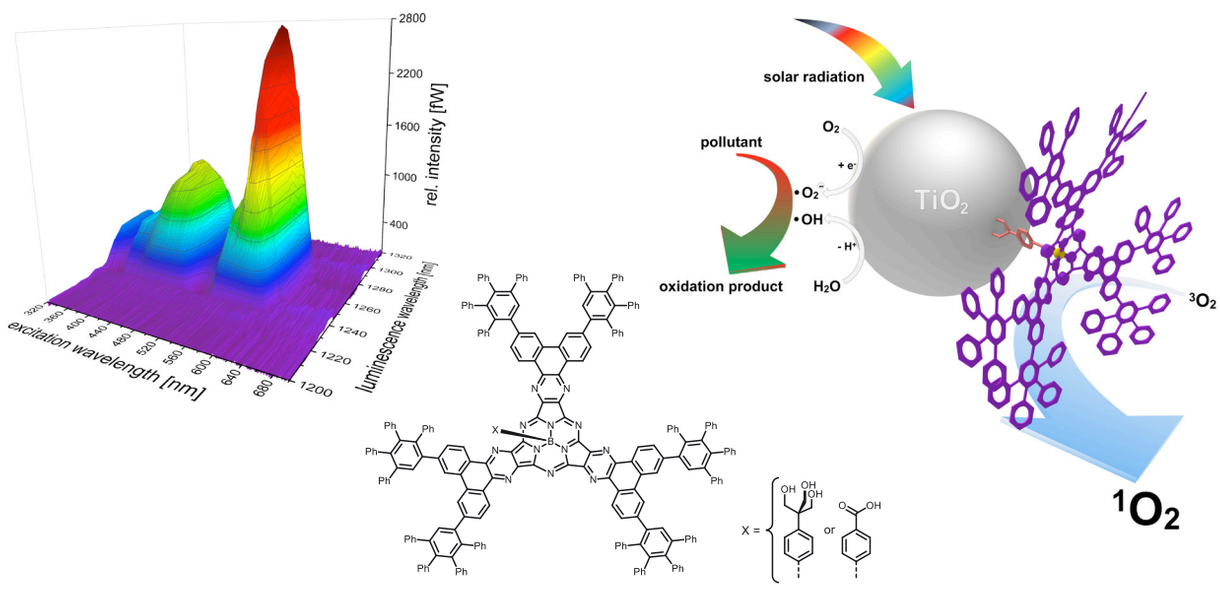
Subporphyrazine/TiO_2–Hybrids for Dual Pathway Photocatalysis

Roman Münnich, **Rüdiger Faust**

University of Kassel, Institute for Chemistry and CINSaT – Center for Interdisciplinary Nanostructure Science and Technology, Heinrich-Plett-Str. 40, 34132 Kassel, Germany. (r.faust@uni-kassel.de)

Subphthalocyanines and their analogues, the subporphyrazines (SubPz), are currently of broad interest due to their photophysical and electrochemical properties that make these versatile chromophores attractive for a variety of applications, among them nonlinear optics,[1] host-guest chemistry,[1,2] solar energy conversion[1] or photocatalysis.[3] Particularly in the area of photocatalysis, the pronounced photosensitizing ability of the SubPz offers exciting possibilities. In hybrid materials of SubPz and TiO_2 the photocatalytic activity (i.e. the photoinduced generation of active oxygen species) of the inorganic component in the UV can be complemented by the visible-light induced singlet oxygen generation of the organic dye.

We have shown recently that peripheral polyphenylation of the SubPz core leads to soluble and efficient singlet oxygen photosensitizers.[3] We report here the introduction of an hydroxyl-based anchoring group as the axial substituent of the boron in polyphenylated SubPz and demonstrate a firm SubPz-attachment to oxidic surfaces. We will discuss details of the synthesis of the functionalized SubPz and of the hybrid materials derived from them along with an evaluation of pertinent photophysical properties with relevance to photocatalytic activities.



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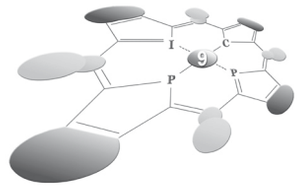

Development of acoustic wave sensors based on cobalt corroles for carbon monoxide detection

Mario L. Naitana[a], Claude P. Gros[a], Valentin Quesneau[a], Nicolas Desbois[a], Stéphane Brandès[a], Meddy Vanotti[b], Virginie Blondeau-Patissier[b], Sylvain Ballandras[c]

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Carbon Monoxide is a well known dangerous compound acting as a "silent killer" due to its undetectable features: colourless, tasteless and odourless. For the human body cells CO manifest its quick deadly action when the organism is exposed in a concentration above 30 ppm and recently the World Health Organization has established a risk assessment in the concentration order of 10 ppm for 8 hours of exposure. Therefore, there is still an ongoing necessity to develop a device able to detect with high sensitivity and specificity the presence of low CO concentration in indoor air. Recently, we have reported the outstanding affinity an infinite selectivity of cobalt(III)corroles for CO over O_2 and N_2 [1] and in this present project, founded by the French National Research Agency (ANR), we describe the development of an efficient and cost-effective surface acoustic wave (SAW)-based sensor, exploiting cobalt corroles as sensing material for CO detection. Several cobalt corroles bearing targeted functional group were tested in order to enhance the interaction of CO vs N_2 and O_2, to optimize the textural properties of the sensing layer and increase the long-term stability of the incorporated metallocorrole.[2]

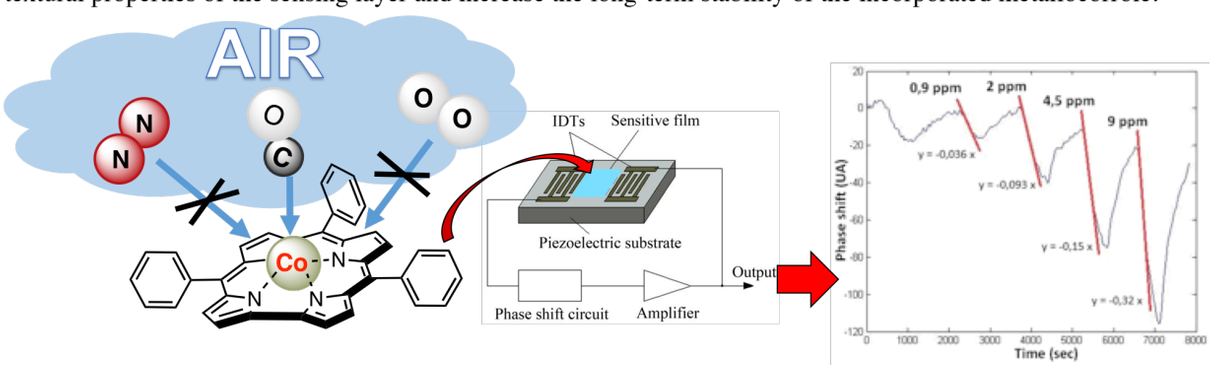

Figure 1

This research is supported by the "Agence Nationale de la Recherche" (ANR) through the CO3SENS project and the "Conseil Régional de Bourgogne" (FEDER and program PARI II CDEA). V.Q. thanks the "Conseil Régional de Bourgogne" for allocating him a "Jeune Chercheur Entrepreneur" PhD. fellowship.

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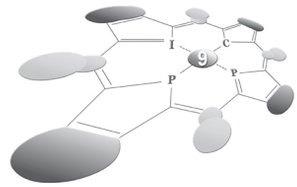

Nitrocorroles as potential agents against human cytomegalovirus infection

Mario L. Naitana[a], Nicolas Desbois[a], Franck Gallardo[b], Claude P. Gros[a]

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Human Herpes viruses massively infect population worldwide and cannot be cured. The human Cytomegalovirus (hCMV) is a highly prevalent virus that causes severe diseases in immune-deficient patients such as HIV positive persons. The hCMV is the first cause of blindness in HIV patients and the first cause of fetal malformations in case of primo-infection during pregnancy. While several inhibitors of Herpes virus progression have been developed so far, nearly all of them target a single step in the virus life cycle, the DNA replication mechanism. As resistant viruses emerge, development and validation of a new generation of drugs that target new pathways during Herpes virus infection is a priority for worldwide healthcare. Therefore, we are interested in synthesizing and evaluating different substituted nitroporphyrinoid derivatives as potential inhibitors of virus infection and propagation. Interestingly, two nitrocorroles display strong activity against human Cytomegalovirus with IC_{50} < 0.5 µM. These compounds also possess antiproliferative activities without detected *in vivo* toxicity. Therefore, nitrocorroles appear for the first time as potential active compounds that can be applied in human health.

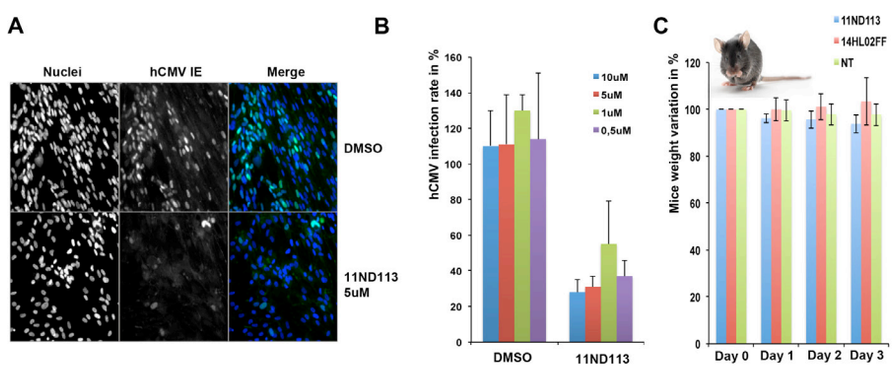

Figure. A) Primary human fibroblasts MRC5 infected with hCMV TB40 (clinical strain) and treated with DMSO 0.5% or « hit » corrole **11ND113**. Infected cells are visualized by the staining of the hCMV Immediate early protein (IE). **B) 11ND113** shows hCMV IC_{50} below 0.5 µM. **C)** « Hit » corrole **11ND113** and one of its variant **14HL02FF** do not display *in vivo* toxicity.

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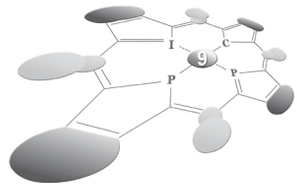

Synthesis of Phthalocyanine Derivatives as Synergists for Improving Contrast Ratio of Liquid Crystal Displays

Jin woong Namgoong[a], Sei-won Chung[a], Jae Moon Lee[a], Se Hun Kim[a], Jae Pil Kim[a*]

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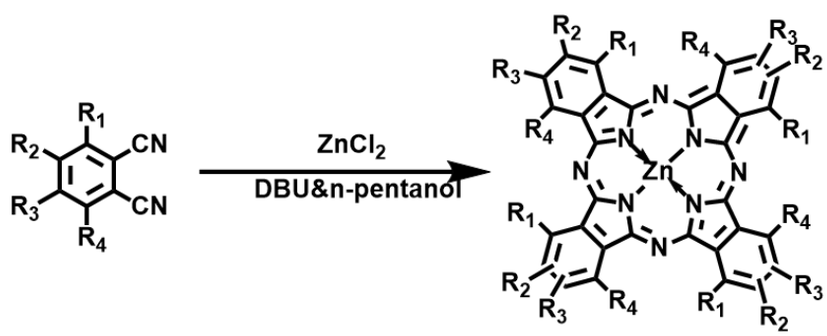
Contrast ratio is one of the most important properties of liquid crystal displays and can be improved by minimizing the light scattering of the pigment particles. Synergists interact both pigments and dispersants so as to inhibit aggregation and improve dispersion of the pigment particles. Therefore, synergists are applied to increase the contrast ratio of liquid crystal displays. Here, phthalocyanine dyes as green color synergists were synthesized for improving contrast ratio of liquid crystal displays. Synergists that have different functional group showed various properties and performance. Moreover, by using various types of dispersant which have different amine and acid value, how synergists interact with dispersant effectively can be investigated. Spectral properties and thermal stability of the dyes were investigated by UV-Vis absorption spectroscopy and thermogravimetric analysis (TGA). Average size and size distribution of the millbase was measured by dynamic light scattering (DLS). Chromatic properties, thermal stability and contrast ratio of color filters using the dyes as synergists were also investigated. Consequently, the contrast ratio increased by adding the synergists and this study showed that the phthalocyanine derivatives with proper functional group can effectively improve the performance of liquid crystal display panels..



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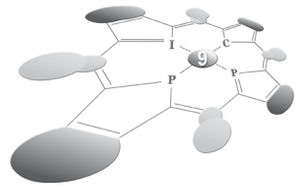

Rest Potentials of Electrolyte Solutions and Threshold Voltages of Organic Electric-Double-Layer Transistors with Platinum Phthalocyanine

- Chihiro Nanjo[a], Michio M. Matsushita[a] , Kunio Awaga[a]–

[a] *Department of Chemistry, Graduate school of Science, Nagoya University, Japan*

There is a growing attention to the electric-double-layer (EDL) transistors, in which electrolytes are adopted as gate dielectrics, because a strong electric field produced by EDL improves transistor performance. In our previous works, we concluded that the performance of these transistors was governed by the so-called rest potential, which is defined as the potential difference between reference and working electrodes and therfore reflects the potential of working electrode. Namely, we revealed the ionic-liquid dependence of the rest potential and a linear relation between the rest potentials and the threshold voltages for the EDL transistors with various ionic liquids [1]. In the present study, we examined the binary mixtures of ionic liquids and the polyethylene glycol (PEG) solutions of various ionic salts for the gate dielectrics of EDL transistors, combining a semiconducor, platinum phthalocyanine (PtPc), which had an excellent stability in the ionic liquids and the PEG solutions.

We prepared various binary mixtures of ionic liquids, combining DEME-TFSI and four kinds of ionic liquids shown in the inset of Fig. 1 and changing their mixing ratios. Then, we measured the rest potentials and the transistor threshold voltages of the EDL transistors of PtPc. Figure 1 shows the relation between the two parameters, clearly indicating a linearity, though there was no linear relation that rest potentials themselves and the mixing ratio beween the parent ionic liquids. This means that the threshold voltage can be controlled continuously by changing the mixing ratio of the ionic liquids.

We also tested the PEG solutions of ionic salts for the EDL tranisistors of PtPc, taking advantage of the facts that PEG dissolves various kinds of ionic salts and the EDL transistors can be tested under vacuum due to a low vapor pressure of PEG, and obtained the essetially the same conclution as done for the ionic-liquid EDL transisitors.

We will discuss the performace of the EDL transistors with the PEG solutions, based on its dependence on the components (cation and anion) in the solutions.

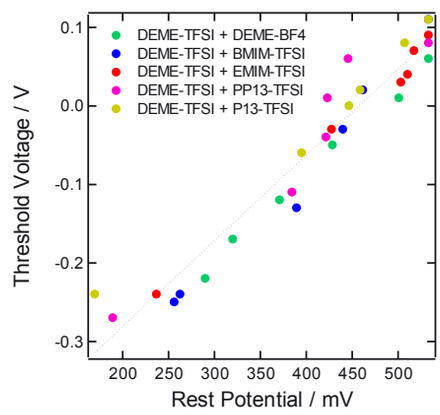

Figure 1. Relation between rest potentials of binary ionic liquids and threshold voltages.

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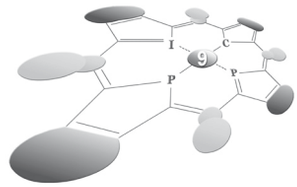

Photophysics and photochemistry of boron porphyrin and boron porphyrinoid complexes

Nina I. Novikova[a,b,c,e], **M. Cather Simpson**[a,b,c,d,e], **Penelope J. Brothers**[a,c]

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[c] *MacDiarmid Institute for Advanced Materials and Nanotechnology*
[d] *The University of Auckland, Department of Physics, 23 Symonds Street, Bldg 301, Auckland 1010, New Zealand*
[e] *The University of Auckland, Photon Factory, 23 Symonds Street, Bldg 301, Auckland 1010*

Boron porphyrin and porphyrinoid complexes are a family of compounds with unusual coordination motifs and surprising versatility in structure.[1,2] The common feature in all the boron porphyrin complexes is the coordination of two boron atoms within a single porphyrin cavity that results in core distortions, the most unusual of which is the tetragonal elongation of the porphyrin core along the B-B axis. Much prior research links the tunability of porphyrin properties to the distortions that occur in the porphyrin core, but the effect of the type of distortion observed in boron porphyrins is largely unknown. Boron coordination to other porphyrinoid ligands such as corrole and calixphyrin results in complexes with either a single or a double boron coordination, further expanding their versatility. The photophysical and photochemical properties of boron porphyrin and boron porphyrinoid complexes were examined using femtosecond and nanosecond transient absorption spectroscopy, quantum chemical calculations and static spectroscopy methods. The dynamics of the transient species produced after photoexcitation of several boron complexes were monitored using transient absorption spectroscopy by exciting a molecule using ultrashort light pulses at the wavelengths corresponding to the Soret and Q band absorptions and monitoring the relaxation by recording UV/Vis absorption spectra at a series of specific time delays after excitation, using a supercontinuum probe pulse. Two time scales of the excitation and probe pulses were used: (i) ~100 fs pulses were used to monitor the ultrashort dynamics on fs to ps timescale and (ii) ~7 ns pulses were used to monitor longer lived transitions.

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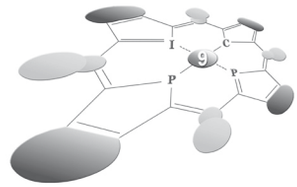


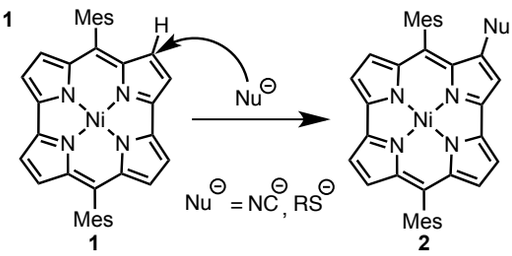
Synthesis and Properties of Stacked Antiaromatic Norcorrole Dimer

Ryo Nozawa[a], **Soji Shimizu**[b], **Ichiro Hisaki**[c], **Won-Young Cha**[d], **Dongho Kim**[d], **and Hiroshi Shinokubo**[a]

[a] *Graduate School of Engineering, Nagoya University, Japan*
[b] *Graduate School of Engineering, Kyushu University, Japan*
[c] *Graduate School of Engineering, Osaka University, Japan*
[d] *Department of Chemistry, Yonsei University, Korea*

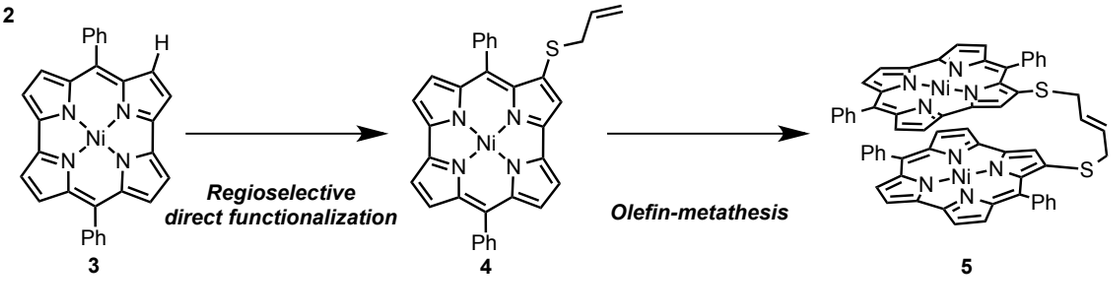
Norcorrole Ni(II) complex **1** is a stable porphyrinoid which shows distinct antiaromaticity. Recently, we have reported that the reaction of norcorrole **1** with nucleophiles affords functionalized norcorrole Ni(II) complexes **2** with perfect regioselectivity (Scheme 1).[1)]

Scheme 1



On the basis of this methodology, we have succeeded in the synthesis of stacked norcorrole dimer **5** (Scheme 2). Schleyer[2)] and Fowler[3)] predicted that stacked antiaromatic compounds would exhibit three-dimensional aromaticity. However, such a stacked antiaromatic compound has not yet synthesized. In this presentation, we will disclose the structure, optical property, and electronic property of this compound.

Scheme 2



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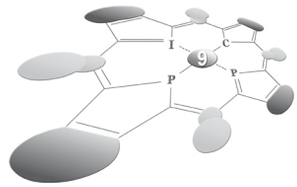

Fabrication of Single Crystalline Thin Film of Non-Peripheral Hexyl-Substituted Phthalocyanine and Its Crystal Structure Analysis with Grazing Incidence Wide-Angle X-ray Scattering Method

Masashi Ohmori, Takashi Uno, Chika Nakano, Akihiko Fujii and Masanori Ozaki

Division of Electrical, Electronic and information Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

The fabrication of the single crystalline thin film of 1,4,8,11,15,18,22,25-octahexylphthalocyanine ($C6PcH_2$), which exhibits an ambipolar high carrier mobility, was realized by using bar coating method. The crystal structure in the thin film was confirmed with Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) method and the simulation using the single crystal structure.

The conditions of bar coating, such as, bar speed, used solvent, substrate temperature and so on, were optimized for controlling the balance of the deposition rate and crystal growth rate. The uniform thin film could be fabricated in an appropriate condition, and exhibited the obvious optical anisotropy.

Figure 1 (a) shows the X-ray diffraction (XRD) patterns when the incident X-ray was parallel to the sweep direction of the bar coating method. The measured XRD patterns completely coincided with the simulated patterns as shown in Fig. 1 (b) by using the data of $C6PcH_2$ single crystal structure in Fig. 1 (c).The film forming direction of the bar coating method was similar to the crystal growth direction of $C6PcH_2$ because of the high crystal growth rate along the direction of the molecular stacking.

Figure 2 shows the azimuthal dependence of the XRD patterns, which was measured with GIWAXS method while rotating the thin film. The dotted XRD pattern means the low alignment distribution in the azimuthal direction. The results of GIWAXS indicate that the molecular packing structure in the thin film three-dimensionally coincided with the $C6PcH_2$ single crystal structure, that is, the thin film consisted of the uniformly oriented $C6PcH_2$ single crystals.

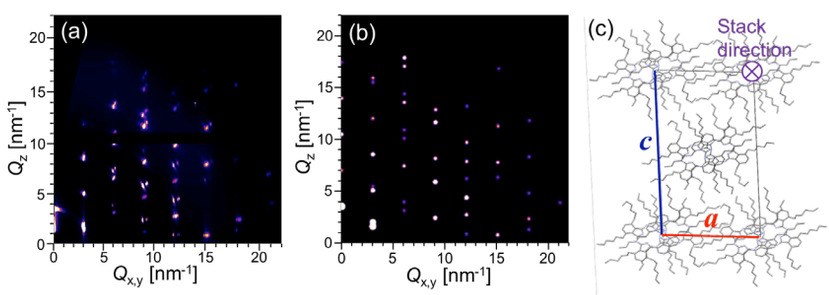

Figure 1 Measured XRD patterns (a) and simulated patterns (b) by using the $C6PcH_2$ single crystal structure (c)

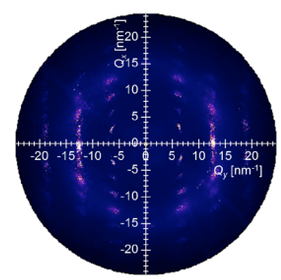

Figure 2 Azimuthal dependence of the XRD patterns

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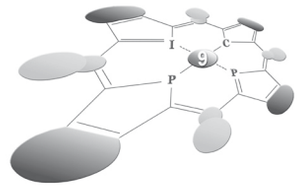

Synthesis of Non-planar Porphycene Dimers for New n-type Organic Semiconductors

Takuya Okabe[a], **Daiki Kuzuhara**[a], **Naoki Aratani**[a], **Hiroko Yamada**[a]

[a] *Graduate School of Materials Science, Nara Institute of Science and Technology*

Recently, non-fullerene acceptors with non-planar structures have attracted attention as novel n-type materials for organic solar cells (OSCs) [1]. In particular, non-planar structures lead to advantageous properties of an isotropic electron transportation and a donor-acceptor phase separation. Porphycene, which is a structural isomer of porphyrin, has strong absorption bands in the visible to near infrared region and shows an electron-accepting property [2]. Thanks to these properties, porphycene is expected to be applied to n-type organic semiconductors for OSCs. We have reported a key intermediate of 3-iodoporphycene which was obtained by iodination reactions of 2,7,12,17-tetrahexylporphycene (**THPc**) with *N*-iodosuccinimide (NIS) in the present of additive [3]. In this work, we have synthesized porphycene dimers with *m*-phenylene (**DPc-mP**) and thienylene (**DPc-T**) linkages via cross-coupling reactions from 3-iodoporphycene (Figure 1).

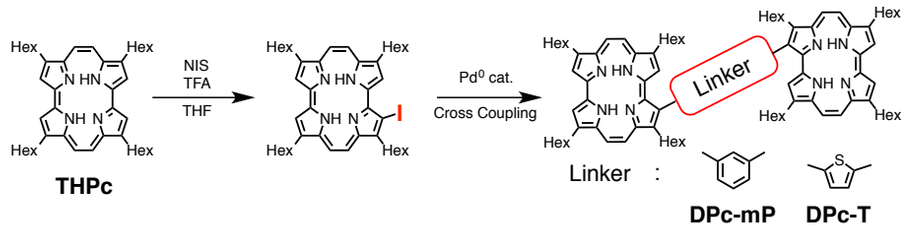

Figure 1. Synthesis of porphycene dimers, **DPc-mP** and **DPc-T**.

The structural information of **DPc-mP** and **DPc-T** were obtained from the X-ray diffraction analysis (Figure 2). The crystal structure of **DPc-mP** showed that two porphycene units are located nearly vertical to each other with a dihedral angle of 103°. On the other hand, the crystal structure of **DPc-T** showed two porphycenes located nearly parallel positions. We fabricated OSCs based on these porphycene dimers as n-type materials. The optical properties and photovoltaic performances of these porphycene dimers will be discussed.

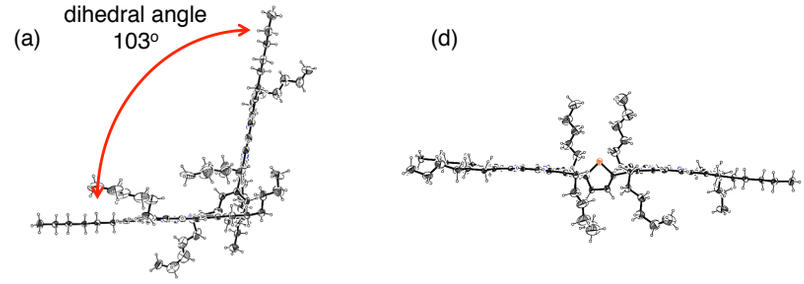

Figure 2. Crystal structure of (a) **DPc-mP** and (b) **DPc-T**. Thermal ellipsoids represent 20% probability.

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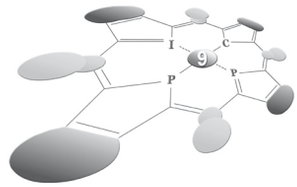

Synthesis, Structures and Properties of Pyrrole-Fused Azacoronene Derivatives Containing 7-Membered Rings

Kosuke Oki[a], **Yoshiki Sasaki**[a], **Masayoshi Takase**[a], **Shigeki Mori**[b], **Tetsuo Okujima**[a], **Hidemitsu Uno**[a]

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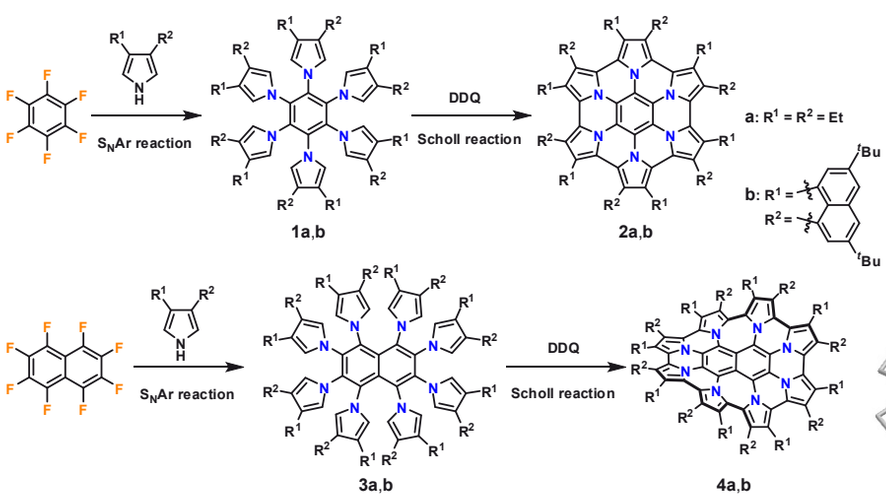
There is a considerable demand for the synthesis of large two-dimensional molecules with extended π conjugation such as polycyclic aromatic hydrocarbons (PAHs). Nitrogen incorporation to PAHs can influence the electronic nature without modifying the structure. For example, pyrrole-fused azacoronene derivatives such as hexapyrrolohexaazacoronene (HPHAC, Figure 1) have an extended π conjugation with multiple interior nitrogen atoms and display stable oxidation states[1,2]. Herein, we report the synthesis of different types of HPHAC **2** and naphthalene-centered azacoronene derivative **4**.

Aromatic nucleophilic substitution (S_NAr) reaction of hexafluorobenzene and octafluoronaphthalene with excess amount of pyrrole afforded hexapyrrolylbenzene (HPB **1a**,**b**) and octapyrrolylnaphthalene (OPN **3a**,**b**), respectively. Then, HPHAC **2a**,**b** and fused-OPN **4a**,**b** containing two 7-membered rings were synthesized by Scholl reaction with dichlorodicyanobenzoquinone (DDQ) (Scheme). The structures were determined by X-ray crystallographic analysis, showing curved π planes of both **2b** and **4a** (Figure 2). The new compounds were also characterized by NMR, UV-vis-NIR absorption and electrochemical analyses.



Scheme.

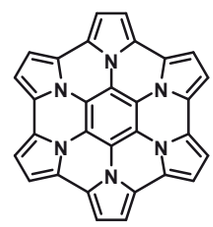


Figure 1.

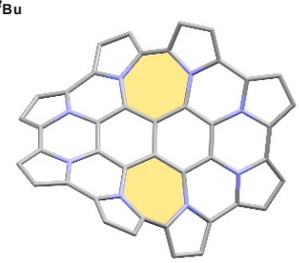


Figure 2. **4a**

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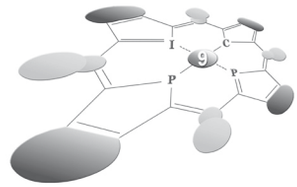

Synthesis of a Mono-substituted Phthalocyanine Conjugated to Monoclonal Antibody for Targeted Therapy

Elizabeth Akinyi Okoth, Benson Getenga Ongarora, Zehua Zhou, J. Michael Mathis, M. Graça H. Vicente

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA

Phthalocyanines exhibit excellent thermal stability, photostability and chemical stability, features that contribute to the interest in developing them as photosensitizers for photodynamic therapy of cancer.[1] Despite these attractive features, there is still a need for specific delivery of photosensitizers to cancer cells as compared to normal cells in order to reduce overall systemic toxicity and increase the photosensitizer's therapeutic effects. Conjugation to tumor specific antibodies increases their affinity for cancer cells.[2] More than 35 monoclonal antibody conjugates have been FDA approved for treatment of blood disorders, cancer and other auto-immune diseases.[3] Phthalocyanines conjugated to a monoclonal antibody have been reported to target cancer cells about 37 times more than the free dye, a factor attributed to antibody-mediation.[4]

My research is focused on the synthesis of a mono-functionalized phthalocyanine dye with a short polyethylene glycol (PEG) group. Attachment of a PEG group increases the solubility and serum life of phthalocyanines in aqueous media. The PEG group is terminated in a carboxylic acid for amide bond formation with bovine serum albumin and a monoclonal antibody. The conjugations were carried out using DIEA, HOBt and TBTU coupling reagents. These syntheses produced photosensitizer conjugates with various degrees of labeling. The phthalocyanine and its analogues were characterized using UV/Vis spectroscopy, NMR spectroscopy and high resolution electrospray ionization mass spectroscopy. The conjugates biological activity is investigated in cell and animal models.

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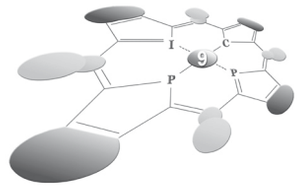


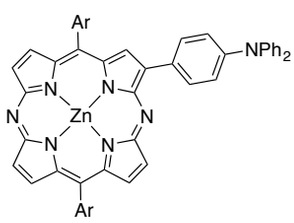
Synthesis and Properties of β-Aryl-5,15-diazaporphyrin Derivatives with Large Charge Transfer Character

Satoshi Omomo [a]; Kenichi Sugiura [b]; Tomohiro Higashino [b]; Hiroshi Imahori [b]; Yoshihiro Matano [c]

[a] *Department of Fundamental Sciences, Graduate School of Science and Technology, Niigata University*
[b] *Department of Molecular Engineering, Graduate School of Engineering, Kyoto University*
[c] *Department of Chemistry, Faculty of Science, Niigata University*

5,15-Diazaporphyrins (DAP) are a class of azaporphyrins with two meso-nitrogen atoms. Recently, we successfully established general methods for the synthesis and regioselective functionalizations of the β-unsubstituted DAPs.[1] Due to high visible-light-harvesting property and electron-accepting ability, donor–acceptor-type DAPs are promising sensitizers for use in dye-sensitized solar cell (DSSC). To our knowledge, however, little attention has been paid to this kind of application.[2]

To develop a new class of DAP-based functional dyes, we have established a convenient method for the introduction of an aryl group to the peripheral β carbon by using Suzuki-Miyaura cross-coupling reactions. It was found that *p*-$Ph_2NC_6H_4$-ZnDAP **1** showed broad absorption and emission bands with the large charge–transfer (CT) character from the triphenylamine (donor) to ZnDAP (acceptor) units.[3] We envisioned that this kind of CT character would be beneficial for the efficient formation of a charge-separated state in DSSC. With this in mind, we synthesized new DAP derivatives bearing anchoring carboxylic groups (**2** and **3**) and elucidated their optical and electrochemical properties to use them in DSSC. The donor–acceptor-type dye **3** showed broad absorption and emission bands like **1**. The optical HOMO–LUMO gaps of **2** and **3** were determined as 2.1 and 1.9 eV, respectively. In the DSSC measurements, **3** showed high power-conversion efficiency compared with **2**. In this presentation, the optical and electrochemical properties of **1–3** will also be discussed in detail.



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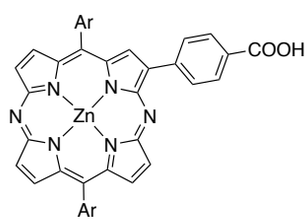

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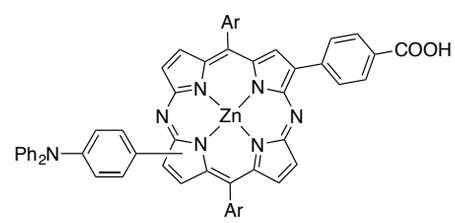

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Azacorroles from Nitrogen Bridged Bisdipyrrins

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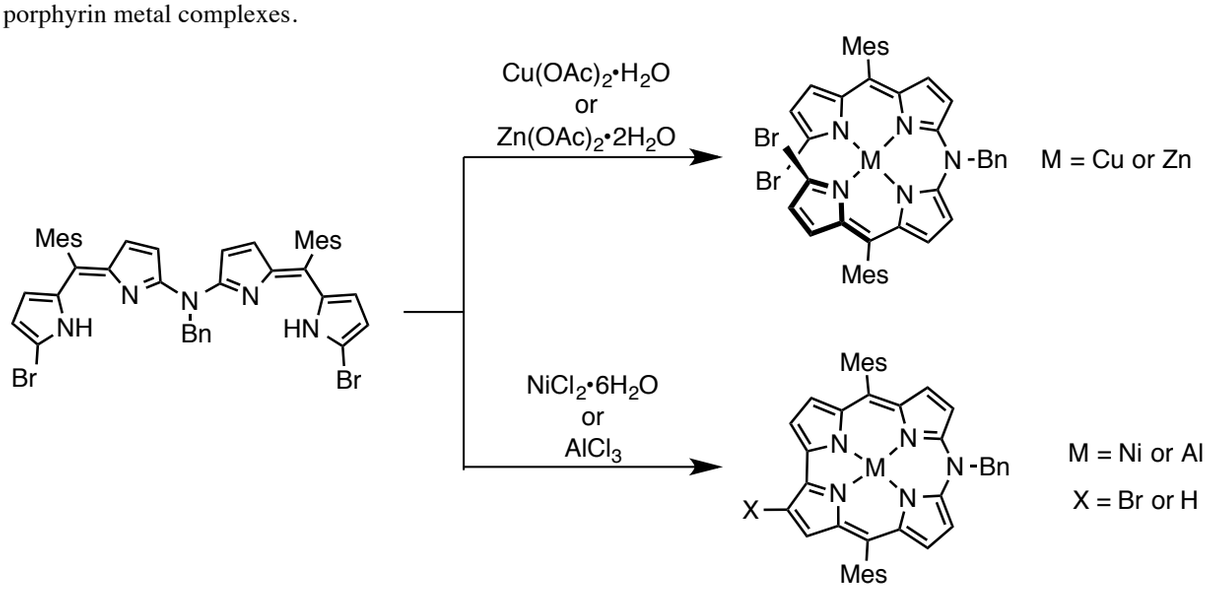
Porphyrinoids have attracted much attention due to their interesting properties. In particular, replacing carbon atoms of porphyrinoids with heteroatoms can change their photophysical and electronic characteristics. Azacorrole is a corrole analogue containing a nitrogen atom at one of the meso positions. The synthesis of azacorroles, however, has been limited.[1]

We have achieved the synthesis of Ni^{II} and Al^{III} azacorroles through coordination-induced cyclization of nitrogen bridged bisdipyrrins.[2] Palladium-catalyzed amination of α,α'-dibromodipyrrin provided nitrogen bridged bisdipyrrins. Treatment of the bisdipyrrins with Cu^{II} and Zn^{II} ions afforded the corresponding metal complexes. On the other hand, heating of the bisdipyrrins with Ni^{II} and Al^{III} ions furnished monobromoazacorroles and azacorroles. In the case of Ni^{II}, the bromo substituent was selectively introduced at the C2 position. Because the ionic radii of Ni^{II} and Al^{III} are much smaller than that of Cu^{II} and Zn^{II}, they serves as templates to bring two reacting centers closer and facilitate the cyclization reaction.

Al^{III} azacorroles showed fluorescence with moderate quantum yield in the solution state. This is the first example of emissive azacorroles. Moreover, UV-vis absorption spectra and cyclic voltammograms revealed that Ni^{II} and Al^{III} azacorroles exhibits significantly different optical and electrochemical properties from the corresponding porphyrin metal complexes.



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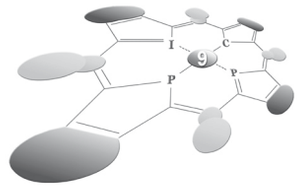

Electrochemical Fluoroalkylation of Organic Compounds Catalyzed by Vitamin B_{12} Derivative

Toshikazu Ono [a,b], **Kosuke Wakiya** [a], **Hossain M. Jakir** [a], **Yoshio Hisaeda** [a,b]

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[b]*Center for Molecular Systems (CMS), Kyushu University*

Trifluoromethylation is an important reaction because trifluoromethyl (CF_3) group provides an enhancement of pharmacological activity to pharmaceutical agents. In this context, introduction of CF_3 groups and perfluoroalkyl groups to the organic compounds is recently considerable attention in scientific communities[1,2]. Here, we report electrochemical trifluoromethylation and perfluoroalkylation of organic compounds mediated by vitamin B_{12} derivative as a novel catalyst as follows (Figure 1). Co(I) species of vitamin B_{12} derivative, which were prepared under -0.8 V vs. Ag/AgCl, reacted with CF_3I, producing Co-CF_3 complex. Then, the complex released CF_3 radical under irradiation of visible light (> 420 nm). The CF_3 radical directly reacted with non-activated substrate such as 1,3,5-trimethoxybenzene due to the high reactivity of CF_3 radical (c.a. 50% yield). Using the different reagent such as C_3F_7I, we successfully performed perfluoroalkylation of organic compounds such as 1,3,5-trimethoxybenzene as well. We will talk about their experimental details and discussion in the poster presentation.

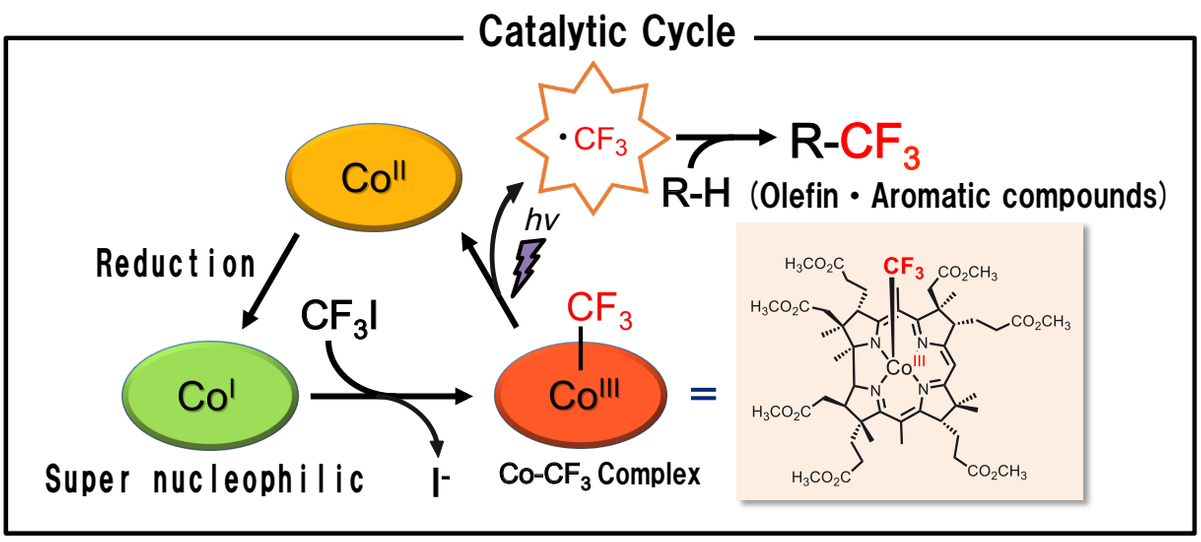

Figure 1. Concept of this study. Radical trifluoromethylation of organic compounds mediated by vitamin B_{12} derivative.

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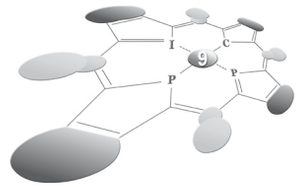


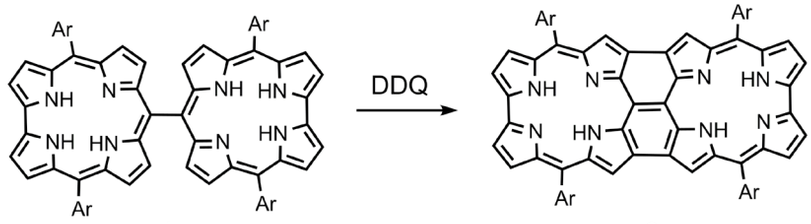
Triply Linked Corrole Dimers

Shota Ooi[a], **Takayuki Tanaka**[a] **and Atsuhiro Osuka**[a]

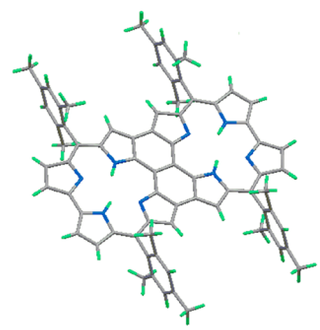
[a] *Department of Chemistry, Graduate School of Science, Kyoto University*

Corrole is a ring-contracted porphyrin bearing a direct pyrrole–pyrrole linkage. In most cases, corroles bear three pyrrolic protons (*3H*-corroles) and those bearing two pyrrolic protons (*2H*-corroles) are electronically frustrated and very rare. After reliable synthetic protocols have been invented in early 2000s, *meso*-aryl substituted corroles have been widely used as chromophores, sensors, and catalysts. Despite these studies, only a limited number of directly linked corrole dimers have been reported so far. For example, doubly 2,18-linked dimer and doubly 3,5-linked dimer were synthesized via oxidative fusion reaction by DDQ from corresponding singly linked dimers[1,2]. Interestingly, 2,18-linked dimer exists as an open-shell, singlet biradicaloid molecule, while 3,5-linked dimer is a closed-shell, nonaromatic molecule with a partially helicene-like structure. Obviously, the triply linked corrole dimer can be a milestone in fused porphyrinoid chemistry, which was actually envisioned by Gryko in 2007 but have not been successful to date[3]. Here we report the synthesis and characterization of triply linked corrole dimers for the first time.

Triply linked corrole dimer **2** was synthesized via DDQ-mediated oxidative fusion reaction of *meso-meso* linked corrole dimer **1**. **2** exhibits characteristic ^{1}H NMR and absorption spectrum, attributable to the nonaromatic yet fully conjugated nature. Interestingly, **2** is fairly stable despite its unusual *2H*-corrole structure, which is ascribed to the presence of three direct connections between the individual corrole units as well as effective intramolecular hydrogen bondings. The structure of **2** was confirmed by X-ray diffraction analysis. While the isolation of the reduced *3H*-forms was hampered because the reduced form was highly unstable and easily reverted back to oxidized *2H*-form, we have successfully observed aromatic *3H*-corrole tape in situ generated by $NaBH_4$. The Zn(II) complex and Cu(II) complex were obtained. The structures and properties of these novel triply linked corrole dimers will be reported in this presentation.



1 **2**



Triply-linked 2H-corrole dimer

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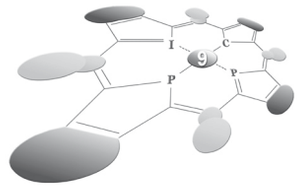


Novel *meso*-amide corroles

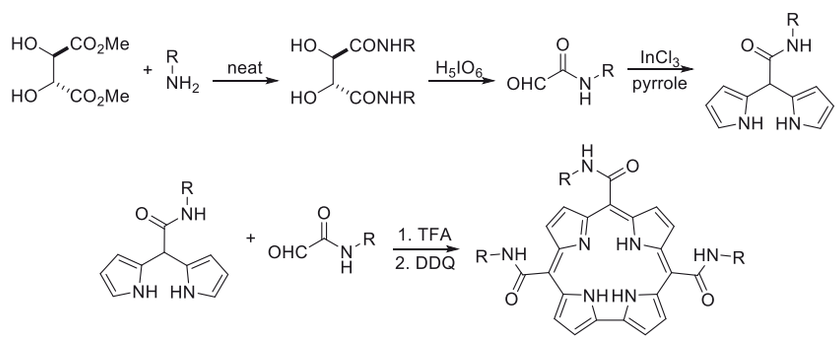
Rafał Orłowski[a] and Daniel T. Gryko[a]

[a]*Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*

Self-assembly as a strategy towards creating large, highly organized structures from relatively simple building blocks is an attractive goal and the design of organic compounds with the ability to adopt specific compact conformations continues to be a flourishing area of research.[1] Nevertheless self-assembly of the corrole based scaffolds is much less studied in comparison with other aromatic tetrapyrroles.

The stabilization of free-base corroles however, requires strong electron-withdrawing substituents, such as pentrafluorophenyl groups, steric hindrance of which, hampers inter-macrocycle overlap, crucial for the assemblies efficient energy-transport properties.[2, 3]

Herein, we would like to present novel *meso*-amide corroles, which are promising alternative to the corroles possessing bulky aryl groups in the *meso*- positions. The presence of such moieties both stabilizes molecule and provides convenient sites for hydrogen bonding. Final products possess promising photo-physical properties.



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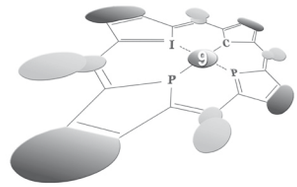


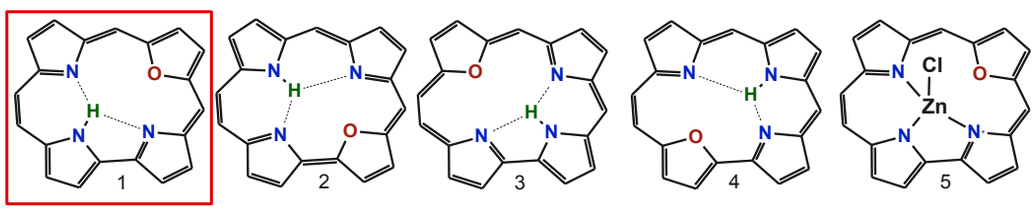
Synthesis of oxahemiporphycene

Jakub Ostapko, Jacek Waluk

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224, Warsaw, Poland, jostapko@ichf.edu.pl

Since the synthesis of porphycene[1], tetrapyrrolic macrocyclic compounds are considered as convenient models for investigations of intramolecular hydrogen bond and proton transfer processes. The tunablity of nitrogen cavity shape and size, crucial in the context of intramolecular hydrogen bond, may be achieved by introduction of proper substituents to the macrocycle or by rearrangement of pyrrole and methine subunits. This geometrical diversity of pyrrole macrocycles inspired wide-ranging discussions of hydrogen bond nature[2]-[5].

Another structural change, besides nitrogen cavity shape tuning, that may have a significant influence on intramolecular hydrogen bond features is the replacement of one of the nitrogen atoms by oxygen. In such a mixed system, the oxygen atom should be considered as a weaker hydrogen bond acceptor with respect to the nitrogen atoms. Moreover, the tautomeric form of the macrocycle with the hydrogen atom located on the oxygen should have a higher energy, which limits the number of possible tautomeric species. In the case of a low symmetry macrocycle, such as hemiporphycene and its oxa analogs, each of the tautomeric forms should exhibit a different arrangement of hydrogen bond lengths and angles.



These elementary considerations inspired us to propose four possible monooxa analogs of hemiporphycene **1**-**4**; each of them possessing three different tautomeric forms. This library of possible structures of monooxahemiporphycenes should provide data that would allow extracting important information on the hydrogen bond nature, e.g., the contributions from the N···N distance and the N-H···N angle.

Here we present the synthesis of one of the possible isomers of monooxahemiporphycene. The 21-oxahemiporphycene **1** was obtained *via* McMurry olefination of an appropriate α,ω-dialdehyde, followed by oxidation. The aromatic macrocyclic product was isolated in the form of its zinc complex **5**.

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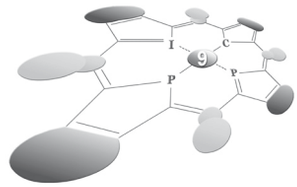

Functionalized cobalt triarylcorrole covalently bonded with graphene oxide: highly efficient electrocatalyst for oxygen reduction reaction in alkaline media

Jijun Tang[a,b], Zhongping Ou[a]*, Rui Guo[a], Yuanyuan Fang[a], Dong Huang[b], Jing Zhang[b], Jiaoxia Zhang[b], Song Guo[c]*, Fredrick M. McFarland[c], Yang Song[d], Karl M. Kadish[d]*

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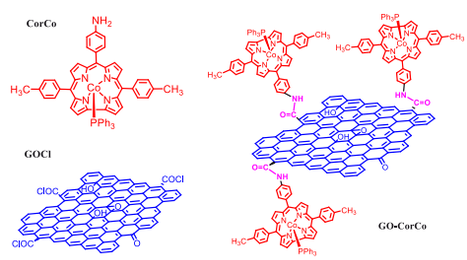
[b]*Schoole of Materials, Jiangsu Science and Technology University, Zhenjiang 212013, China*
[c]*Department of Chemistry and Biochemistry, The University of Southern Mississippi, Hattiesburg, MS 39406,USA*
[d]*Department of Chemistry, University of Houston, Houston, Texas 77203-5003, USA*

Study and examination of novel catalysts for the oxygen reduction reactions (ORR) is one of the hot topics in the field of fuel cell [1] and the metallocorroles have received more and more attention because they can catalyze a variety of reactions including the ORR [2]. In the present work, a functionalized cobalt triphenylcorrole (CorCo) covalently bonded with graphene oxide (GO) was synthesized in the first time and characterized by UV/Vis, fluorescence, FT-IR, micro-Raman, HRTEM, TGA, XRD, XPS and AFM. Electrocatalytic activities of the GO, CorCo, a mixture of GO and CorCo as well as the covalently bonded GO-CoCor (see structures in Chart 1) towards the reduction of dioxygen were examined in both homogeneous and heterogeneous systems by cyclic voltammetry and linear sweep voltammetry using a rotating electrode (RDE) in air-saturated 0.1 M KOH and 0.5 M H_2SO_4 solutions. The results indicate that the GO-CoCor is a highly efficient electrocatalyst for the 4-electron reduction of dioxygen in alkaline media. Support from Natural Science Foundation of China (21501070) and Foundation of Jiangsu University (15JDG131, 05JDG051).

Chart 1. Structures of examined catalysts



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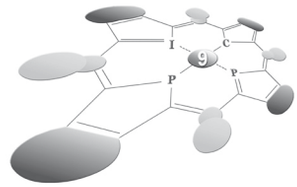
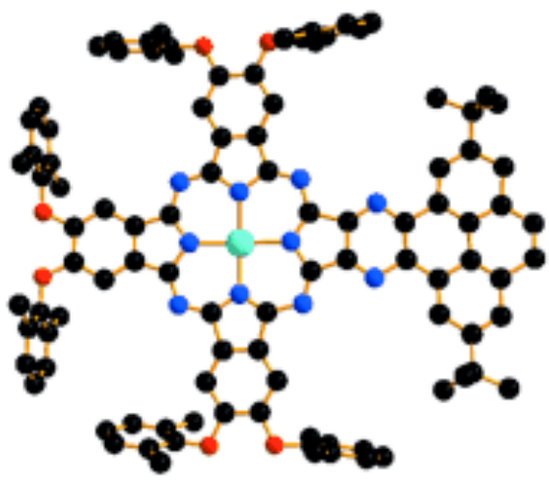


Unsymmetrical Pyrene-Fused Phthalocyanine Derivatives: Synthesis, Structure, and Properties

Houhe Pan, [a] **Chao Chen,** [a] **Kang Wang,** [a] **Wenjun Li,** [a] **and Jianzhuang Jiang**[a]

[a]*Beijing Key Laboratory for Science and Application of Functional Molecular and Crystalline Materials Department of Chemistry, University of Science and Technology Beijing*

Novel pyrene-fused unsymmetrical phthalocyanine derivatives 2,3,9,10,16,17-hexakis(2,6-dimethylphenoxy)-22,25-diaza(2,7-di-tert-butylpyrene)[4,5]phthalocyaninato zinc complex Zn[Pc(Pz-pyrene)(OC8H9)6] (1) and 2,3,9,10-tra(2,6-dimethylphenoxy)-15,18,22,25-traza(2,7-ditert-butylpyrene)[4,5]phthalocyaninato zinc compound Zn[Pc(Pz-pyrene)2(OC8H9)4] (2) were isolated for the first time. These unsymmetrical pyrene-fused phthalocyanine derivatives have been characterized by a wide range of spectroscopic and electrochemical methods. In particular, the pyrene-fused phthalocyanine structure was unambiguously revealed on the basis of single crystal X-ray diffraction analysis of 1, representing the first structurally characterized phthalocyanine derivative fused with an aromatic moiety larger than benzene.



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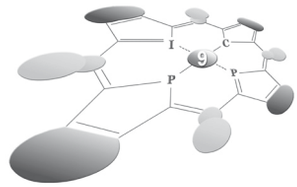
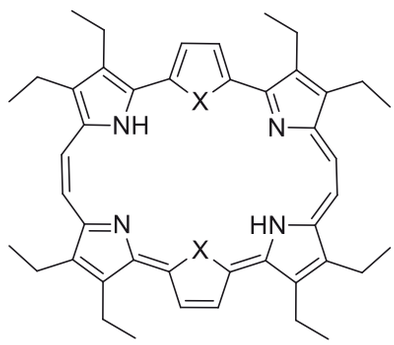


First solid state structural characterization in novel bronzaphyrins: Synthesis and photophysical properties

M. V. Nanda Kishore and Pradeepta K. Panda

School of Chemistry, University of Hyderabad, Hyderabad – 500 046

Bronzaphyrin is a 26-π aromatic hexaphyrin, first reported by Johnson et al.[1] The name bronzaphyrin is derived due to their characteristic bronze color in chloroform solution. So far only very few bronzaphyrins reported with macrocycle possessing SS, SN and SO as the two central heterocycles (S: thiophene; N: pyrrole; O: furan).[2,3] Owing to the synthetic difficulty associated with their synthesis and the reported lack of stability of other derivatives viz. NN and OO, probably led to dwindling interest in this macrocycle, with no report pertaining to their solid state structure.[1,2] Herein, we wish to report synthesis and photophysical properties of three different bronzaphyrins (NN, SS and OO).We could able to synthesize the first stable all-azabronzaphyrin and dioxabronzaphyrin. In addition, we could ascertain solid state structure of bronzaphyrins (NN and SS) for the first time. Both macrocycles display interesting structural diversities along with strong absorption in the near infrared region.



X: NBn, S, O

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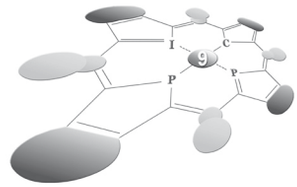

Meso-expanded calix[4]pyrroles: Hosts for simultaneous cooperative binding of anion and neutral molecule guest pair

B. Sathish Kumar, Pradeepta K. Panda*

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Anion recognition is of great significance in the field of supramolecular chemistry, owing to their biological relevance.[1] Designing a specific host for a specific anion is quite challenging because of the factors involved viz. basicity of anions, its size and shape, and also the solvent medium used. On the other hand, binding of small neutral receptors are even a more onerous task due to absence of any significant supramolecular interactions. Therefore, simultaneous binding of an anion and a neutral receptor by a supramolecular host is so far not been envisaged. Recently, we have designed and synthesized a new type of expanded calix[4]pyrrole derivative **1**, which stabilizes an infinite 1D water chain in solid state.[2] We found macrocycles **1-3** show preferential binding towards fluoride ion and interestingly, macrocycle **2** binds to water bridged difluoride moiety with two units of it forming a sandwich complex in the solid state. On the other hand, in presence of ethanol, the macrocycle exhibits, hitherto not seen simultaneous binding of fluoride ion and an ethanol molecule as an interacting guest pair.

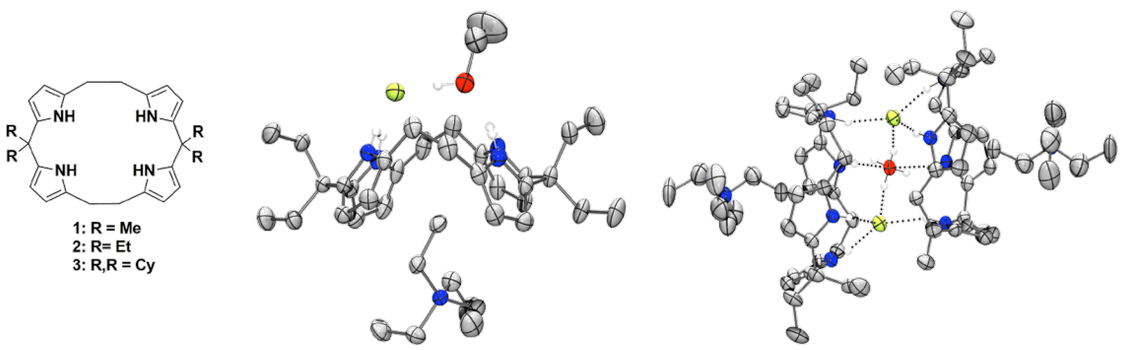

Figure 1: View of Host-Guest structures of macrocycle **2** in solid state *i.e.* **2.TEAF.EtOH & (2.TEAF)$_2$.H$_2$O**

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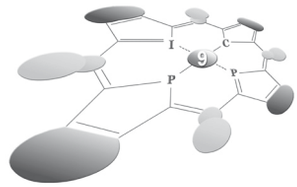

Oxidizing Chromene-annulated Chlorin

Nisansala Hewage,[a] Matthias Zeller,[b] and Christian Brückner*,[a]

[a] *Department of Chemistry, University of Connec*ticut
[b] *Department of Chemistry, Purdue University*
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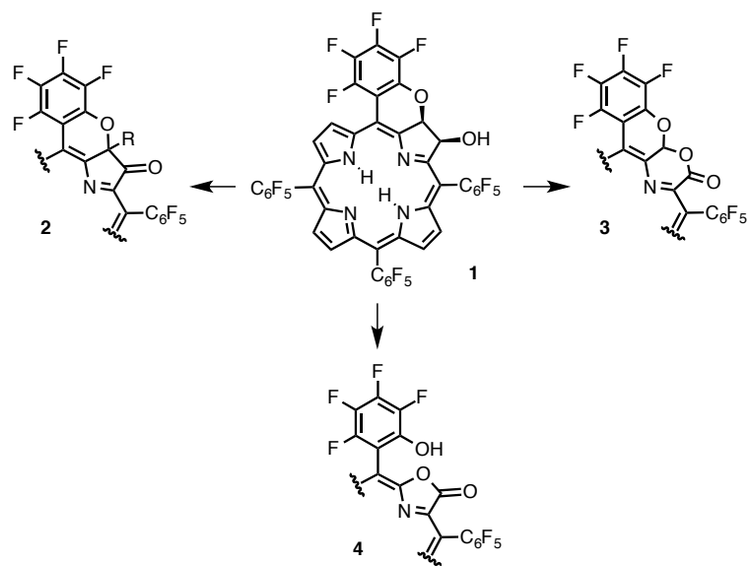
Mono-chromene-annulated *meso*-(pentafluorophenyl)chlorin **1** is accessible by an intramolecular nucleophilic aromatic substitution of the corresponding diolchlorin. Its synthesis and red-shifted optical properties when compared to the non-annulated chromophore of this, and related, chlorins were reported previously.[1] We investigated now the oxidative conversions of mono-chromene-annulated *meso*-(pentafluorophenyl)chlorin **1** under a range of different oxidation conditions (e.g., using CrO_3, $KMnO_4$, etc). A range of products (such as ketone **2**, five- and six-membered lactones **4** and **3**, respectively) with varying oxidation states of their β-positions were observed, all possessing optical properties reflective of their architectures. Many of the products were not accessible by oxidation of the non-annulated diolchlorin analogue.



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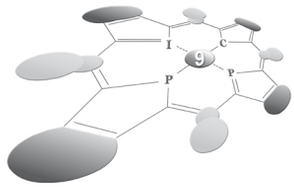

Porphyrinoid-based bio- and nanodevices for theranostic applications

Oriol Planas, Beatriz Rodríguez-Amigo, Ester Boix-Garriga, Rubén Ruiz-González, Montserrat Agut and Santi Nonell

Institut Químic de Sarrià, Universitat Ramon Llull, Via Augusta 390, Barcelona 08017, Spain

Theranostic nanomedicine is a new modality for cancer detection and treatment which combines the targeting and delivery properties of organic and/or inorganic nanoparticles with drugs able to exert both a diagnostic and a therapeutic effect. In this regard, the combination of nanotechnology with photosensitizers (PSs) offers a unique opportunity to develop novel phototheranostic probes that efficiently accumulate in malignant cells and can be detected through fluorescence imaging. Moreover, the intrinsic production of reactive oxygen species (ROS) by the PSs allows the eradication of the targeted cells.
In this study, bio- and nanodevices based on porphyrins and porphycenes have been prepared and assessed for their potential in anti-cancer and anti-microbial applications.

Acknowledgements
This work has been supported by grant CTQ2013-48767-C3-1-R from the Spanish Ministerio de Economía y Competitividad. Oriol Planas thanks the European Social Funds and the SUR del DEC de la Generalitat de Catalunya for his predoctoral fellowship (grant No 2016 FI_B200100).

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Triazole linked porphyrin-cyclo-[2]-malonate conjugates - a new building block for fullerene chemistry

Maximilian Popp, **Andreas Hirsch***

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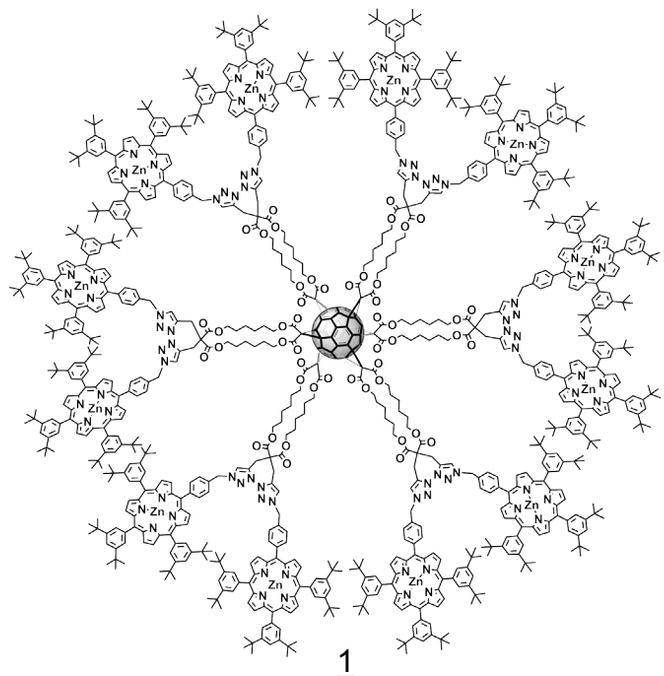
Porphyrins covalently bound to fullerenes are widely described in literature. Due to the high absorption rate of porphyrins and the excellent electron acceptor properties of fullerenes, these conjugates are often used to mimic the photosynthetic reaction centre and to transform light into chemical energy. [1] So far, the attachment is achieved in several ways, including ether and amid bonds as well as click-chemistry[2], but mostly on the open side chain of malonates, that are used for cyclopropanation in the Bingel-Hirsch reaction to exohedrally functionalize fullerenes.[3]

Here we report a novel molecular system, utilizing cyclo-[2]-hexylmalonate as rigid spacer, instead of open malonate chains. By copper mediated Huisgen 1,3-dipolar cycloaddition we were able to bind two azido-porphyrins to alkyne substituted cyclo-[2]-malonates, resulting in the fullerene hexakis adduct **1** bearing twelve porphyrins.



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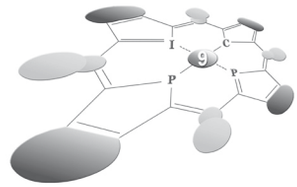

Inhibition of Heme Protein Function by Nitrosoarene/alkane Coordination

Samantha Powell, Bing Wang, Guan Ye, Daniel M. Copeland and George B. Richter-Addo

Price Family Foundation Institute of Structural Biology and Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019, USA

Mammals utilize dioxygen (O_2) for respiration. The blood protein hemoglobin (Hb) and the muscle protein myoglobin (Mb) are involved in O_2 binding, transport (Hb), and storage (Mb). Both Hb and Mb utilize heme sites for O_2 binding to the central iron atoms. Nitrosoalkanes and nitrosoarenes (RN=O; R = alkyl or aryl) are valence isoelectronic with O_2, and exhibit complementary binding to heme Fe. These RN=O compounds are generated either by oxidative metabolism of amines (RNH_2) or by reductive metabolism of organic nitro compounds (RNO_2). Once generated, these RN=O metabolites are known to bind to the Fe centers in heme proteins to inhibit their function. Thus, there is intense interest in determining how these RN=O compounds form and bind to the heme centers. We have prepared the nitrosobenzene adduct of Mb, and characterized it by X-ray crystallography to 1.75 Å resolution. The crystal structure shows that the PhNO sits in the distal pocket 2.2 Å from the iron core. In another crystal structure, a second PhNO/PhNHOH ligand is found to occupy the Xe1 binding site at the proximal site beneath the heme macrocycle. This strongly suggests an O_2-storage capability of this Xe1 site in the natural aerobic environment.

We have extended our investigations to the binding of a known amphetamine metabolite to both Hb and Mb. We were able to obtain suitable crystals of the nitrosoamphetamine adduct with the Mb H64A mutant, and were successful in obtaining its crystal structure to 1.73 Å resolution. In addition to the N-binding of the ligand, we show that the hydrophobic end of the ligand protrudes into the hydrophilic solvent region, an observation that was not readily predicted. We now show that the reaction of N-hydroxyamphetamine with wt swMb also results in the formation of the Mb-AmphtNO adduct. These results will be presented and discussed in the context of RNO_X biochemistry.

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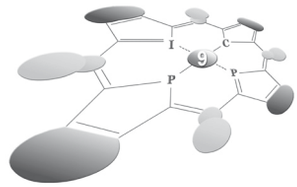

Synthesis and Exploitation of MetalloPorphyrins for Organic Photovoltaic Devices (OPV)

Rajesh Pudi, Werther Cambarau, Lydia Cabau, Cristina Rodríguez, Anton Vidal-Ferran, Pablo Ballester and Emilio Palomares

Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans, 16, 43007 Tarragona, Spain

It has become evident from the past two years that remarkable power conversion efficiency (PCE) values, obtaining from porphyrin based electron donor materials in OPV, emerge them as a strong competitor to the other organic small molecule and as well as to the polymeric based electron donating materials [**1-3**]. Most of the porphyrin derivatives that have been studied so far in OPV are metalated with Zn. This is mainly attributed to the generation of the efficient photoinduced singlet electron transfer processes of Zn-complexes to electron accepting material in the resulting solar device. The triplet excited state properties of metallo porphyrin derivatives, however, have not been exploited in organic photovoltaic devices yet. Taking into account this consideration, the objective of work is to synthesize the heavy metal based porphyrin systems and to study the effect of the heavy metal center in the porphyrin on the electron transfer processes and thereby the performance of resulting solar device.

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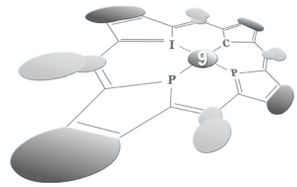

Synthesis and Properties of Xanthene Bridged Optically Actived Porphyrin Dimers

Mingfeng Qin[a], Xu Liang [a,*], Minzhi Li[a], and Weihua Zhu[a,*]

[a]*School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China*

Numerous examples of porphyrinic chromophores involved in chirality-transfer processes, in which the chirality is transferred from an enantiomerically pure ligand to a metal center, are known in the literature. However, the transfer of chiral information from a chiral amino acid unit to porphyrin dimers are less synthesized previously. On the other hand, porphyrin oligomers with macrocyclic rings that are covalently linked in a cofacial configuration have received considerable attention in recent years due to their unique electronic structures and novel optical properties. Several types of conjugated porphyrin oligomers have been reported such as, doubly- or triply-fused co-planar porphyrins, alkyne-bridged porphyrin strands, and *p*-phenylene-bridged twisted/planar porphyrin dimers. Interest of porphyrin dimers with linking moieties, especially those that adopt a face-to-face manner has been increasing in recent years. Porphyrin dimers with face-to-face conformations exhibit an increased ability to bind two metals ions in a suitable geometry, opening up the possibility of mimicking the activity of heme and nonheme iron and copper-binding bioproteins such as oxidase, oxygenase, and oxygen transport proteins, which have binuclear active sites. In this poster presentation, a series of free base porphyrin chiral dimer bridged by a flexible amide-bonded xanthene moiety and its binuclear zinc(II) complex were synthesized and characterized. Electronic structure of these two compounds were in-depth characterized by spectroscopy, electrochemistry and theoretical calculations. This work is financial support was provided by the NSFC of China (No. 21171076)

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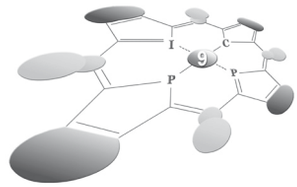

Vibrational spectroscopy to study the heme-redox sensory kinase MA4561

Christine Joy U. Querebillo[a], Hoang Khoa Ly[a], Kerstin Fiege[b], Nicole Frankenberg-Dinkel[b], Inez M. Weidinger[a], Peter Hildebrandt[a]

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[b]*Technische Universität Kaiserslautern, Department of Biology, Erwin-Schrödinger-Str. 56, 67663 Kaiserslautern*

Most heme-based sensors contain non-covalently bound b-type heme proteins. The multi-domain sensory kinase MA4561 from *Methanosarcina acetivorans* was the first reported cytoplasmic protein to incorporate a covalently attached heme co-factor. This protein was found to be crucial in regulating dimethyl sulfide (DMS)-dependent methyltransferase and is believed to have a redox/DMS signalling function. Signal output is activated by phosphoryl transfers and autophosphorylation, which is dependent on the heme-redox state[1]. Thus, by probing the structural changes with its redox state, we may be able to further understand the underlying mechanism in its signalling functions.

Here, we performed resonance Raman spectroscopy and the electronic configurations in both the chemically reduced and oxidized states of the protein. Spectroelectrochemical studies were also carried out with protein samples immobilized on roughened silver or gold electrodes using potential-dependent surface enhanced resonance Raman spectroscopy (SERRS) and surface enhanced infrared absorption (SEIRA) spectroscopy combined with electrochemistry. These studies provide insight into the coupling between redox transitions and ligation and spin state changes and thus may contribute to an improved understanding of the molecular function of this redox sensor.

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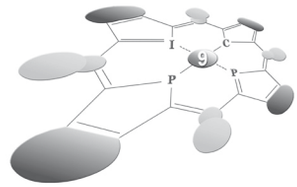


Porphyrin-derivatives linked to Ir(III)-Complexes as potential Materials for OLEDs

David Reger, Ann-Kristin Steiner, Dominik Lungerich, Norbert Jux*

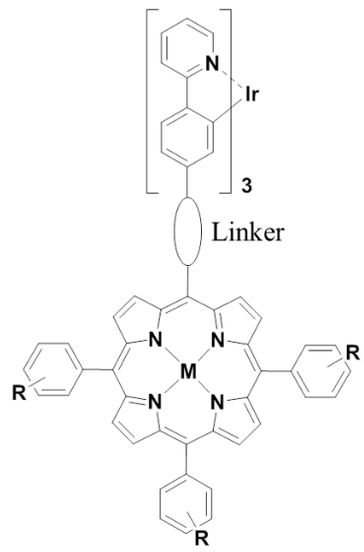
Department of Chemistry and Pharmacy & Interdisciplinary Center for Molecular Materials (ICMM), Friedrich-Alexander-University Erlangen-Nürnberg, Organic Chemistry II, Henkestraße 42, 91054 Erlangen, Germany (david.reger@fau.de)

Organic Light Emitting Diodes (OLEDs) have attracted huge attention in the last decades as very interesting materials for digital displays. Hereby OLEDs offer several advantages over todays commonly used displays. Hence extensive research was carried out and the technology was even commercialised.[1],[2]

Ir(III)-complexes are among the most common and promising materials for luminescent devices as strong spin-orbit-coupling in heavy metals leads to enhanced intersystem crossing and therefore allows harvesting of both, singlet and triplet excited state. Numerous materials based on those complexes were already synthesised and successfully tested in devices. Furthermore porphyrin-derivatives, especially ones with Pt(II) metal-centre, have already been used as active materials in OLEDs.[1],[2],[3],[4]

Therefore we want to investigate both active molecular systems covalently linked to each other (see figure). The combination and interaction of those might reveal interesting properties and give access to new luminescent materials. The fine tuning of the materials should be possible not only by different substituents on the phenylpyridine or porphyrin, but also by different metals complexed by the porphyrin.

Furthermore metal-metal interactions between the porphyrin metal-centre and the Ir(III) could be studied on our systems.



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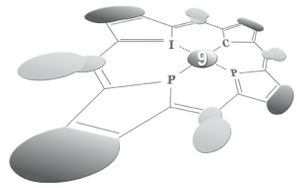

Effects of the Flexibility of Alkylthio Substituents on the Photophysical Properties of Porphyrazines

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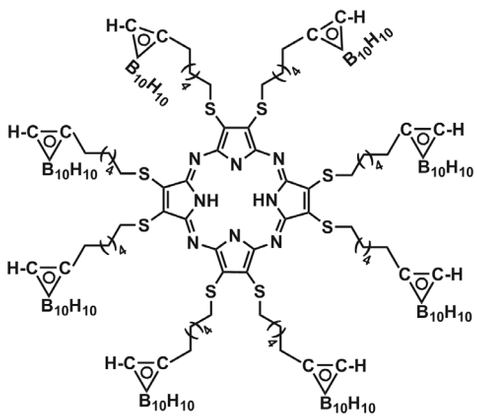
Alkylthioporphyrazines (ATPzs) are a widely investigated class of tetrapyrroles because of their potential applications in high-tech fields and biomedicine. Dissimilar from alkylthioporphyrins and arylsubstituted porphyrazines, which show luminescence and $^1O_2$ photosensitizing properties, ATPzs are only weakly fluorescent, if any.[1] Upon photoexcitation into the intense near-IR Q-band ATPzs undergo fast radiationless decay, that makes them promising candidates in photothermal therapy (PTT) of cancer. The photophysical behavior of ATPzs has been investigated using 2,3,7,8,12,13,17,18-octakis-(1,2-dicarba *closo*-dodeca-boran-2-*yl*)hexylthio-5,10,15,20-(21*H*, 23*H*) porphyrazine, H_2HEHCSPz, as a case study.[2]



H_2HEHCSPz

This molecule, which has been synthesized by innovative, "soft" methods, has the advantage to conjugate the biologically relevant characteristic of being free from transition metals with high potential in both, PTT and boron neutron capture therapy (BNCT) of cancer. To ascertain whether the encumbering carboranyl cages can influence the flexibility of the alkylthio groups, the carboranyl-free ethylthioporphyrazine, H_2OESPz, has also been studied. The photophysical behavior of H_2HEHCSPz and H_2OESPz has been investigated by ultrafast transient absorption spectroscopy in solution and interpreted with the help of dynamic ^{1}H NMR experiments and density functional theory (DFT) and time-dependent DFT (TDDFT) calculations.

It is found that, following photoexcitation, ATPzs deactivate by the pathway $S_1(\pi,\pi^*) \rightarrow S_n(C_\beta\text{-}2p_z/S_{l.p.},\pi^*) \rightarrow$ ground state. The presence of quenching singlet excited states with $C_\beta\text{-}2p_z/S_{l.p.},\pi^*$ character immediately below the primarily photogenerated $S_1(\pi,\pi^*)$ state is a consequence of the electronic structure changes induced by the inherent flexibility of the alkylthio chains.

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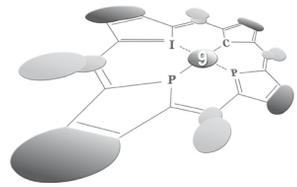

Charge Effects on the Reactivity of Polycationic Compound I and Compound II Mimics: a DFT Analysis

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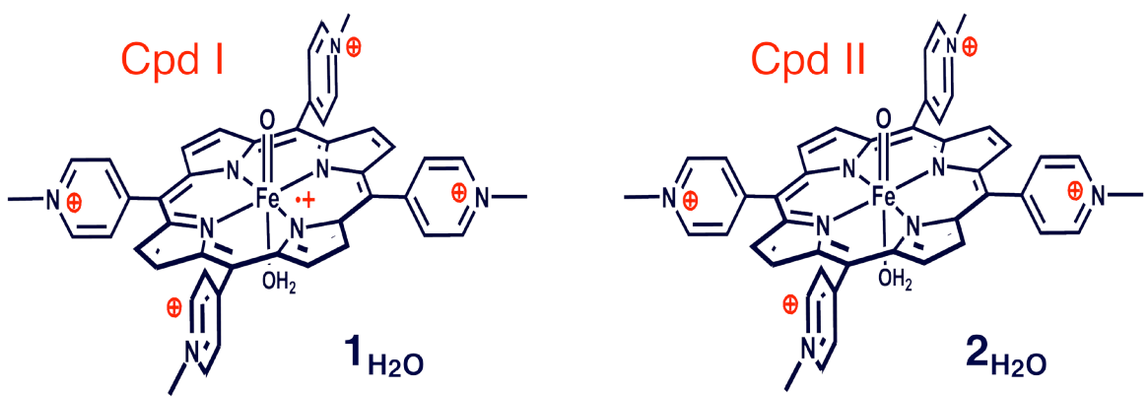
The charge effects on the reactivity of the polycationic Compound I (Cpd I) and Compound II (Cpd II) mimics experimentally investigated by Bell and Groves[1] are analyzed by DFT calculations.[2] Specifically, we consider the Cpd I model $[(4\text{-THPyP})^{+\bullet}(H_2O)\text{-}Fe^{IV}{=}O]^{5+}$ (THPyP = 5,10,15,20-tetrakis(N-hydro-4-pyridinium) porphyrinate), $\mathbf{1}_{H_2O}$ and its Cpd II counterparts $[(4\text{-THPyP})Fe^{IV}{=}O]^{4+}$, **2**, and $[(4\text{-THPyP})(H_2O)Fe^{IV}{=}O]^{4+}$, $\mathbf{2}_{H_2O}$.
In gas phase simulations it is found that all positive charges enhance the reactivity. According to a detailed electronic structure analysis in the gas phase of the reactant complexes *en route* to the transition state, the positive charges stabilize the electron acceptor orbital (EAO) of the catalyst more than the electron donor orbital (EDO) of the substrate, thereby reducing the energy gap between these orbitals and, hence, the H-abstraction barrier.
The effect of the peripheral charges residing on the pyridinium groups is dampened in water solution by screening effects of the solvent. However, the effect of the positive charge residing on the porphyrin ring of the Cpd I mimic is not much diminished by the solvent.
The well known stronger oxidizing capability of Cpd I mimics relative to their Cpd II counterparts is ascribed to the effect on the frontier orbitals of the positive charge on the ring, rather than to the presence of a hole *per se*.



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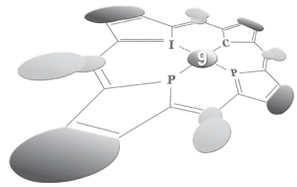

Improved Synthesis and Optical Properties of Functionalized Arylated Tetrabenzoporphyrins

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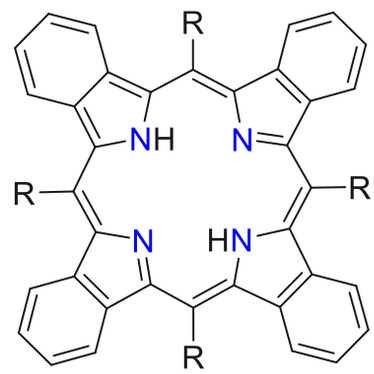
Tetrabenzoporphyrins (TBPs) have considerably red-shifted absorption bands compared to porphyrins. These unique optical properties and their aromatic nature give rise to possible applications as near-infrared organic light emitting diodes[1] and for optical upconversion[2]. Nevertheless, the synthesis of TBPs is accompanied by challenging synthetic requirements and moderate yields. Herein we present an easy and universal protocol for the synthesis of various functionalized arylated tetra-benzoporphyrins using modified Lindsey conditions.



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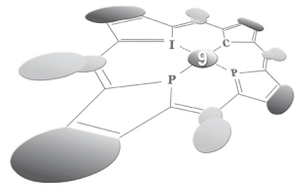

Supramolecular Assembly between a Monomeric Quadruply Ring-Fused Porphyrin and Fullerenes

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Recently, we have reported the synthesis of the Zn(II) complex of a quadruply fused porphyrin (ZnQFP), which bears four fused five-membered rings at the periphery.[1] The structure of ZnQFP changes from the most stable planar form to a concave one by the axial coordination of pyridine at the Zn(II) center. Herein, we utilized the π-conjugated concave surface of a pyridine-coordinated ZnQFP derivative to recognize the convex surfaces of fullerenes.[2]

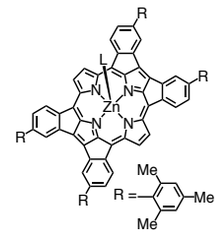

Figure 1. Molecular structures of ZnOFP derivatives.

In this study, we used a ZnQFP derivative (**1**) having mesityl groups at the fused benzene rings to improve the solubility (Figure 1). As a result of the surface-shape matching, the 2:1 supramolecular complexes with ZnQFP and fullerenes were formed even in the solution. UV/Vis titration experiments of **1**-py with C_{70} in 1,2-dichrolobenzene at 298 K gave the association constant (K) for the 2:1 complex to be $(2.9 \pm 0.2) \times 10^7$ M^{-2}. This association constant is quite larger than those reported for planar monomeric porphyrins. For further confirmation of formation of the supramolecular complexes in solution, ^{1}H NMR titration experiments were also performed in 1,2-dichrolobenzene-d_4. Addition of C_{70} to the solution of **1**-py induced upfield shift of the ^{1}H NMR signal for the β-protons of **1**-py and downfield shift of that for the o-CH_3 groups of the mesityl groups.

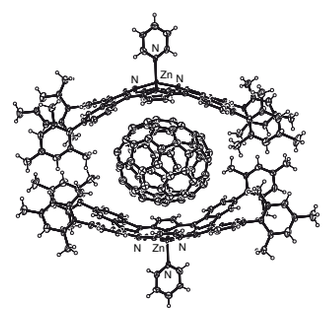

Figure 2. Crystal structure of the associated complex between **1**-py and C_{70}.

The structures of supramolecular assemblies of **1**-py with fullerenes have been revealed by single-crystal X-ray diffraction analysis (Figure 2). The concave surface of **1**-py and the convex surface of fullerenes are well matched with each other to form a 2:1 assembly on the basis of strong π-π interactions.

The association between **1**-py and fullerenes affect the redox potentials of **1**-py and fullerenes. The redox potentials of **1**-py in 1,2-dichrolobenzene were positively shifted in the association complex with C_{70}, whereas those of C_{70} exhibited negative shifts. The tendencies of the potential shifts can be accounted for by the charge–transfer interaction from **1**-py to the C_{70}.

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Symmetrical and Unsymmetrical Porphyrin-Perylenebisimide Donor-Acceptor Molecular Dyads

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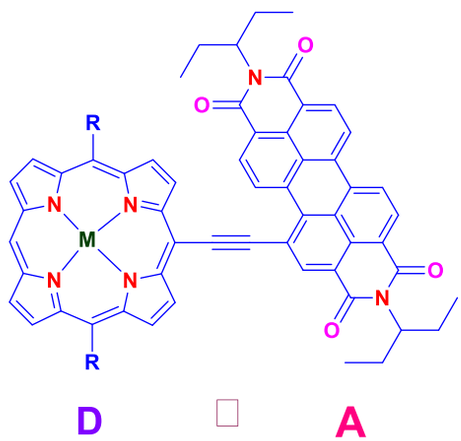
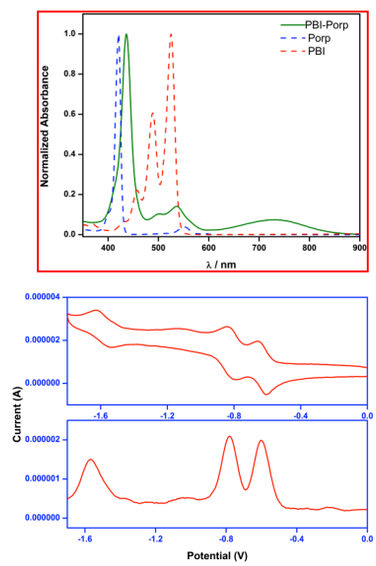
Many recent efforts have been targeted towards the development of new and efficient organic sensitizers that are suitable for practical use. Among the various pigments members of the porphyrin family are attractive candidates for light harvesting due to their high molar absorption coefficients and excited state energy transfer characteristics. Though porphyrins absorbs blue light strongly they have very limited absorption in the rest of the visible region and are less stable than other analogues. Efficient light harvesting from these macrocycles is realized by introducing various accessory pigments. Perylenebisimides can be ideal accessory system for porphyrins as they absorbs strongly in the visible region where porphyrin absorption is limited and are exceptionally stable. They have long excited state life times and can be modulated synthetically for various applications.In this current talk, recent results on these molecular systems and a few selected larger assemblies will be highlighted.





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Boronic Ester Appended Porphyrins as Anion Sensors

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Boronic esters appended porphyrins are of considerable interest owing to their ability to form covalently linked di/tri/tetra or octameric porphyrins, covalent organic framework (COF) and potential precursors for DSSCs and PDT.[1] The Lewis acidity boron atom has been utilised for the detection of anions[2a] and the boronic acid tighthly binds to substances containing 1,2-diols. Thus, porphyrin-boron cojugates can be employed to detect fluoride and cyanide ions,[2b,c] carbohydrates and biologically important neurotransmitters, such as L-DOPA (L-dihydroxyphenylalanine), dopamine and related species.[2] Herein, we present the synthesis, structural, photophysical and redox properties of 5,10,15,20-*tetrakis*(4'-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)porphyrin (**2**) and its Zn(II) complex (**2a**) and their utilization for the detection of basic anions.[3] The deprotection and protection statergy of borylated porphyrin (**2**) is shown in Figure 1a. The colorimetric responses and their corresponding UV-Vis spectral changes of **2a** are shown in Figure 1b.

(a) (b)

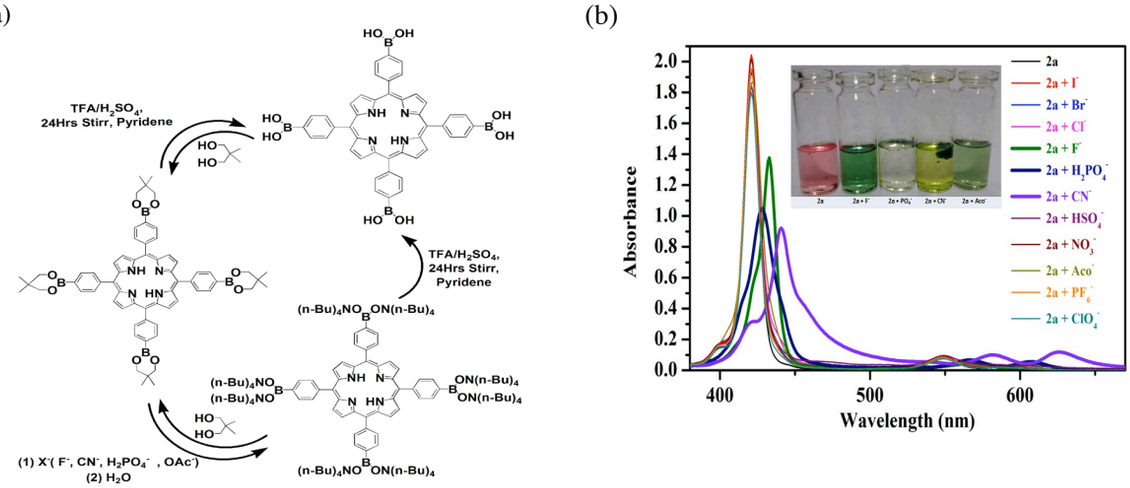

Figure 1. (a) Deprotection-protection statergy of borylated porphyrins; (b) the colorimetric responses and the correspoding UV-Vis spectral changes of **2a** with anions ($F^{\square}$, $CN^{\square}$, $OAc^{\square}$ and $H_2PO_4^{\square}$).

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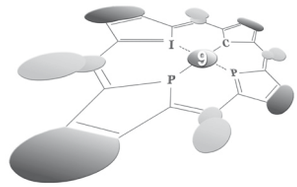

β-Octachlorovanadylporphyrin as Highly Efficient and Selective Epoxidation Catalyst for Olefins

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Selective oxidation of olefins to epoxy compounds has always been an interesting area of research for chemists owing to their great importance in the production of highly valued commodity chemicals such as polyurethanes, unsaturated resins, glycols, surfactants, and other products.[1] Metalloporphyrins have been found to be efficient catalysts for alkene epoxidation using various oxygen atom donors due to their high chemical and thermal stability, interesting physicochemical properties and flexible architectural modification to tailor redox properties and conformational features.[2,3] Iron and manganese porphyrin complexes were widely utilized as effective homogenous catalysts for such oxygenation reactions in last few decades. The major drawbacks of homogenous MTPP-based catalysts are (i) the macrocyclic ring is liable for oxidative self-destruction; (ii) aggregation of metalloporphyrins through π-π interactions; (iii) lower turnover frequency (TOF) and; (iv) poor product selectivity. So, there is a quest for highly efficient metalloporphyrin catalyst for the selective oxidation of olefins.

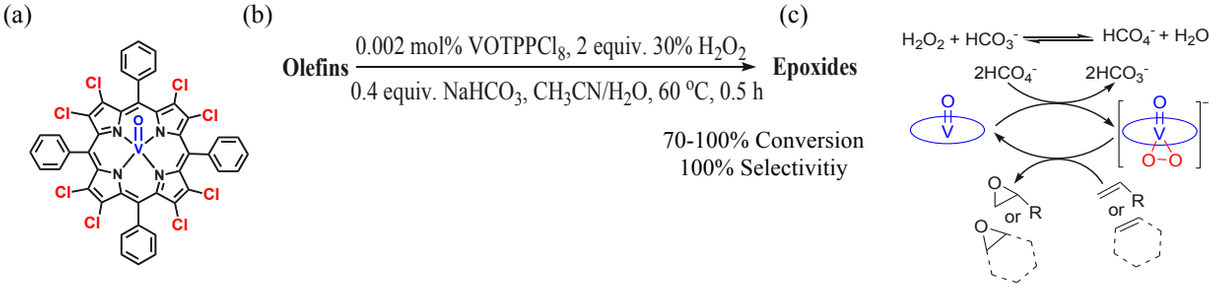

Figure 1. (a) Molecular structure of $VOTPPCl_8$; (b) reaction conditions for the catalytic conversion; (c) plausible catalytic mechanism for the conversion of olefins to epoxides using $VOTPPCl_8$ catalyst.

In this presentation, we will discuss about the selective epoxidation of olefins using biological important oxidant H_2O_2 catalyzed by robust $VOTPPCl_8$ using $NaHCO_3$ as promoter with high selectivity and very high TOF numbers (8200-9560 h^{-1}).

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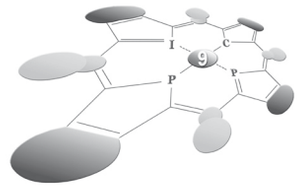

Synthesis and Spectroscopic Studies of Biomimetic Light-Harvesting Porphyrin-Peptoid Conjugates

Jiwon Seo, Boyeong Kang, Woojin Yang

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Much effort has been made to construct a defined arrangement of porphyrins, particularly, in a face-to-face arrangement of two porphyrin π planes. Herein, we present an efficient strategy for (1) face-to-face arrangement of porphyrins, and (2) energy donor-acceptor dyad synthesis using Zn-porphyrin and free base porphyrin on peptoid (or oligo-N-substituted glycine) helices. Distance and orientation of porphyrins are precisely defined, which results in distinct optical properties and energy transfer efficiency of the porphyrin-peptoid conjugate.
A set of porphyrin-peptoid conjugates displaying porphyrins in various spatial arrangements was synthesized and characterized by UV-Vis, circular dichroism and fluorescence emission spectroscopy, which provided strong evidences for intermolecular and intramolecular interactions between porphyrins. In addition, donor-acceptor molecular dyads were constructed using zinc porphyrin and free base porphyrin, and energy transfer efficiency was evaluated depending on the relative orientation and distance of donor and acceptor. The porphyrin-peptoid conjugates will be useful for understanding the optoelectronic behavior of porphyrins and potentially for the development of novel photosensitizers and light-harvesting systems.

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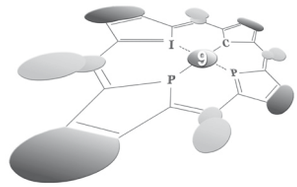

β-Alkyloxazolochlorins: Ozonation of Octaalkylporphyrins

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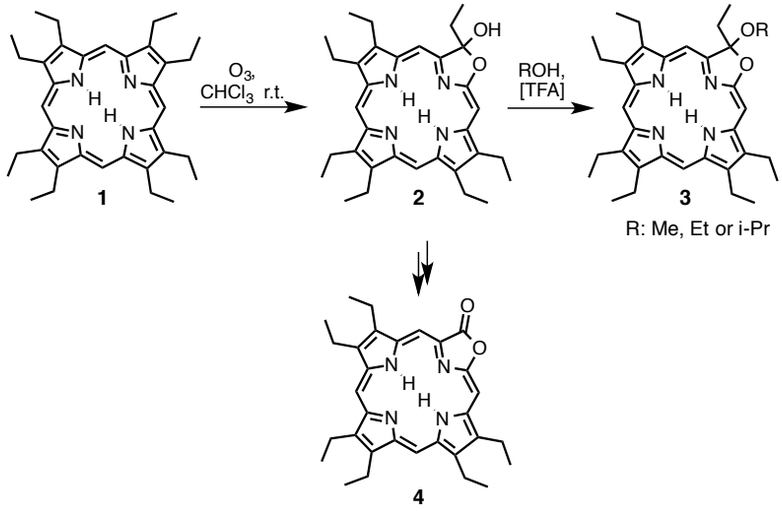
In 1933, Fischer and Deželić reported that porphyrins with saturated β-substituents (such as etioporphyrin) converted into chlorin-like chromophores, with an intensified λ_{max} band at ~650 nm, upon passing dilute ozone streams (~1%) over short time spans into a solution of the porphyrins.[1] However, they could not decipher their structures. In 1977, Shul'ga *et al*. determined these chlorin-like compounds to be oxozolochlorins, such as **2** (as the product from octaethylporphyrin (OEP)). Intrigued by these reports, and our long-standing interest in oxazolochlorins,[3] we reinvestigated the ozonation of β-alkyporphyrins. Heptaethyloxazolochlorin **2** is indeed formed by ozonation of OEP, but it is exceedingly sensitive to acid, light, and heat. Like in the *meso*-aryloxoazolochlorins, we were able to increase the stability of the hemiacetal **2** by conversion to acetals **3**. Like other oxazolochlorins,[3] they are characterized by hyperchromic electronic spectra, when compared to the spectra of the parent octaethylchlorin. We also report on the dehydroxylation of **2** and its conversion to hexaethylporpholactone **4**, the first example of a β-alkylporpholactone. We further describe the oxazolochlorin-type ozonation products of etioporphyrin I, thus confirming the connectivity of the products Fischer and Deželić observed 83 years ago.



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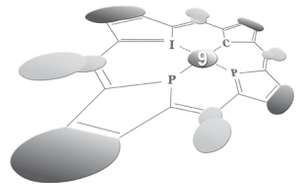
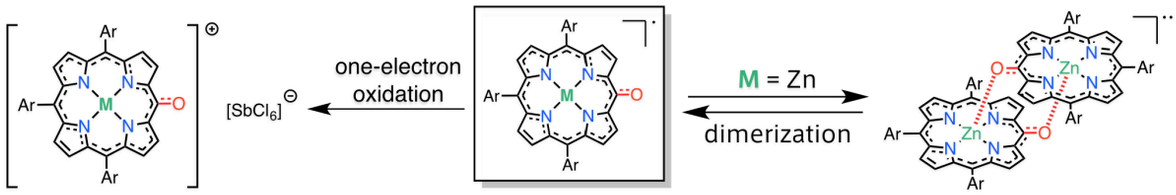


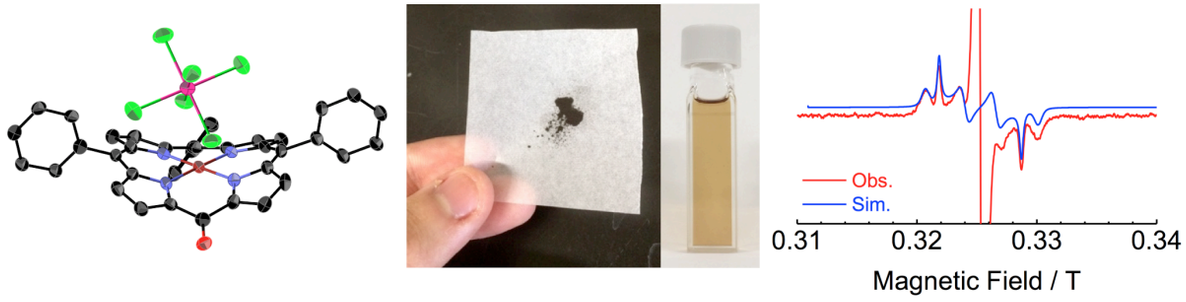
Triarylporphyrin *meso*-Oxy Radicals: Remarkable Stabilities, Properties, and Oxidation to Oxophlorin π-Cations

Daiki Shimizu, **Atsuhiro Osuka**

Department of Chemistry, Graduate School of Science, Kyoto University

5-Hydroxy-10,15,20-triarylporphyrin (oxophlorin) and their Ni(II) and Zn(II) complexes were oxidized with PbO_2 to give the corresponding porphyrin *meso*-oxy radicals as remarkably stable species. These radicals were fully characterized with X-ray diffraction analysis, UV/vis/NIR absorption and ESR spectroscopies, magnetic susceptibility measurement, electrochemical studies, and theoretical calculations. Free-base radical and its Ni(II) complex have been shown to exist as a monoradical in solution, while the Zn(II) complex exists in an equilibrium between monomer (doublet monoradical) and dimer (a non-Kekulé singlet biradicaloid) with a dimerization constant of $K_D = 3.0\times10^5$ M^{-1} in non-coordinating CH_2Cl_2 at room temperature but becomes a pyridine-coordinated monoradical upon addition of pyridine. Variable temperature magnetic susceptibility measurements of these radicals revealed different magnetic interactions in the solid-states, which has been interpreted in terms of their different packing structures in a microscopic sense. These radicals undergo one-electron oxidation and reduction in a reversible manner within narrow potential windows of 0.57 ~ 0.82 V. Finally, one-electron oxidation of Ni(II) and Zn(II) porphyrin *meso*-oxy radicals with tris(4-bromophenyl)aminium hexachloroantimonate furnished oxophlorin π-cations, which displayed non-aromatic closed-shell character, NIR absorption, and significant double bond character of the C–O bond.





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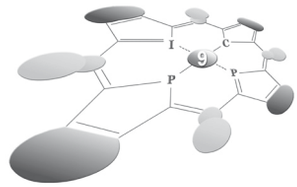

Electrode modification using nanocomposites of boron or nitrogen doped graphene oxide and cobalt (II) tetra aminophenoxyphthalocyanine nanoparticles

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Department of Chemistry, P.O. Box 94, Rhodes University, Grahamstown, South Africa (email: t.nyokong@ru.ac.za)

Research into carbon based materials is increasing due to their potential applications in areas including as sensors, and in electrocatalysis.**[1]**. Reduced graphene oxide nanosheets (rGONS), reduced boron doped graphene oxide nanosheets (rBDGONS) and reduced nitrogen doped graphene oxide nanosheets (rNDGONS) and their composites with cobalt (II) tetra aminophenoxyphthalocyanine nanoparticles (CoTAPhPc**NP)** were employed towards the detection of hydrogen peroxide. The nanomaterials were characterized by absorption spectroscopy, transmission electron microscopy, scanning electron microscopy, Raman spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy linear sweep voltammetry and cyclic voltammetry. rNDGONS showed excellent electrooxidation and electroreduction of hydrogen peroxide supported by superior surface coverage values. The inclusion of nanosized Pc significantly lowered the reduction overpotential. CoTAPhPcNP-rNDGONS-GCE gave a sensitivity of 39.302 mA/M, catalytic rate constant of 1 x 10^3 $M^{-1}s^{-1}$ and a detection limit of 8.24 nM. An adsorption equilibrium constant and Gibbs free energy of 1.26 x 10^3 M^{-1} and -17.69 $kJmol^{-1}$ respectively was observed.

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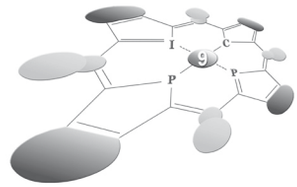

Chiral crystals of 5,10,15-tris(pentafluorophenyl)corrole

Justyna Sniechowska,[a] Piotr Paluch,[a] Grzegorz Bujacz,[b] Marcin Gorecki,[c] Jadwiga Frelek,[c] Daniel T. Gryko,[c] and Marek J. Potrzebowski[a]*

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Corroles, one carbon shorter analogues of porphyrins emerged a few years ago as an independent area of research. Their synthesis, chemical transformations, coordination chemistry, photophysics, non-linear properties and electrochemistry have recently been studied in great detail[1,2]. Number of experimental techniques have been used to characterize corroles both in the liquid[3] and solid state[4]. The unique solid state NMR technique Very Fast MAS with a sample spinning rate over 40 kHz was employed for screening and selection of corrole crystals suitable for X-ray diffraction studies. The host-guest approach and formation of inclusion complexes were efficient methods for the synthesis of chiral crystals from free base corroles possessing an extremely low racemization barrier. Our data show that the intrinsic features of corroles, including the dihedral angle saddling effect and distortion of the macrocyclic rings out of planarity have no influence on the tendency for "mirror-symmetry breaking".

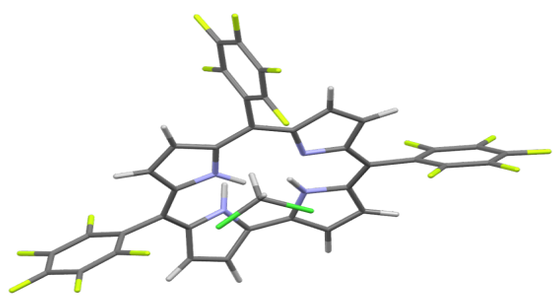

Figure 1. X-ray structure of 5,10,15-tris(pentafluorophenyl)corrole

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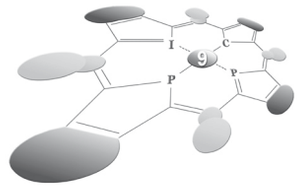

Liposome Bearing Zinc Phthalocyanine and Gadolinium Ions for Magnetic Resonance Imaging and Phodynamic Therapy

Lukasz Sobotta[a], Paulina Skupin-Mrugalska[a], Beata Wereszczynska[b,c], Alicja Warowicka[b], Tomasz Zalewski[b], Marcin Jarek[b], Jadwiga Mielcarek[a], Jacek Gapinski[b,d], Stefan Jurga[b,c]

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Liposomes are very attractive vehicles for drug delivery. It can encapsulate molecules of different character, e.i. lipophilic or lipophobic. Liposomes easily can be modified by introducing various phospholipids and other modifiers. Liposomes are ideal lipid vehicles for developing multifunctional nanoplatforms, combining diagnostic and therapeutic modalities. Above features enabled us to obtain gadolinium incorporated liposomes for simultaneous delivery of a contrast agent and drug molecule. The main objective of this study was to develop a new liposomal vehicles (GdLip) for photodynamic therapy, and to study its properties. GdLips were prepared according to a standard thin layer method. Singlet oxygen quantum yield was evaluated for zinc phthalocyanine incorporated into GdLip. We showd that singlet oxygen generation was not affected by the presence of gadolinium ions. The relaxivity parameters r1 and r2 were determined for different proton frequencies. Results suggest that GdLip possess promising properties as potential contrast agents influencing T1 and T2 relaxation times. T2 weighted MRI images revealed high contrast between GdLip and a blank sample. In vitro cellular studies were performed to assess GdLip toxicity in dark and with light irradiation. The results showed no toxicity against cancer cells (HeLa) and human fibroblasts in the dark. Whereas cell viability was decreased by over 90% following light exposition of cells.

Acknowledgements
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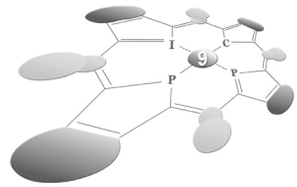

Analysis of the *In vitro* and *In vivo* effects of Photodynamic Therapy on Prostate Cancer by using protoporphyrin IX-polyamine derivatives

Chloë Fidanzi-Dugas,[a] Bertrand Liagre,[a] Guillaume Chemin,[a] Aurélie Perraud,[b] Claire Carrion,[c] Robert Granet,[a] Vincent Sol,[a] David Yannick Léger[a]

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Aims and Scope: Photodynamic therapy (PDT), using porphyrins as photosensitizers (PS), has been approved for the treatment of several solid tumors. We developed a new vectorization strategy based upon the chemical derivatization of Protoporphyrin IX (PpIX) with the two polyamines (PA), spermidine (PpIX-dSd) and spermine (PpIX-dSm). PA, as well as their porphyrin derivatives (PpIX-PA), are actively transported and accumulated into cancer cells by the Polyamine Transport System (PTS). Phototoxicities of PpIX-PA have been assessed after red light irradiation of two Chinese hamster ovarian cell lines, CHO and CHO-MG (which differ from each other by their PTS activity), along with the human healthy prostate cell line RWPE-1 and three human prostate cancer cell lines, PC-3, DU 145 and LNCaP.

Results: PA derivatization increased PS efficiency. Photoactivation of PpIX-PA triggered the intrinsic apoptotic pathway and also activated the COX-2/PGE_2 pathway, known as an inducer of apoptosis resistance (through the p38/MAPK protein which is pro-apoptotic but also a positive regulator of COX-2). However, inhibition of COX-2 did not increase PDT efficiency and inhibition of p38/MAPK resulted in increased PDT-induced apoptosis. These PS also induced a reduction in expression of NF-κB, a pro-survival factor. I*n vivo* phototoxicities of PpIX-dSd and PpIX-dSm have been tested on PC-3 subcutaneous xenografts performed in nude mice. Tumor irradiation by red light of PpIX-dSd treated mice resulted in growth slowing and histological studies showed a drop in both the proliferative marker Ki67, and the anti-apoptotic protein Bcl-2 levels. Nevertheless, *in vitro* PpIX-dSm efficiency failed to be confirmed *in vivo*.

Conclusion: PA-derivatization increased PpIX *in vitro* phototoxicity. Activation of the COX-2/PGE_2 pathway did not seem to reduce PDT efficiency. Only PpIX-dSd, was found somewhat active on a murine model. Nevertheless, these data showed that these new PS could be good candidates in the context of prostate cancer treatment by PDT.

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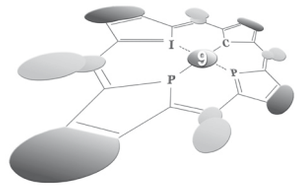

Chlorin-*p*6/PEI - Cellulose Nanocrystal Hybrids: *in vivo* Evaluation as New Potential Anticancer Agents for Application in Photodynamic Therapy.

Nicolas Drogat,[a] Frédérique Brégier, [a] Shihong Qiu, [a] Gautier Ndong Ntoutoume, [a] Jean Pierre Mbakidi, [a] Chloé Fidanzi-Dugas, [a] Youness Limani, [a] Fabrice Lalloué, [b] Claude Couquet,[c] Gaelle Begaud-Grimaud, [a] Caroline Le Morvan,[a] David Yannick Léger, [a] Bertrand Liagre, [a] Vincent Chaleix, [a] Robert Granet, [a] Vincent Sol [a]

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We report the synthesis of water-stable and water-soluble photosensitizer-conjugated nanoparticles (PS-CNCs) composed of cellulose nanocrystals (CNCs) bearing polyaminated chlorin *p6* (chlorin-*p*6/PEI). These nanoparticles were characterized by electron microscopy, zeta potential, UV-visible spectroscopy, DLS experiments and were tested for singlet oxygen production. *In vitro* tests were conducted on the glioblastoma cell line U87MG: cellular uptake of PS-CNCs was attested by confocal microscopy and photocytotoxicity tests showed that IC_{50} values fall within the nanomolar range. An *in vivo* model consisting of U87MG cells grafted onto the chorioallantoic membrane (CAM) of developing chick embryo has been built; this model allowed to evidence the tumor targeting properties of PEI/CNCs nanoparticles (rendered fluorescent after reaction with FITC). It also allowed to show the antiangiogenic properties of PEI/CNCs. Then, *in vivo* studies showed tumor growth inhibition in PDT- treated mice after intravenous injection of CNCs covalently labeled with chlorin-*p*6/PEI. This tumor-vectorized photosensitizer possess a remarkable therapeutic efficacy against glioblastoma tumor, with an inhibition ratio of 85%. To the best of our knowledge, this is the first *in vivo* demonstration of the tumor-targeting and anticancer properties of photosensitizers grafted to cellulose nanocrystals. These results indicate that this multifunctional nanoconstruct is a promising PDT agent for solid tumor treatment and this finding may serve as a "green" natural platform for future non invasive deep-cancer therapy.

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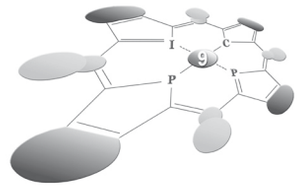

Electrochemistry and acid/base properties of free-base octabromo triarylcorroles in nonaqueous media

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Electrochemistry and acid-base properties are described for two series of free-base triarylcorroles in dichloromethane (CH_2Cl_2), benzonitrile (PhCN) and pyridine (py). One series possesses only *meso* substituents and the other has both *meso* and β-pyrrole substituents. The structure of the examined compounds are shown in Chart 1 and represented as $(tdcc)H_3$, $(tpfc)H_3$, $(Br_8tdcc)H_3$ and $(Br_8tpfc)H_3$, where tdcc and tpfc is the trianion of tri-(2,6-dichlorophenyl)corrole and tri-(pentafluorophenyl)corrole, respectively. Different electrochemical properties are observed for the octabromocorroles as compared to the non-brominated corroles, due in part of the corrole ring distortion and in part to the strong electron-withdrawing properties of the Br groups. The octabromocorroles are easier to deprotonate than the non-brominated corroles in solution and this was confirmed by both electrochemistry and spectroelectrochemistry as well as by measurements of the protonation/deprotonation constants during titration of the compounds with different acids and bases in CH_2Cl_2 or PhCN. The electrochemistry of the protonated and deprotonated corroles is presented and comparisons made with previously published data for other protonated and deprotonated corroles under the same solution conditions.

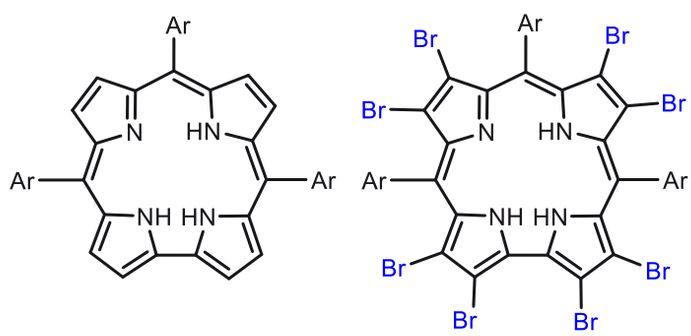

Chart 1. Structures of investigated free-base corroles.

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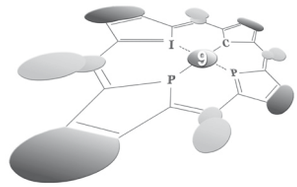

Syntheses and Characterizations of Internally Bridged Expanded Porphyrins

Takanori Soya, Hirotaka Mori, and Atsuhiro Osuka

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Expanded porphyrins have attracted considerable attention since they are nice platforms to realize Hückel aromatic and antiaromatic molecules and Möbius aromatic and antiaromatic molecules.[1,2] In recent years internally bridged expanded porphyrins have been revealed to serve as aza-annuleno(aza-annulene) variants displaying dual electronic properties. Despite their interesting properties, there have been only a few reports on this class of compounds.[3] In this presentation, we report the syntheses and characterizations of internally bridged octaphyrins(1.1.1.0.1.1.1.0), decaphyrins(1.1.1.1.1.1.1.1.1.1), and dodecaphyrin(1.1.1.1.1.1.1.1.1.1.1.1).
Acid catalyzed condensations of 1,4-phenylene or 2,5-thienylene bridged bis-dipyrromethane tetracarbinols with corresponding oligopyrroles followed by oxidation afforded internally bridged expanded porphyrins. Their structural and electronic properties were revealed by X-ray crystallographic analyses, NMR spectra, and absorption spectra.

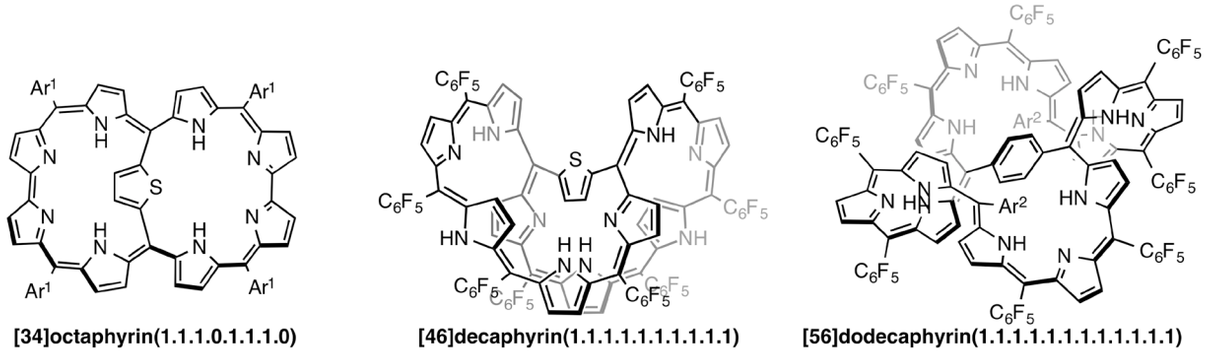

Figure. Structures of internally bridged expanded porphyrins. Ar^1 = *p*-octyloxyphenyl. Ar^2 = 2,6-dichlorophenyl.

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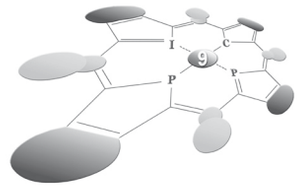

Different synthetic Pathways toward Porphyrin substituted Hexaphenylbenzenes

Marcus Speck, Sofia Rohde, Ute Pinkert, Andreas Hirsch*

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Hexabenzocoronenes (HBCs) possess interesting electronic and optical properties as building blocks for graphene and related compounds.[1] For better solubility, we used alkyl substituted porphyrin moieties to act as substituents on the HBC moiety, respectively the Hexaphenylbenzene system as immediate precursor of HBC. The fine-tuning of the physical properties through the substituents of the porphyrins may lead to interesting model compounds for artificial photosynthesis and light harvesting complexes.[2]
As starting materials soluble porphyrindipyrromethanes and bifunctionalized diphenylacetylene were used in a common one pot-synthesis to obtain the target molecules. In case of low yield of the final condensation step to the target porphyrin oligomers, other synthetic routes are tested.
Characterization has been carried out by standard analytical methods. Widespread NMR investigations show interesting geometric effects of the interaction of the porphyrin systems.
In this contribution synthetic pathway, product stability and NMR investigations will be discussed.

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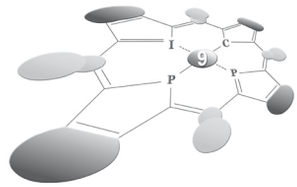

Computational and Spectroscopic Studies in the Design of Novel Porphyrins for Solar Cell Applications

Angel (Qi Wen) Zhang[a], Satoshi Yamamoto[b], Lydia Kwan[a], Nagao Kobayashi[b], Mutsumi Kimura[b], Martin Stillman[a]

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Currently, porphyrins are being studied intensively as photosensitizers for dye-sensitized solar cells and for singlet oxygen production in photodynamic cancer therapy. In both cases extending the Q band into the red is required. One limitation in the general use of photodynamic therapy is that it can only be used to treat tumours where light can reach. The optimal wavelength for tissue penetration lies between 670 and 910 nm. For solar cells, the Q band (or any S1 transition) needs to match the electrochemical properties of the electron transport system used. Chlorophyll has a Q band that lies within this optimal wavelength range and is therefore a great starting point for the design of porphyrins with intense red-shifted Q bands.
To aid in directing the design of porphyrins with different substituents that will exhibit these red-shifted bands in a systematic manner, a Δ[(LUMO+1)-LUMO] trend is being constructed from the calculated electronic structures of a range of compounds. This trend will help direct future synthetic plans. A Δ[HOMO-(HOMO-1)] trend was previously proposed by the Stillman, Kobayashi, et al. in 2005 to help in the design of porphyrins with strong absorption in the near IR region1. Since the two HOMOs can only be split by so much, to further decrease the gap between HOMO and LUMO, substituents and ring modifications that will split the two LUMOs need to be determined. The splitting of the two LUMOs will provide intense red-shifted Q bands, that will likely lead to novel electrochromic properties1.

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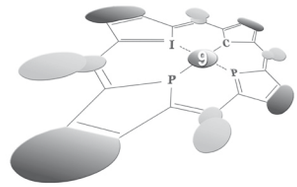

Hydrogen-Bond-Assisted Selective Formation of Monoprotonated Dodecaphenylporphyrin and the Photodynamics of Intermolecular Electron Transfer

Wataru Suzuki[a], Hioarki Kotani[a], Tomoya Ishizuka[a], Kei Ohkubo[b,c], Shunichi Fukuzumi[b,c,d], Takahiko Kojima[a]

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In the protonation of a freebase porphyrin (H_2P), one-step formation of a diprotonated porphyrin (H_4P^{2+}) has been mainly observed rather than stepwise protonation involving a monoprotonated porphyrin (H_3P^+). This results from the higher basicity of H_3P^+ due to the saddle distortion induced by the electrostatic repulsion among inner protons than that of H_2P. However, there is no report on an effective strategy to stabilize H_3P^+; thereby, the properties and reactivity of H_3P^+ have yet to be clarified. Herein, we describe selective formation of a monoprotonated porphyrin in the protonation of saddle-distorted dodecaphenylporphyrin (H_2DPP) in the presence of a polar protic solvent. In addition, we report photoinduced electron-transfer properties of monoprotonated H_3DPP^+, including the first determination of reorganization energy (λ) of electron transfer (ET) of H_3P^+.

Addition of methanol as a polar protic solvent to an acetone solution of H_2DPP with 1 eq of trifluoroacetic acid (TFA) resulted in selective formation of H_3DPP^+, as confirmed by spectroscopic measurements and X-ray crystallography (Fig. 1). One methanol molecule was found to form hydrogen bonding with H_3DPP^+ in the crystal, which should be important for the selective formation of H_3DPP^+. The selectivity of H_3DPP^+ formation, evaluated by a ratio ($[H_3DPP^+]/[H_2DPP]_0$), increased with increasing the portion of methanol (0-10%) in acetone. The ratio showed saturation relative to the methanol concentration to indicate the stabilization of H_3DPP^+ by hydrogen bonding methanol, as reflected on the thermodynamic parameters of H_3DPP^+ formation. Femto- and nano-second laser flash photolysis were applied to elucidate the photodynamics of H_3DPP^+ in intermolecular photoinduced ET from ferrocene derivatives as one-electron donors to the triplet excited state of H_3DPP^+ as an electron acceptor in acetone/methanol (3%). The second-order rate constants of the ET reactions were evaluated in light of the Marcus theory of ET. The reorganization energy (λ) of ET was determined to be 1.86 eV, which is slightly larger than that of H_4DPP^{2+} in acetonitrile (1.69 eV),[1] due to larger structural change of H_3DPP^+ than that of H_4DPP^{2+} after ET, as confirmed by DFT calculations.

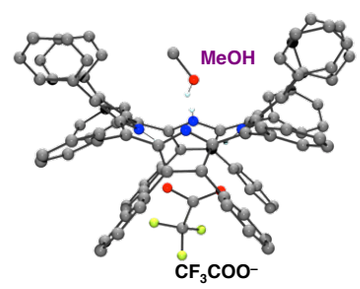

Fig. 1. Crystal structure of $H_3DPP^+(CF_3COO^-)(MeOH)$

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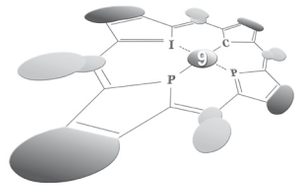

Toward aceneporphyrinoids – syntheses, properties and coordination chemistry of phenanthriporphyrinoids

Bartosz Szyszko, Marcin Małecki, Anna Berlicka, Michał J. Białek, Agata Białońska, Kamil Kupietz, Ewa Pacholska-Dudziak and Lechosław Latos-Grażyński

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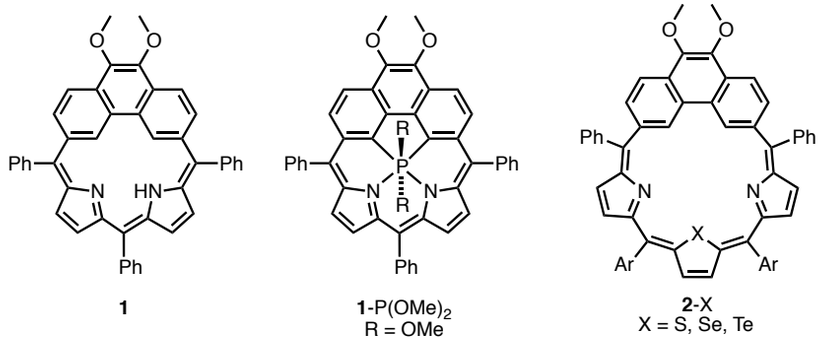
Altering of the archetypical porphyrin frame realized through the replacement of pyrolle ring with other carbocycle creates innovative routes for the exploration of coordination chemistry confined in a macrocyclic environment. Molecules that link structural features of polycyclic aromatic hydrocarbons and polypyrrolic macrocycles in a way, which allows for electronic communication - aceneporphyrinoids - exemplify this approach. Such compounds can demonstrate peculiar electronic and molecular structures. For example the incorporation of a phenanthrene moiety into a porphyrin framework results in the formation of hybrid macrocycles—phenanthriporphyrin **1**,[1] and 32-heterophenanthrisapphyrins **2**-X.[2] In the case of **1** the structural features of the molecule result in its distinct antiaromaticity, while the highly folded molecules of heterophenanthrisapphyrins manifest very limited π-electronic conjugation.
Phenanthriporphyrin **1** adopts the trianionic {CCNN} core, and was proven to be suitable for the incorporation of a phosphorus(V) center to form a hypervalent organophosphorus(V) derivative **1**-P(OMe)$_2$.



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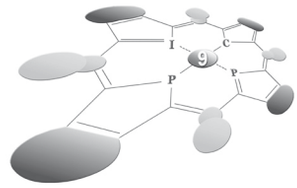

Protonation Behavior and Aromaticity in Thiaporphyrins

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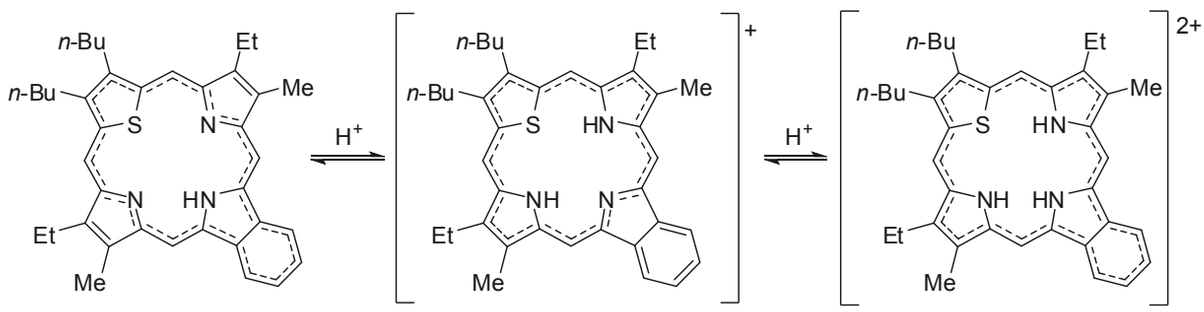
It is well known that free-base porphyrins are easily protonated to give the corresponding diprotonated forms, and the monoprotonated forms are hardly observed both in crystalline[1] and solution states[2]. The protonation behavior and the changes in aromaticity on protonation were reported for core-modified porphyrins[3](*e.g.* benzipoprhyrin, carbaporphyrin and N-confused porphyrin). In thiaporphyrins, the difference in size of core cavity might affect on protonation abilities. However, protonation behavior of the thiaporphyrins have not been investigated in detail. We investigated the protonation behavior of bicyclo[2.2.2]octadiene-fused (BCOD-fused) thiaporphyrin **1** and thiabenzoporphyrin **2**. In the acid titration experiment, the absorption spectra of both thiaporphyrins gradually changed to monoprotonated form **1**·H^+ and **2**·H^+, then to diprotonated forms **1**·$2H^+$ and **2**·$2H^+$. where isosbestic points were clearly observed, respectively. Fortunately crystal structures of **1** (neutral form), **2**·H^+ (monoprotonated form), and **1**·$2H^+$ (diprotonated form) were cleary revealed. Based on the atomic geometries, the NICS (neucleus independent chemical shift) and HOMA (harmonic oscillator model of aromaticity) values for the protonated forms were calculated. Considering from the calculated results, the ^{1}H-NMR and absorption spectra, the nature of the π-system will be discussed (Scheme).



Scheme. Stepwise protonation and the proposed resonance structures of neutral, monoprotonated, and diprotonated forms of **2**.

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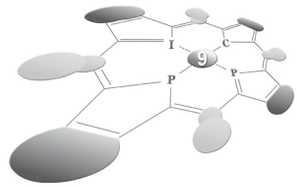

Synthesis of chlorophyll derivatives possessing a sulfanyl, sulfinyl or sulfonyl substituent at the 3^1-position and their optical properties

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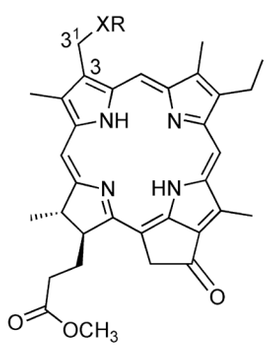
Sulfur-containing chlorophyll derivatives were identified in sediments of an Antarctic lake and their related compounds have been already synthesized. However, no report is available for the preparation of chlorophyll derivatives possessing a thiomethyl group at the 3-position (X = S in Fig. 1). Here we report on syntheses of such sulfide, sulfoxide, and sulfone as well as their optical properties [1].

Methyl pyropheophorbides **2** and **3** possessing an *S*-alkylated or arylated sulfanylmethyl group at the 3-position were prepared by the reaction of 3-hydroxymethyl-chlorin **1** with the corresponding thiols in the presence of zinc iodide. The resulting sulfides **2/3** were readily oxidized to the corresponding sulfoxides **2a/3a** and sulfones **2b/3b** and the chlorin free bases were smoothly transformed to their metal complexes. Their Qy absorption maxima in dichloromethane were dependent on the *S*-functional groups at the 3^1-position and bathochromically shifted by an increase of their electronegativities (Table 1). The observation was due to their electron-withdrawing effect through homoconjugation of the 3^1-substituents with the chlorin π-system via a methylene moiety. Their fluorescence emission quantum yields were similarly affected by the 3^1-substituents and increased with suppression of the electron-donating ability of the *S*-atom. The partial fluorescence quenching in the sulfides would be ascribable to photoinduced electron transfer from the 3^1-S to the singlet excited state of the chlorin moiety in a molecule.



1: X = O, R = H
2: X = S, R = C_6H_4(*p*-CH_3)
3: X = S, R = $(CH_2)_8H$

2a: X = SO, R = C_6H_4(*p*-CH_3)
2b: X = SO_2, R = C_6H_4(*p*-CH_3)
3a: X = SO, R = $(CH_2)_8H$
3b: X = SO_2, R = $(CH_2)_8H$

Fig. 1. Molecular structures of chlorophyll-*a* derivatives, methyl pyropheophorbides possessing an *O*/*S*-substituent at the 3^1-position

Table 1. Absorption maxima (nm) in CH_2Cl_2

Compounds	Soret	Qy
2/3	412/412	663/663
2a/3a	412/412	667/669
2b/3b	412/412	669/671

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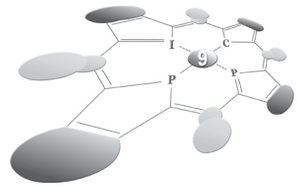

Self-aggregation of bacteriochlorophyll-*d* amino-analogs in an aqueous micelle solution

Hiroaki Watanabe, Tadashi Mizoguchi and Hitoshi Tamiaki

Graduate School of Life Sciences, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan

There are a large amount of alcohol-type chlorophyll pigments including bacteriochlorophyll(BChl)-*d* in the light-harvesting antennas of green photosynthetic bacteria, called chlorosomes. Inside a chlorosome, BChl-*d* molecules spontaneously form *J*-type self-aggregates using intermolecular hydrogen-bond between the 3^1-OH and 13-C=O, coordination between the 3^1-OH and central Mg, and π-π interaction of the chlorin skeletons. As the model of self-aggregative BChl-*d*, we synthesized chlorophyll-*a* derivatives possessing an amino group at the 3^1-position (left drawing of Fig. 1) [1]. The synthetic animo-chlorins were monomeric in polar organic solvents such as THF. In an aqueous micelle solution, their Qy-absorption maxima were shifted to longer wavelengths and intensive circular dichroism bands appeared at the red-shifted Qy region. These spectral changes indicated that they self-aggregated in the solutions to form large oligomers similarly as in natural chlorosomes (right drawing of Fig. 1). The epimerically pure samples (middle drawing of Fig. 1) formed different self-aggregates dependent on the $C3^1$ chirality in an aqueous micelle [2]. We will report on the mechanism of self-aggregation of such amino-chlorins as well as their physical properties and nano-structures, compared with those of natural and artificial hydroxy-chlorins.

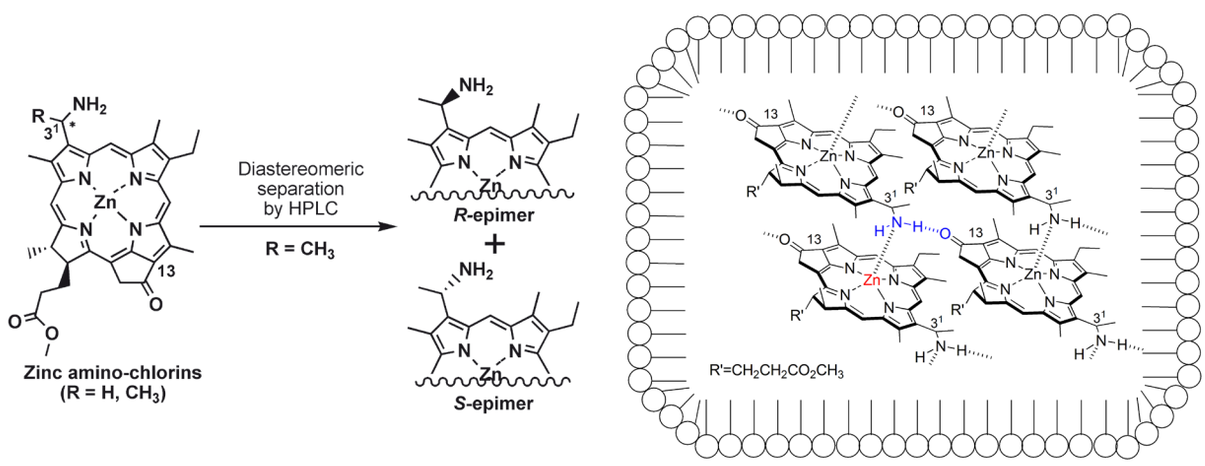

Fig. 1. Diastereomeric separation (middle) of zinc amino-chlorins as the model of BChl-*d* (left) and the schematic drawing of their self-aggregats in an aqueous micelle (right)

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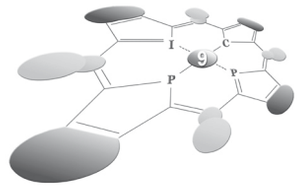


Fullerene Linked Benzoporphyrins for Solution-Processed Organic Photovoltaic Material

Yuto Tamura[a], Daiki Kuzuhara[a], Mitsuharu Suzuki[a], Hiroko Yamada[a]

[a] *Graduate school of Material Science, Nara Institute of Science and technology, 8916-5, Takayama-cho, Ikoma, Nara, Japan*

Organic photovoltaics (OPVs) are electric generation system using charge separation between donor (D) and acceptor (A) material at interface in a solid film. One of the most efficient structure to improve device performance is bulk heterojunction (BHJ) structure which is given from blended D and A material thin film. This structure provides nanoscale domains to form a large interface between D and A for charge separation. However, it is often difficult to control nanostructure of crystalline material such as benzoporphyrin (**BP**) in BHJ structure. Our recent report revealed that Fullerene linked **BP** dyad molecule (**BP–F**) provides more smooth and homogeneous morphology to improve device performance compare with blended **BP** and **PC$_{61}$BM** [1]. We synthesized triad type compound (**BP–F2**) using extremely soluble precursor [2] of **BP** (**CP–F2**) as next generation (Figure 1). Here, the application for OPV will be report.

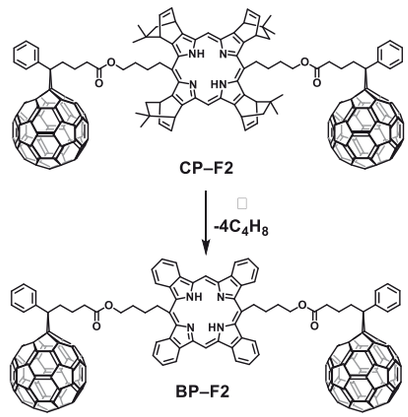
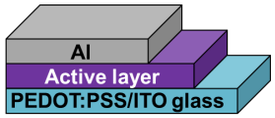


Figure.1 Chemical structures of **CP–F2** and **BP–F**

Configuration of fabricated OPV cells and device performances under AM 1.5 illumination are shown in Figure 2 and Table 1, respectively. **BP–F2** showed better performance than blended **BP**:**PC$_{61}$BM**. Furthermore, J_{sc} value of **BP–F2** was much improved than **BP–F** to show the best PCE of 0.41% examined here. We believe that around 10 times higher carrier mobility of **BP–F2** than **BP–F** induced this improvement of J_{sc} value (Table.2). We will also report comparison of optical properties, film morphology and evaluation of device performances in **BP–F** and **BP–F2**.



Active layer =
BP–F2 or **BP–F** or **BP**:**PC$_{61}$BM**

Figure.1 Configuration of fabricated OPV cells

Table.1 Device performances

	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF	PCE [%]
BP–F2	2.20	0.57	0.32	0.21
BP–F	1.12	0.45	0.29	0.15
BP:**PCBM**	0.57	0.14	0.23	0.02

Table.2 Carrier mobility of BP–F2 and BP–F estimated by SCLC measurement

	Hole mobility [cm^2 V^{-1} s^{-1}]	Electron mobility [cm^2 V^{-1} s^{-1}]
BP–F2	5.6×10^{-5}	2.0×10^{-5}
BP–F	2.6×10^{-6}	3.1×10^{-6}

Hole only device: ITO / MoO_3 / **BP–F2** or **BP–F** / MoO_3/Al
Electron only device: ITO / ZnO / **BP–F2** or **BP–F** / LiF / Al

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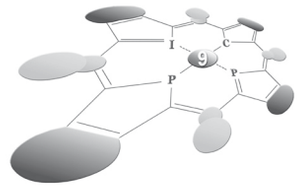

Syntheses and Properties of [28]Hexaphyrin Ge(IV) and Sn(IV) Complexes

Takayuki Tanaka,[a] Mondo Izawa,[a] Shin-ichiro Ishida,[a] Atsuhiro Osuka[a]

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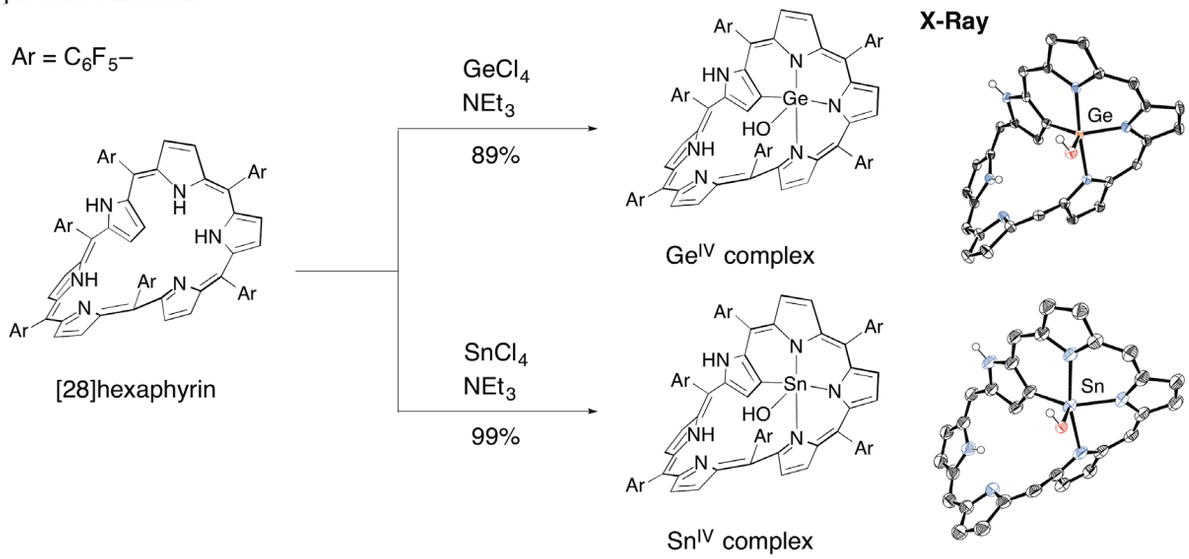
Expanded porphyrins, which consist of more than four pyrrolic subunits, have attracted considerable interests in light of their intriguing structural and photophysical properties.[1,2] A further arousing attribute of them is their ability to serve as effective platforms for realizing Möbius aromatic molecules. Recent investigation recognized us that singly twisted macrocycles possessing Möbius topology are intrinsically chiral, and can be separated to enantiomeric pairs, *P*-twist and *M*-twist.[3]

In this presentation, we will report efficient syntheses of [28]hexaphyrin Ge^{IV} and Sn^{IV} complexes and their physical properties. Both complexes showed distinct 28π Möbius aromaticity as seen in their ^{1}H NMR and UV/vis/NIR absorption spectra. They displayed twisted structures rigidified by the central 5-coordinated atoms with trigonal bipyramidal geometry. The axial ligand of Ge^{IV} complex, -OH, could be exchanged for alkoxy, phenoxy, and thiophenoxy groups. Their properties and enantiomeric separation of Ge^{IV} complex will be presented in detail.



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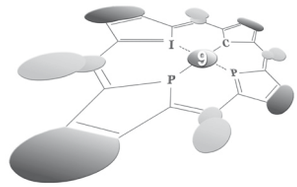

Synthesis of Boron Porphyrinoids

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[b]*MacDiarmid Institute for Advanced Nanomaterials, New Zealand,*

In the past two decades, the Brothers' research group has synthesised boron porphyrins and corroles by inserting boron into their N_4 cores using boron trihalides and their derivatives. This has yielded rich chemistry for both the boron and the ligands such as the presence of diboryl complexes, several unique coordination modes for the boron such as B-O-B, B-H-B and B-B bonding as well as tetragonal distortion of the ligands.[1,2] As an extension of this work, two new classes of porphyrinoids have been investigated for boron coordination: calixphyrins and porphyrazines. Calixphyrins and porphyrazines have received increased interest due to improvements in their synthesis. Calixphyrins, containing both sp^2 and sp^3 *meso* carbons, are considered to be a hybrid of porphyrins which contain only the former and calixpyrroles which only have the latter.[3] Similarly, porphyrazines are structural hybrids of porphyrins and phthalocyanines.[4]

A series of mono and diboron calixphyrins (Calix) have been synthesised using BF_3, BCl_3 and $PhBCl_2$ as the boron source. The reaction with BF_3 produces both the mono-BF_2 or diboron B_2OF_2 products. Due to the presence of both dipyrrin and dipyrromethane bonding sites, two structural isomers of both compounds have been isolated. In the case of B_2OF_2(Calix), the steric bulk of the groups on the periphery of the ligand directs the bonding site to which the boron coordinates. The reaction with $PhBCl_2$ in the presence of $N(^iPr)_2Et$ results in the unexpected reduction of the calixphyrin ligand; however, this does not occur when the reaction is carried out without base.

The insertion of boron into porphyrazines (Pz) has been achieved using BCl_3 and $PhBCl_2$. The reaction with BCl_3 forms an air- and moisture-sensitive intermediate which can be converted into the stable B_2OF_2(Pz) using BF_3 as the fluorine source. The reaction with BF_3 does not produce a boron porphyrazine product. The reaction with $PhBCl_2$ forms two diboron products, PhBOBPh(Pz) and PhBOBOH(Pz). No mono-boron products have yet been observed.

The structural similarities of boron porphyrinoids with BODIPYs as well as the tripyrrolic subporphyrinoids lead to the possibility that these new classes of compounds could have a potentially wide range of applications.

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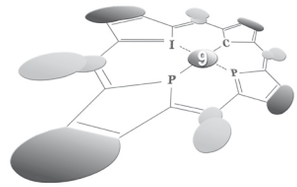

The Influence of Substituent Orientation on the Photovoltaic Performance of Phthalocyanine-Sensitized Solar Cells

Lara Tejerina[a], M.V. Martínez-Díaz[a], Mohammad Khaja Nazeeruddin[c], and Tomás Torres[a,b]

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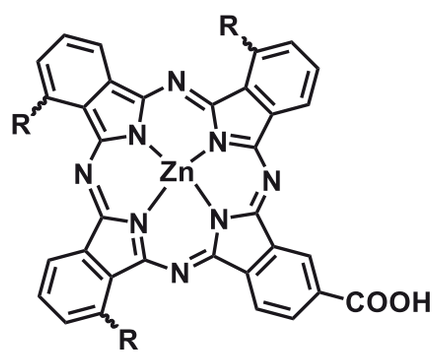
[c] *Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, 1951 Sion (Switzerland)*

Phthalocyanines (Pcs) are used as sensitizers in dye-sensitized solar cells (DSSCs) because of their stability and intense absorption in the red and near-IR regions. Impressive progress has been made in photovoltaic efficiencies by introduction of bulky peripheral substituents to help suppress macrocycle aggregation. To reach benchmark efficiencies reported for other related dyes, new designs need to be explored [1]. Single carboxy-ZnPc regioisomers substituted at the non-peripheral positions by aryl and aryloxy groups have now been studied, which has shed light on the influence of steric hindrance and/or orientation of the substituent around the anchoring group on the photovoltaic response [2]. The regioisomers bearing the group far away from the anchoring group produces a more effective sensitization of the TiO_2 films and higher short-circuit photocurrent density (J_{sc}).



R = Ar, OAr

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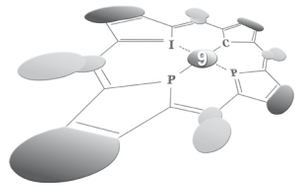

Unsymmetrical Phthalocyanines for Dye-sensitized Solar Cells

Gülenay Tunç[a], Yunus Yavuz[b], Betül Canımkurbey[b,c], Sait Eren San[b], Ferda Hacıvelioğlu[a], Vefa Ahsen[a], Ayşe Gül Gürek[a]

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In the last few years, phthalocyanines (Pcs)have attracted strong interest in the field of dye-sensitized solar cells (DSSCs) and have proved to be realistic candidates for replacing the successful but costly ruthenium-based sensitizers.[1] However, conversion efficiencies are still lower than those of related porphyrins, which are the most effective organic molecules in this area. Structural modifications at the peripheral aryloxy groups and variations on the linker between the Pc and the anchoring group have recently been reported, giving rise to many new nonaggregated carboxy ZnPcs derivatives which have reached excellent efficiency values close to 6.5%[1,2].
In this work, unsymmetrical tetra and octa substituted Zn(II)Pcs have been designed and synthesized which consist of two different carboxylic acids and hexylthia groups at the peripheral positions. These Zn(II)Pcs were synthesized by a statistical condensation reaction between two different phthalonitrile derivatives. The effect of substituted groups will be investigated on photophysical, photochemical properties and on point of view DSSC performance.

ACKNOWLEDGEMENTS
The Scientific and Technological Research Council of Turkey (TUBITAK) is gratefully acknowledged for the funding of these works (project 114M478 coupled to the COST Action MP1307)

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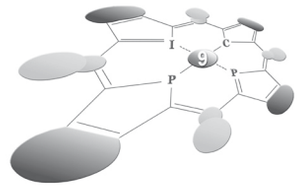


Synthesis and Characterization of *peri*-Naphthoporphyrins

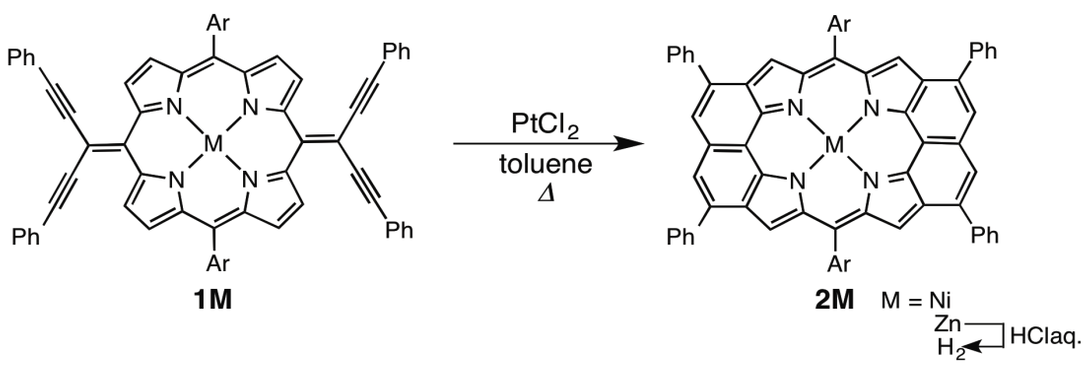
Masataka Umetani, Koji Naoda, Takayuki Tanaka, Atsuhiro Osuka

Department of Chemistry, Graduate School of Science, Kyoto University

In recent years fused porphyrinoids have attracted much attention because of their promising properties as NIR-absorbing and emitting dyes, pigments of photodynamic therapy, non-linear optical materials, and electron conducting materials.

meso-meso, *β-β, β-β* Triply-linked porphyrin arrays (porphyrin tape)[1] possess a unique position in light of their remarkable bathochromic absorption shifts reaching infrared region that arise from the effective electronic delocalization over the whole molecules. Various porphyrins fused with other aromatic segments such as anthracene-fused porphyrin[2] and BODIPY-fused porphyrin[3] have been explored. In these examples, the aromatic characters of the porphyrin segments were mitigated due to the electron delocalization onto the fused outside segments. Wu *et al*. reported fused quinonoidal porphyrin[4] that exhibits a nonaromatic nature intrinsic to the quinonoidal conjugation as a result of acquiring stabilization due to four Clar's sextet benzenes. They also synthesized phenarenyl-fused porphyrin[5] that was an open-shell biradical and was easily oxidized by air to form oxygenated derivatives. In these cases, two or more aromatic units are linked by triple C—C bonds, giving rise to formal naphthalene segments directly on the porphyrin peripheries. Thus, we naturally became interested in the common interior core, namely di-*peri*-dinaphthoporphyrin, the conjugation circuit of this unique fused porphyrin cannot be simply delineated as usual porphyrin 18π circuit.

Di-*peri*-dinaphthoporphyrins **2M** have been synthesized via $PtCl_2$-mediated cycloisomerization reaction of π-extended quinoidal porphyrins **1M**. **2M** exhibit a characteristic paratropic ring current effect that presumably arises from the 24π antiaromatic circuit as a dominant resonance contributor. UV/Vis absorption spectra, cyclic voltammetry, and excited-state dynamics as well as theoretical calculation support this conclusion.



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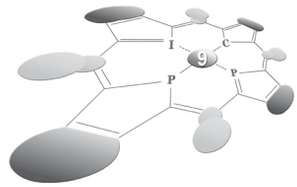

Multifunctional Logic in a Photosensitizer with Triple-Mode Fluorescent and Photodynamic Activity

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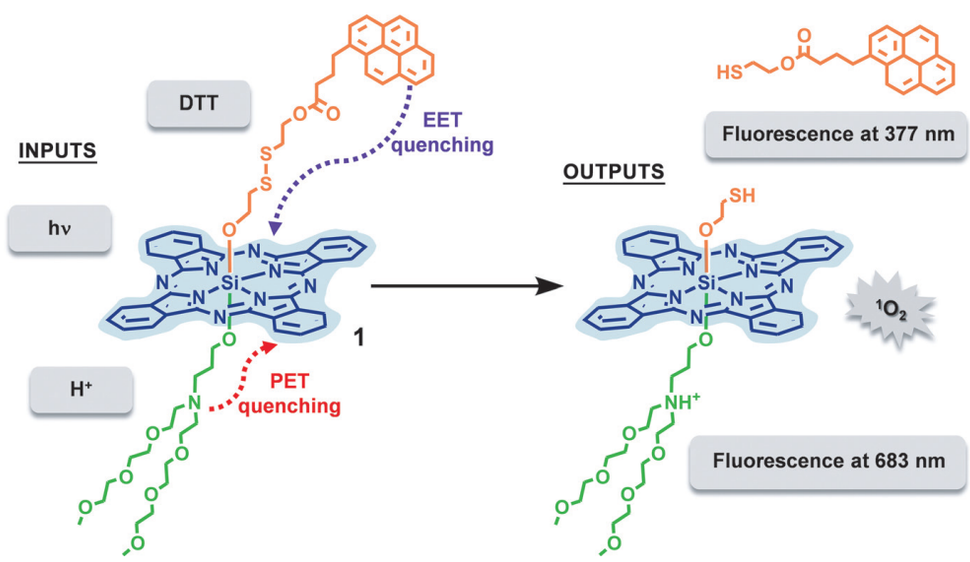
We describe a photosensitizer[1,2] (PS) with the capacity to perform multiple logic operations based on a pyrene-containing phthalocyanine (Pc) derivative. The system[3] presents three output signals (fluorescence at 377 and 683 nm, and singlet oxygen ($^1O_2$) production), which are dependent on three inputs: two chemical (concentration of dithiothreitol (DTT) and acidic pH) and one physical (visible light above 530 nm for $^1O_2$ sensitization). The multi-input/multioutput nature of this PS leads to single-, double-, and triple-mode activation pathways of its fluorescent and photodynamic functions, through the interplay of various interrelated AND, ID, and INHIBIT gates. Dual fluorescence emissions are potentially useful for orthogonal optical imaging protocols while $^1O_2$ is the main reactive species in photodynamic therapy (PDT). We thus expect that this kind of PS logic system will be of great interest for multimodal cellular imaging and therapeutic applications.



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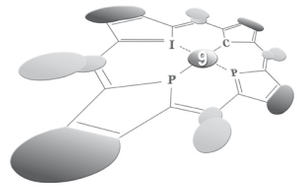

On the Twists and Turns of the Siamese-Twin Porphyrin upon Oxidation

Anastasia Vogel[a], **Sebastian Dechert**[a], **Michael John**[a], **Christian Brückner**[b], **and Franc Meyer**[a]

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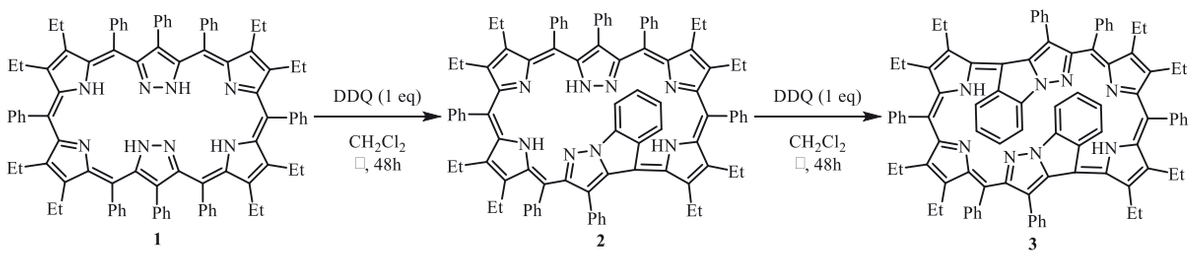
Siamese-Twin Porphyrins[1] **1** are non-macrocycle-aromatic, expanded porphyrins that are composed of two porphyrin-like subunits that are fused through two pyrazole moieties. Each $\{N_4\}$-pocket exhibits its own conjugation pathway. Building upon the redox non-innocence of the Siamese-Twin Porphyrin in its metal complexes[2] oxidations of **1** with carefully controlled amounts of the two-electron, two-proton oxidizing agent DDQ were performed.[3]



Surprisingly, the strain on the macrocycle in its free-base form **1** led upon oxidation to the formation of product **2** incorporating a single N^{pz}-$C^{o\text{-}Ph}$ linkage between the pyrazole unit with a neighboring *meso*-phenyl group, forming a pyrazolo[1,5-*a*]indole moiety. Repeated treatment with a second equivalent of the oxidant yielded a doubly *N*-fused species **3**, involving a second pyrazole moiety. The fusions strongly alter the conformation of the macrocycles, as shown by X-ray diffraction. UV-vis and NMR-spectroscopic investigations indicated the presence of highly delocalized but non-macrocycle-aromatic π-systems. This behavior of the Siamese-Twin Porphyrin in response to oxidation is in contrast to the behavior of related all-pyrrole-based expanded macrocycles that can be switched by redox processes and protonation between Hückel and Möbius-aromatic states.[4]
The syntheses, structures and properties of **1**, **2** and **3** are presented here.

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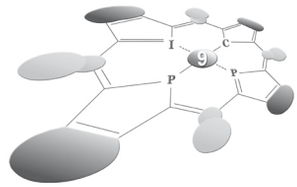
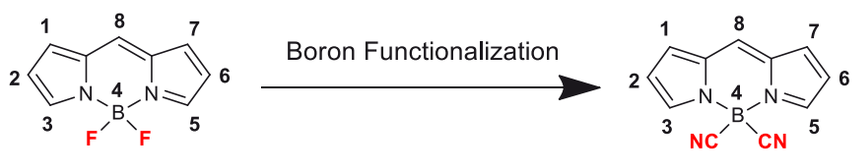


Synthesis and Investigation of 4,4'-dicyano-BODIPY Derivatives

Maodie Wang, Alex L. Nguyen, M. Graca H. Vicente

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA

BODIPY dyes are widely used as fluorescent labels and sensors, due to their high molar extinction coefficients, biocompatibility, sharp fluorescence with high quantum yields and photochemical stability.[1] Although the methods for the functionalization of BODIPYs at the carbon peripheral positions have been intensely investigated, the functionalization of BODIPYs at the boron center has lagged far behind.[2,3] We will report the synthesis of a series of 4,4'-dicyano-BODIPY derivatives,[4] and their stability under acidic and basic conditions. The spectroscopic properties of the BODIPYs, including their absorption and emission wavelengths, fluorescence quantum yields, ^{1}H, ^{13}C and ^{11}B NMR, as well as their structural features will be presented and discussed.



BODIPY
(4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene)

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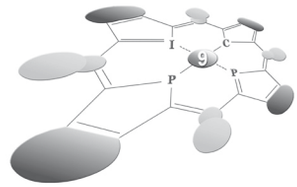
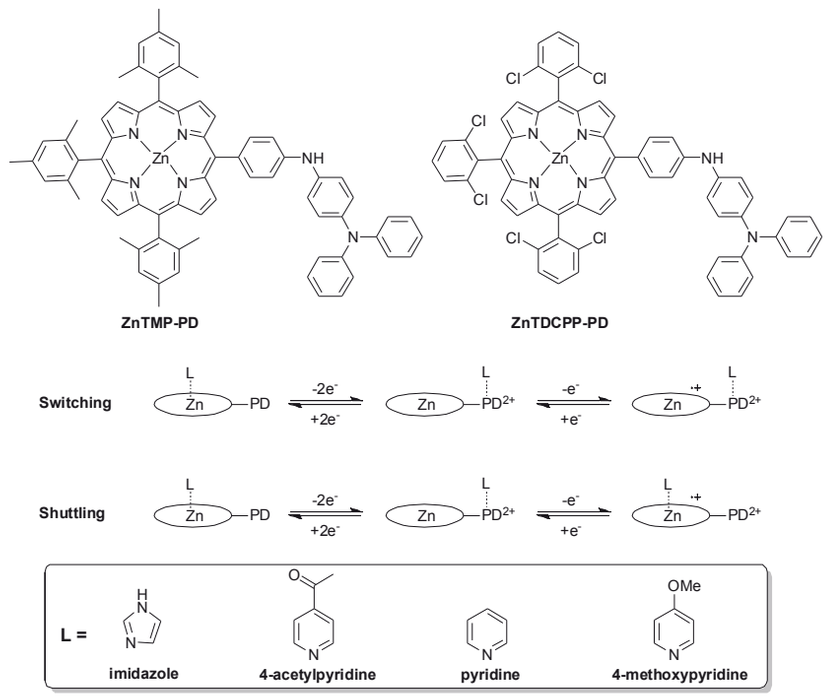


Engineering zinc porphyrin linked with *meso*-phenylenediamine substituent for electrochemically controlled ligand shuttling

Shi-Ju Wang, Guan-Ling Chen, Kuo Yuan Chiu and Yuhlong Oliver Su*

Department of Applied Chemistry, National Chi Nan University 1, University Road, Puli, Nantou Hsien, 545, Taiwan



In our previous research, a series of **ZnTMP-PD** derivatives has been synthesized and also investigated thoroughly. Only ligand switch phenomenon could be observed. In this study, **ZnTDCPP-PD** was synthesized and fully characterized. By using electrochemical and spectroelectrochemical method, ligand shuttling between zinc porphyrin and *meso*-phenylenediamine substituent could be monitored.

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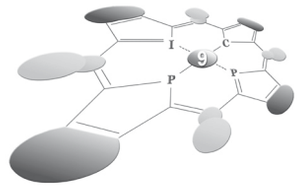

Effect of NO_2 substitution and solvent on UV-visible spectra, redox potentials and electron transfer mechanism of β-nitrocopper triarylcorroles. Proposed electrogeneration of a Cu(I) oxidation state

Lina Ye[a,b], Wenda Wang[a], Zhongping Ou[a]*, Yuanyuan Fang[a], Yang Song[c], Karl M. Kadish[c]*

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Three copper triarylcorroles containing a β-pyrrole nitro substituent were synthesized and characterized as to their spectral and electrochemical properties in nonaqueous media. The examined compounds are represented as β-$NO_2(YPh)_3CorCu$, where Cor is the trianion of a triphenylcorrole and Y is a Cl, H or CH_3 substituent at the *para*-position of the three *meso*-phenyl rings of the compound. The structures of the compounds are shown in Chart 1. UV-visible spectra measured in CH_2Cl_2, DMF and pyridine combined with DFT calculations reveal that the electronic ground state of each copper nitrocorrole exists mainly in its Cu^{II}-$Cor^{\bullet 2-}$ form. Each neutral compound undergoes three one-electron reductions, the first two of which are reversible in the three utilized solvents. The data from electrochemistry and thin-layer spectroelectrochemistry are consistent with electrogeneration of a formal Cu(II) corrole with an unreduced macrocycle, represented as Cu^{II}-Cor^{3-}, after the first one-electron reduction and electrogeneration of a Cu(I) corrole after addition of a second electron to give a species represented as Cu^{I}-Cor^{3-}. This doubly reduced β-nitro corrole has a sharp Soret band at 439 nm and a well-defined Q band at 611 nm in CH_2Cl_2 and exhibits no evidence for reduction at the conjugated π-ring system of the macrocycle. Similar absorption spectra are seen for the three examined doubly reduced nitrocorroles in DMF and pyridine, suggesting a metal(I) species exist in both solvents. Changes in the redox potentials and absorption spectra of the nitrocorroles are examined as a function of the solvent and para-phenyl substituents on the molecule and comparisons are made between spectral and electrochemical data of the newly synthesized compounds and that of structurally related corroles lacking a β-nitro group. Support from Jiangsu Province Ordinary University Graduate Student Research Innovation Project (KYLX-1064), Natural Science Foundation of China (21501070) and Foundation of Jiangsu University (15JDG131, 05JDG051).

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Chart 1. Structures of examined copper corroles

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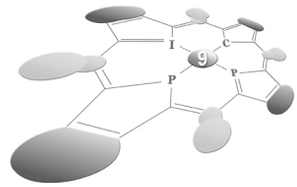

Effect of Chemical Environmental on the Electroreductive Dechlorination of Toxic Lindane

Junxia Wen[a], Xu Liang[a,*] Tingting Huang[a], Minzhi Li[a], Weihua Zhu[a,*]

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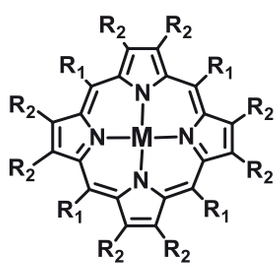
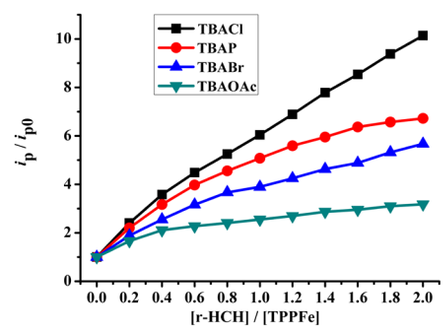
Lindane has been widely used for three decades as a potent pesticide for controlling malaria, typhus and other insect borne diseases but its use in agriculture has been banned in many countries since the mid-1970s because its exposure to human and wildlife can result in severe health problems [1–4]. Under this point of view, facile and highly efficient removal of environmental toxic organochlorides become social challenges. Right now, macrocyclic compounds containing transitionmetal ions can be used as the efficient catalysts for chemical and electrochemical dechlorination of environmental harmful organochlorides. Compared with chemical dechlorination, electrochemical dechlorination of environmental harmful organochlorides catalyzed by metal-porphyrinoids can be more easily achieved. Generally, metallo-porphyrin electrocatalyzed dechlorination reaction produce a σ-bond between organochloride and electrogenerated metallo-porphyrin anion (described as $[(Por)M(I)]^- + RX \square (Por)M(III)(R) + X^-$) as a key intermediate. Thus, chemical environmental may has a large effect on the electroreductive dechlorination of toxic lindane. In this study, we try to use different solvent, temperature and even different supporting electrolyte. Spectroscopy, electrochemistry, spectroelectrochemistry, controlled potential dechlorination, and dechlorination products analysis were carried out to give in-depth understand both reaction kinetics and mechanism of effect of chemical environmental on the electroreductive dechlorination of toxic organochlorides, such as lindane. This work was financially supported by the NSFC of China (No. 21171076).





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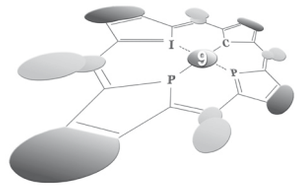

Conjugable Vitamin B_{12} Derivatives

Aleksandra Wierzba,[a] Mikołaj Chromiński,[a] Agnieszka Jackowska,[a] Rashid Nazir,[a] and Dorota Gryko*[a]

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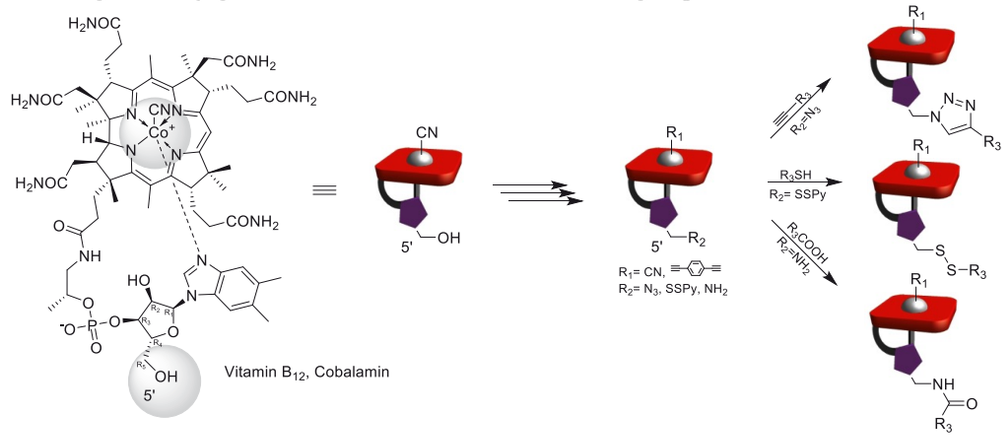
Delivery of an active compound to its site of action is one of the crucial issues in drug development. A promising strategy is to use naturally occurring compounds, such as vitamin B_{12} (cobalamin) due to its unique ability to penetrate cells via a system of transport proteins.[1] These proteins show high tolerance to modifications of two main functionalities on B_{12}; the 5'-OH group and the central cobalt ion.[2]
Russell-Jones's carbamate methodology for conjugation at the 5'-position is currently the most popular approach.[3] However, this method is limited to the conjugation of amines and the resulting carbamate is rather unstable under acidic conditions. We have developed a more robust approach, relying on [1,3] dipolar cycloaddition.[4] Transformation of the 5'OH into an azide proved highly active in the copper catalyzed as well as strain promoted [1,3] dipolar cycloaddition (CuAAC or SPAAC) to alkynes. Subsequent reduction of the azide gave an amine, which can be easily coupled with acids. As disulfide-based conjugates can undergo cleavage in the presence of glutathione (GSH) - the most abundant thiol in mammalian cells, we have also developed a vitamin B_{12} derivative suitably tailored for such conjugation.[5]
The formation of a cobalt functionalized, highly heat/light stable cobalamin derivative was achieved via reduction-free, direct alkynylation of vitamin B_{12}.[6] Moreover, we have developed the methodology allowing for selective orthogonal conjugation at both the Co center and 5'-OH group.[7]



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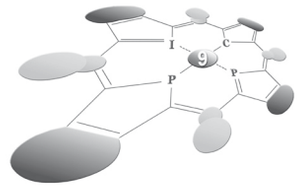

Contemporary Synthesis and Investigation of Peptidic-BODIPY Conjugates

Tyrslai M. Williams, M. Graça H. Vicente

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA

Epidermal Growth Factor Receptor (EGFR) is a cell surface protein that is overexpressed on the surface of various cancerous cells, caused by mutations during binding, particularly colorectal cancer (CRC).[1] This unique instance makes the aggressive targeting of EGFR a great focus of study for both treatment and detection.[2] Imaging these cancer cells with fluorescent molecules that possess CRC selectivity is fundamental for facilitating early detection. BODIPY dyes are very attractive fluorophores mainly due to their desirable photophysical properties. The small fluorescent compounds are easily tunable and are stable in various conditions.[3-4] Exploiting fluorescent imaging has been a huge staple towards the advancements in detecting colorectal cancer, however development of robust fluorescent probes have been quite difficult. Fluorescent probes that possess excellent solubility, selectivity, and durability are difficult to derive. The desire of my research is to synthesize fluorescent BODIPY-peptidic probes that will rally the desired criteria for colorectal cancer detection. The research presented will focus on synthetic routes to achieving BODIPY-peptidic probes through click chemistry. This strategy allows the conjugation of peptidic ligands to BODIPY dyes to occur in a simple more efficient method at ambient temperatures. The click chemistry approach to BODPIY-peptidic conjugates will not only build a foundation for developing future BODIPY probes, but also eliminate past issues seen in synthesis of BODIPY-conjugates.[5-6] The conjugates will be investigated *in vivo* to determine their efficacy towards human colorectal adenocarcinoma cell lines HT-29.

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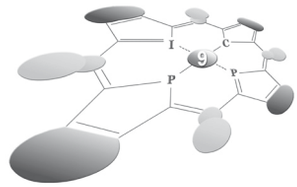

Peroxidase Activity of the Abeta-Heme Complex and Other Heme Binding Peptides

Amelie Wißbrock[a], **Toni Kühl**[b], **Oliver Ohlenschläger**[c] **and Diana Imhof**[a]

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The discovery of Fe(III) heme as an effector molecule has gained increasing attention within the last decades. So far a broad range of proteins such as the heme synthase ALAS-1, the human circadian factor Per-2 and the BK channel Slo 1 have been described as heme-regulated proteins (HRP). Transient Fe(III) heme binding to these proteins leads to a change of their activity and/or stability.[1] In 2006, heme binding to the Amyloid beta (Aβ) peptide was shown.[2] The peptide is well known from its significant role within the neurodegenerative disorder Alzheimer's disease (AD). Interestingly, the Aβ-heme complex possesses a peroxidase-like activity that might take part in the pathology of AD.[2] Within our previous studies we used a combinatorial peptide library approach that gave insight into the sequence specificities of heme-binding sites and eventually led to the prediction and identification of new heme-regulated proteins.[3-5] Our current work focuses on the possible peroxidase-like activity of distinct heme-peptide complexes. Therefore, several Aβ-derived peptides were synthesized and characterized with respect to their heme-binding behaviour as well as their potential peroxidase activity. In addition, a series of heme-binding peptides with different length and different coordinating amino acids was studied with respect to the possible enzymatic activity of the complexes. The results point to the impact of specific residues for the peroxidase activity within the Aβ-peptide. The examination of none Aβ-peptides indicates that besides the sequence length the coordinating amino acid and the sequence composition are relevant for the heme-induced enzymatic activity.

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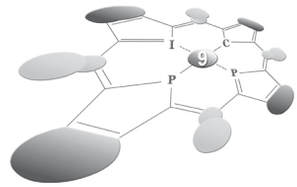

pH-Responsive Zinc(II) Phthalocyanine Dimers in Mesoporous Silica Nanoparticles as an Activatable Photosensitizing System for Photodynamic Therapy

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Photodynamic therapy (PDT) is a non-invasive therapeutic method for the treatment of cancer. Through the interactions of photosensitizers, light, and tissue oxygen, singlet oxygen can be generated to kill neighboring cells and tissues [1]. Much research effort has been devoted to developing sophisticated photosensitizing systems that can achieve tumor selectivity, improved efficacy, and less side effects. Mesoporous silica nanoparticles (MSN) have emerged to be promising nanocarriers to deliver photosensitizers for PDT. Due to their unique structural properties, they exhibit a number of advantages, such as high stability in blood circulation, high loading of theranostic agents, and enhanced permeability and retention effect [2]. Targeted delivery can also be achieved by anchoring different tumor targeting ligands onto the outer surface of MSN [3]. In this presentation, we will report the synthesis, characterization, and pH-responsive properties of MSN loaded with acid-labile zinc(II) phthalocyanine dimers for targeted PDT. The fluorescence intensity and singlet oxygen production of this photosensitizing system can be switched on in acidic condition. After the MSN are internalized into cancer cells, they exhibit much stronger intracellular fluorescence and much higher photocytotoxicity compared to their non-cleavable analogue, rendering this nanosystem a promising theranostic agent for cancer. The in vivo activation of this photosensitizing system will also be reported.

This work was supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region (Project No. 402212).

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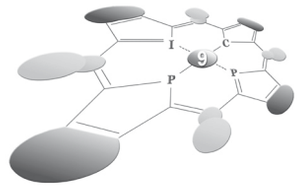

Synthesis and characterization of chlorin dimers

Ruisheng Xiong, Anna Arkhypchuk, Daniel Kovacs, Andreas Orthaber, Eszter Borbas

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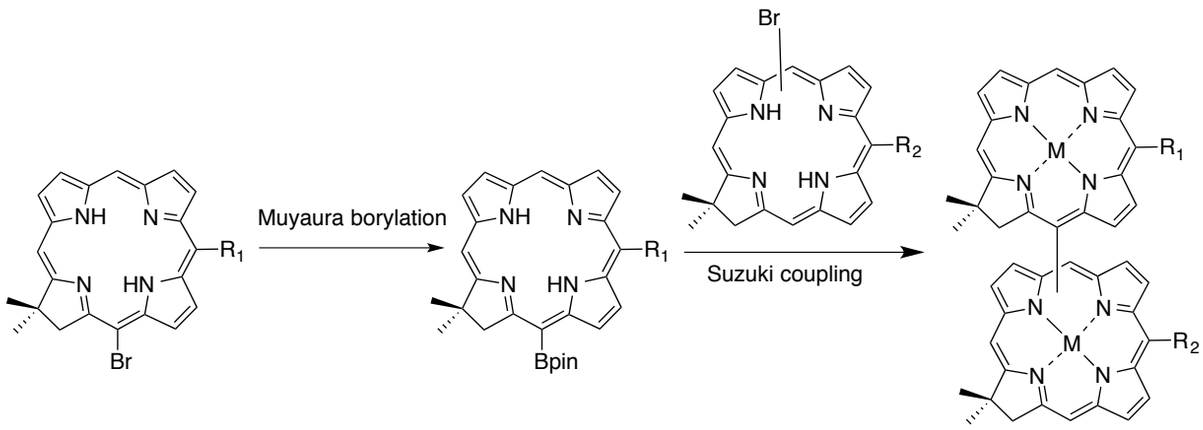
Directly linked porphyrin dimers have been investigated extensively[1]. However, their red-absorbing analogues based on hydroporphyrins (chlorins and bacteriochlorins) have gained very little attention due to the synthetic difficulties involved in preparing such structures. We accessed directly linked chlorin dimers via the Suzuki cross-coupling of chlorin-boronic acid derivatives with halogenated chlorins. Borylated chlorins were synthesized through Miyaura borylation[1b, 2] of the corresponding bromochlorins.[3] With these versatile intermediates a series of directly linked *meso-meso* and β-*meso* linked chlorin dimers were prepared. Metallation with Zn- or Pd-salts afforded the corresponding metal chelates. The photophysical properties of all dimers were investigated, and compared to those of monomeric reference species.



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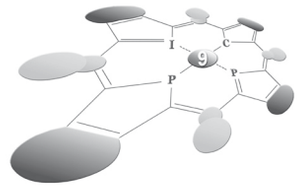
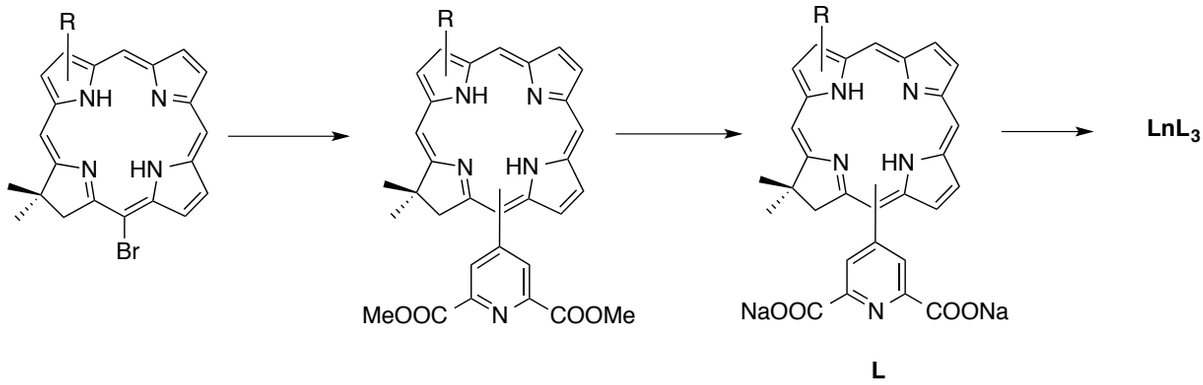


Hydroporphyrin sensitized NIR lanthanide luminescence

Ruisheng Xiong[a], **K. Eszter Borbas**[a]

[a]*Department of Chemistry, Ångström laboratory , Uppsala University, 75120, Uppsala, Sweden*

The spiked, often non-overlapping emission bands of the luminescent trivalent lanthanide ions (Ln) are attractive for multicolor imaging.[1] Yb and Nd, which emit in the near infrared (NIR) can be sensitized by hydroporphyrins (chlorins).[2,3,4] However, previously reported Ln-chlorin dyads have very poor water solubility, which renders characterization difficult, and is detrimental to the photophysical properties. To address this problem, we designed and synthesized a new class of water-soluble Ln-chlorin dyads.



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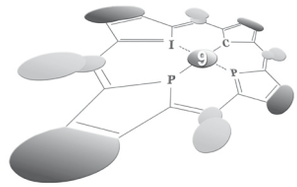

Design, synthesis and photophysical properties of multichromophores based on a truxene platform

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Truxene as a C3-symmetrically fused fluorene trimer, has attracted a great deal of interest. Recently synthesized truxene derivatives including a variety of star-shaped oligomers and dendritic structures with extended π-conjugations such as in light-emitting diodes (OLEDs), non-linear opticals (NLO), molecular wires, two-photon absorption (TPA) and fluorescent probes[1]. The truxene platform is used for the preparation of star-shaped multichromophoric dyes. Presently, extensive efforts have been devoted to develop artificial photosynthetic reaction centers, which can mimic the energy- and electron-transfer processes of photosynthesis. Porphyrins, Corroles and BODIPY dyes are well known for high molar absorbance, as well as high fluorescence quantum yield, good photostability and solubility which are usually utilized as photosensitizing electron donors. In addition, fullerenes C60 is excellent electron acceptors because of its outstanding photophysical and electrochemical features.

Herein, we describe a facile strategy to employ cross coupling reactions for preparing a novel star-shaped systems with three chromophores(Fig.1), in which truxenes are connected to fullerene C60 and Porphyrins, Corroles or BODIPY dyes. Their photophysical properties are being are currently under investigation.

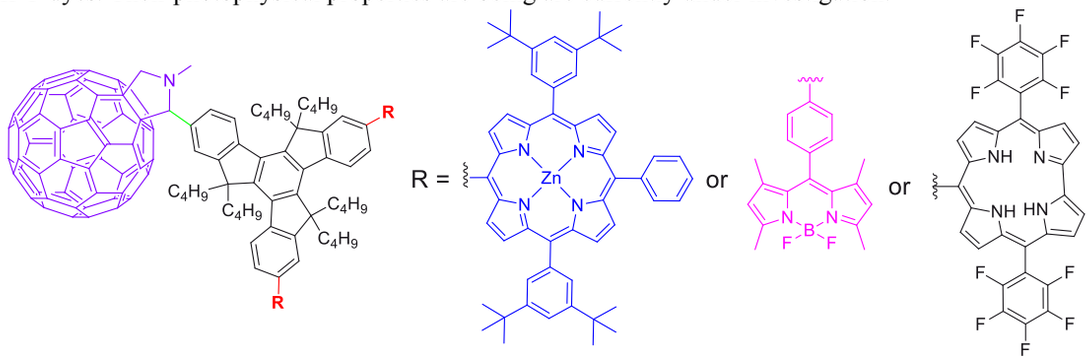

Fig. 1 Structures of the truxene-based dyads

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Self-floating Graphitic Carbon Nitride/Zinc Phthalocyanine Nanofibers for Photocatalytic Degradation of Contaminants in High Bankgrounds of Complicated Constituents

Tiefeng Xu, Dongjing Ni, Xia Chen, Fei Wu, Wangyang Lu*, Hongguang Hu, Zhexin Zhu, Wenxing Chen*

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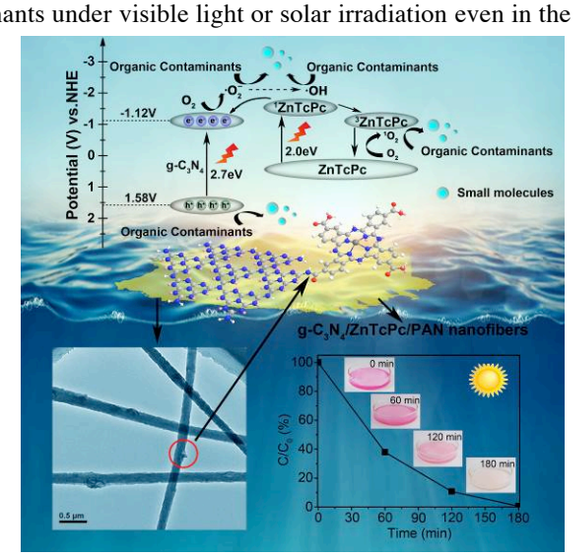
The massive amounts of emerging, anthropogenic contaminants which can raise considerable toxicological concerns in the apuatic environments is one of the key environmental problems afflicting people. The effective elimination of these contaminants in high bankgrounds of complicated constituents by an environmentally friendly method has received extensive attention in recent years. In this study, we prepared a photocatalyst based on polyacrylonitrile-supported graphitic carbon nitride coupled with zinc phthalocyanine nanofibers (g-C_3N_4/ZnTcPc/PAN nanofibers), by introducing g-C_3N_4/ZnTcPc as the catalytic entity and employing the PAN nanofibers as support to help the powder catalyst overcome the defects of easy aggregation and difficult recycling. Herein, Rhodamine B (RhB), 4-chlorophenol (4-CP) and carbamazepine (CBZ) were selected as the target model pollutants. Compared with the typical •OH-induced catalytic system, g-C_3N_4/ZnTcPc/PAN nanofibers displayed the targeted adsorption and degradation of organic contaminants under visible light or solar irradiation even in the presence of high additive concentrations. According to the results of the radical scavenging techniques and the electron paramagnetic resonance (EPR) technology, the degradation of target substrates were achieved by the attack of active species, including photogenerated hole, singlet oxygen ($^1O_2$), superoxide radical ($\bullet O_2^-$) and hydroxyl radical (•OH). The transformation of RhB and CBZ into some biodegradable small molecular acids has been also detected by ultra-performance liquid chromatography and high-definition mass spectrometry (UPLC Synapt G2-S HDMS). Therefore, this study not only presents a method for removing highly hazardous but low-concentration contaminants in high backgrounds of complex constituent, but also sets an example for the design of some photocatalytic systems based on the supported photocatalysts to apply on the real wastewater treatment.



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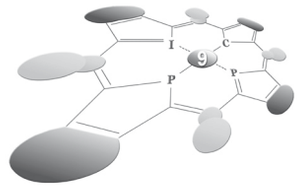

Electrochemistry of aryl-substituted tripyrrinone copper complexes in nonaqueous media. A comparison in redox poperties to the structurally related porphyrins and corroles

Weijie Xu[a], Lina Ye[a], Songlin Xue[a], Wenda Wang[a], Yuanyuan Fang[a], Zhongping Ou[a]*, Yang Song[b], Karl M. Kadish[c]*

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Four aryl-substituted tripyrrinone copper complexes were synthesized and characterized as to their electrochemistry and spectroelectrochemistry in CH_2Cl_2 containing 0.1 M tetra-*n*-butylammonium perchlorate as the supporting electrolyte. The examined compounds are represented as $(YPh)_3TPyO_2Cu$, where $TPyO_2$ is a dianion of the tripyrrinone and Y is a CH_3O, CH_3, H or Cl substitutent on the *para*-position of the three phenyl rings of the compound. The structures of compounds are shown in Chart 1 which also included the structures of related copper porphyrins and corroles with the sane meso-substituents. Each neutral copper tripyrrinone is ESR active and shows a typical d^9 Cu(II) signal in frozen CH_2Cl_2 solution. The Cu(II) compound undergoes three reductions between -0.61 and -1.90 V and two oxidations between 1.00 and 1.24 V vs SCE. The oxidation potentials are similar to that of copper tetraarylporphyrins but the reduction potentials are positively shifted as compared to the tetraarylporphyrins. Thus, the potential difference between the first one-electron ring oxidation and first one-electron ring reduction (HOMO-LUMO gap) of $(YPh)_3TPyO_2Cu$, which ranges from 1.68 to 1.75 V, is smaller than the separation of 2.30-2.37 V for the copper tetraarylporphyrins, or ~2.70 V for copper triarylcorroles under the same solution conditions. Support from the Natural Science Foundation of China (21501070) and Foundation of Jiangsu University (15JDG131, 05JDG051).

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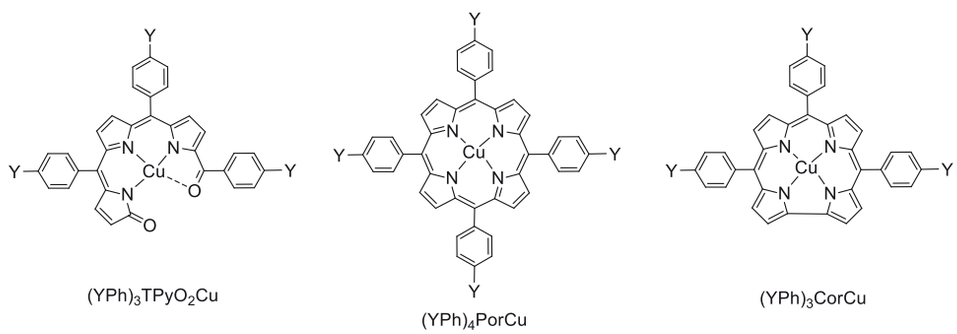

Chart 1. Structures of copper tripyrrinones, copper porphyrins and copper corroles.

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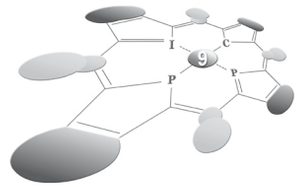

Synthesis and In Vitro Properties of a Series of Carborane-containing BODIPYs[1]

Sunting Xuan, Ning Zhao, Zehua Zhou, Frank R. Fronczek, and M. Graça H. Vicente

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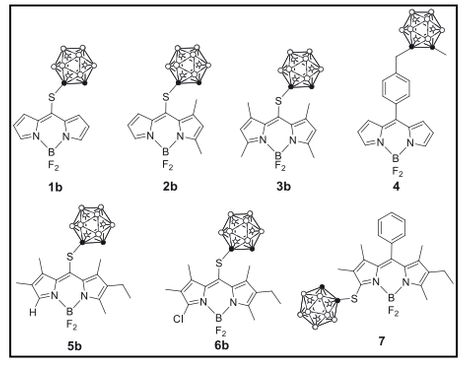
Boron neutron capture therapy (BNCT) is a very promising binary anticancer methodology, especially for the treatment of brain tumors.[2] One major challenge in the BNCT for brain tumors arises from the existence of the blood-brain barrier (BBB) that prevents most drugs from penetrating into the brain and from reaching the targeted tumor cells.[3] Two main characteristics are required for the passive diffusion of molecules across the BBB: 1) MW ≤ 500 Da, and 2) high lipophilicity (log P < 5).[3,4] Also, BNCT drugs need to be soluble in aqueous media to enable systemic administration.[5] Therefore, we designed and synthesized a series of 8 (*meso*)- and 5 (α)-*ortho*-carboranyl-BODIPYs with MW in the range 366-527 Da and log P in the range 1.5-2.7 from the corresponding halogenated BODIPYs by nucleophilic substitution. Their structures were characterized by ^{1}H-, ^{13}C- and ^{11}B-NMR, HRMS, and in the case of 2b and 5b by X-ray analysis. The purity of all compounds (> 95%) was determined by HPLC. Their cytotoxicity and cellular uptake were evaluated in human glioma T98G cells, and their BBB permeability was investigated in human hCMEC/D3 brain endothelial cells. All compounds exhibited low dark- and photo-toxicities and efficiently accumulated within T98G cells. All the compounds showed relatively higher BBB permeability compared to the Lucifer Yellow (LY) standard. The combination of low cytotoxicity, abundant boron moiety, and high BBB permeability render these carboranyl BODIPYs highly promising BNCT reagents used for brain tumors (e.g. glioblastoma multiforme).



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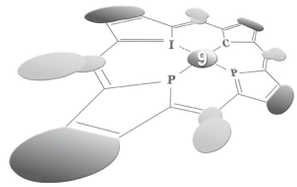

Synthesis and Structures of [14]Tribenzotriphyrin(2.1.1) Metal Complexes

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Subporphyrins are analogues of porphyrinoids that contain only three pyrrole or isoindole rings linked by meso-sp^2 carbon atoms. The first synthesis of tribenzosubporphyrins was reported by Osuka's group in 2006 with very harsh conditions. From then on, lots of subporphyrin analogues have been reported. However, almost all of these reported subporphyrins existed only as bowl-shaped boron complexes and the yields are typically very low (< 5%) due to the formation of tetraarylporphyrins and polymeric materials. In 2008, we reported a facile synthesis of meso-aryl-substituted [14]benzotriphyrin(2.1.1) compounds based on a modified Lindsey condensation method in moderate yields up to 35%.[1] These compounds represent the first example of near planar core-free contracted porphyrinoids with 14-π-electron aromatic systems containing only the standard pyrrole and isoindoline moieties. X-ray diffraction analysis revealed that the triphyrin core is near planar. Till now, eight kinds of [14]Triphyrin(2.1.1)-metal complexes have been synthesized and characterized including Ag(I), Mn(I), Fe(II), Re(I), Ru(II), Pd(II), Pt(II) and Pt(IV).[2-4]

Recently we have prepared another two kinds of metallotriphyrin complexes (Pd(II) and Rh(III)). As compare to the reported metallotriphyrin complexes Pd(II)-TriP shown deep saddle comformation while Rh(III)-TriP shown dome shape structure. [5-6]

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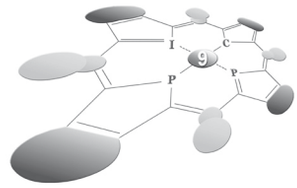

Chemo- and Regioselective Reduction of Diazaporphyrins

Ayaka Yamaji[a], Yoshihiro Miyake[a], Hayato Tsurugi[b], Kazushi Mashima[b], and Hiroshi Shinokubo[a]

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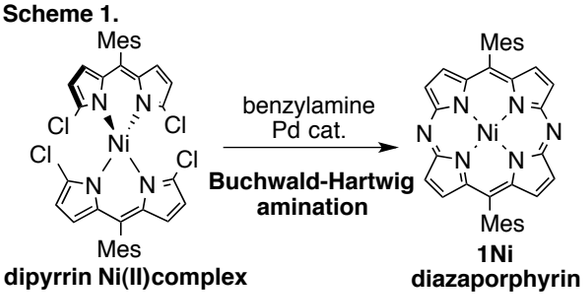
[b] *Department of Chemistry, Graduate School of Enginerring Scienece, Osaka University*

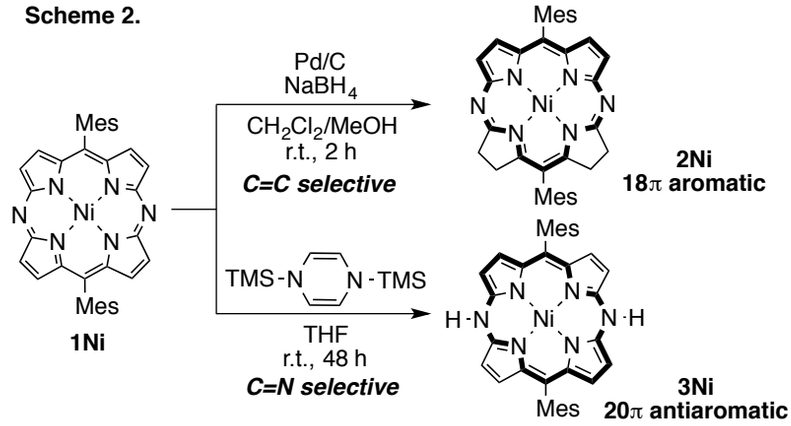
We have recently reported the synthesis of *meso*-aryl-substituted Ni(II) diazaporphyrin **1Ni** via Buchwald–Hartwig amination of a dipyrrin Ni(II) complex with benzylamine through C–N coupling.[1] This metal template strategy using dipyrrin metal complexes was found to be quite effective to create new types of porphyrinoids.[2]

Scheme 1.



Because diazaporphyrin is an electron deficient aromatic compound, we expected that the reaction of diazaporphyrin with reductants would provide novel porphyrinoids. Here, we have found that the reduction of diazaporphyrin **1Ni** with $NaBH_4$ provides isobacteriodiazachlorin **2Ni**. In sharp contrast, we have found that the reaction of diazaporphyrin **1Ni** with *N,N'*-disilyl-1,4-dihydropyrazine provides 20π antiaromatic dihydrodiazaporphyrin **3Ni** selectively.[3] We will present the structures and properties of reduction products and discuss antiaromaticity of dihydrodiazaporphyrins.

Scheme 2.



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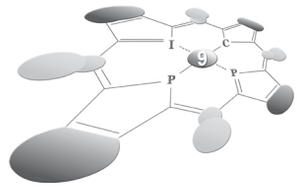

Self-assembled metal thioporphyrazine nanomicrospheres and their photocatalytic activity

Changjun Yang, Bingguang Zhang, Lanchang Gao, Kejian Deng*

Key Laboratory of Catalysis and Material Sciences of the State Ethnic Affairs Commission & Ministry of Education, College of Chemistry and Material Sciences, South-Central University for Nationalities, Wuhan, 430074, China. Tel: +8627-67843930; Fax:+8627-67842752; E-mail: dengkj@scuec.edu.cn;

Metal thioporphyrazines can activate O_2 under visible light irradiation at room temperature producing reactive oxygen species such as □OH, $O_2^{-\bullet}$ and $^1O_2$, which can efficiently degrade organic pollutants [1, 2]. In order to improve the utilization efficiency of sunlight and the recycling of the catalyst, metal thioporphyrazine nanomicrospheres were obtaioned by self-assembly. Zinc thioporphyrazine bearing eight functional outer chains and each with one terminal olefin group could form covalent bond, therefore, the uniform morphology of zinc thioporphyrazine nanomicrospheres were obtained by self-assembly, and the mean diameter of nanomicrospheres between 200 to 300 nm. The zinc thioporphyrazine nanomicrospheres also shown high photocatalytic activity for degradation of dye Rhodamine B (RhB) under mild conditions. Zinc thioporphyrazine nanomicrospheres are potentially useful as a biomimetic catalyst material for water treatment, which is beneficial to the actual application for catalyst in industrial production.

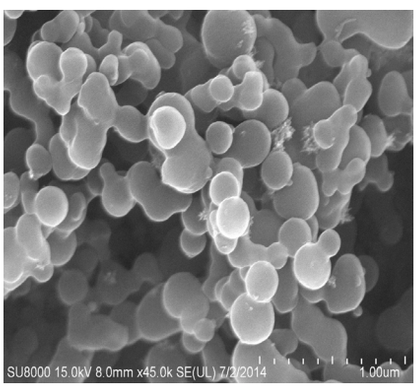

Figure 1：The SEM image of the self-assembled zinc thioporphyrazine nano microspheres

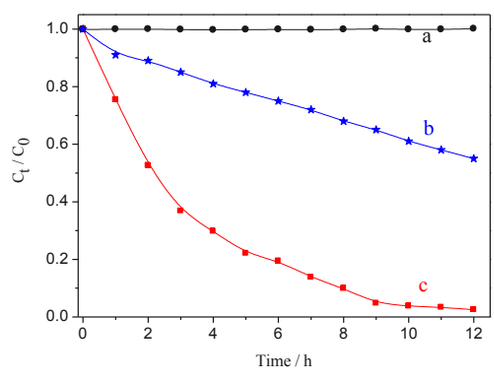

Figure 2：photocatalytic degradation of RhB. a: RhB/Nano sphere/Dark; b: RhB/Visible light; c: RhB/Nanosphere/ Visible light.

Acknowledgement: This work was financially supported by NNSFC(Nos. 20977115 and 21272281), the S&T Plan Innovation team for of Wuhan city (2015070504020220).

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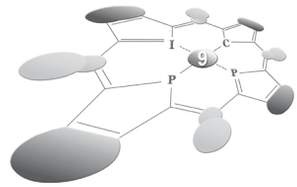

Valuable Metal-Ion Selective Binding Properties of Chemosensor Phthalocyanines

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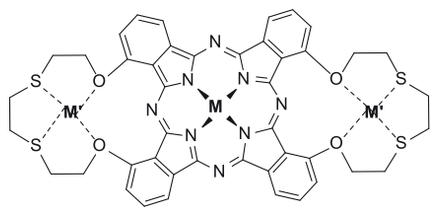
The molecular architecture of the phthalocyanines plays significant role in the binding process. The point of attachment of the substituent bound to Pc ring and their relative orientation in space should influence the ease of metal chelation because of the differences in inter substituent distances. It is of great significance to detect pollutants, such as heavy metal ions for environmental purposes. In this work, photophysical, photochemical and metal ion binding properties of phthalocyanine derivatives (M=Zn, and Co) containing 3,6-dithia-1,8 ocatediol substituents were investigated. Electronic spectra of the modified phthalocyanines exhibited distinct changes in the visible region, both absorbance and fluorescence, in response to treatment with metal ions in solution. Such properties make phthalocyanine derivative intriguing candidates for incorporation into the transducer layers in optically based chemical sensors[1-2].



M=Zn, Co, ; M'=Pd $^{2+}$, Ag^{+}

The structure of the desired complexes were characterized by the spectroscopic tecniques, such as UV-Vis, FT-IR, NMR, MS(MALDI-TOF).

We thank to research funds of SAÜ (BAP-2015,02-04-001), and TUBİTAK (114Z448).

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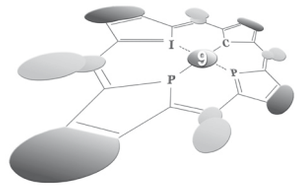

Covalent Immobilization of a Fluorescent Metal-Sensitive Ptholocyanine Dye in Sol–Gel Films

Orhan Güney[a] Mehmet Kandaz[b] and Meryem N. Yarasir[b]

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The immobilization of fluorescence probe into sol-gel silica supports for determination of metal ions has been recently attracted great attention [1]. The porosity of sol-gel matrices allows fluoroprobe to diffuse into the solid support. There are three methods of fluoroprobe immobilization: sol-gel impregnation, covalent binding and chemical doping. A covalent binding of the sensor ptholocyanine (Pc) on carrier matrices improves the practical use because it enables long-term measurements, avoiding leaching and a possible contamination of the sample under investigation.

Our investigations were carried out using a fluorescent metal sensitive Pc consisting of a derivative of Pc with functional groups. One group (isocyanate) is able to bind to a carrier material such as a sol–gel layer. The other functional group (Pc) serves for the receptor function for the detection of metal ions. The functionalized Pc moiety was appended to the functional precursor, 3-isocyanatopropyl triethoxysilane and hence a Pc functionalized silane was obtained. Sol-gel polymeric material was then prepared by a conventional one-pot method with the co-condensation of such Pc-based precursor and the cross-linker, tetramethoxysilane. The immobilization of a isocyanato-functionalized indicator Pc on sol–gel films was actualized by urethane bonding. The advantages of this glassy substrate, compared to hydrogels or polymers, are a wide variability of sol compositions, the formation of very thin films and a relatively simple synthesis of the sols. The sol–gel layers are applied on conventional glass slides by a spin-coating process. These resulting glassy substrates show a good mechanical stability and a transparency for visible light. We focused on the variation of the synthesis-especially concerning Pc concentration, the film thickness, and the resulting properties of the Pc-sol-gel substrate system.

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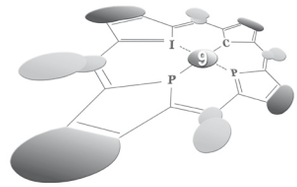

Conformational Fixation of A Rectangular Antiaromatic [28]Hexaphyrin Using Rationally Installed Peripheral Straps

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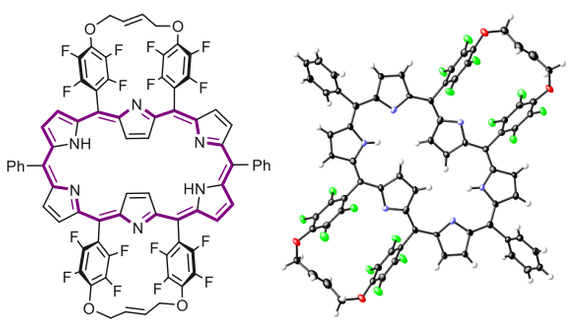
[c]*Graduate School of Science, Kyoto University*

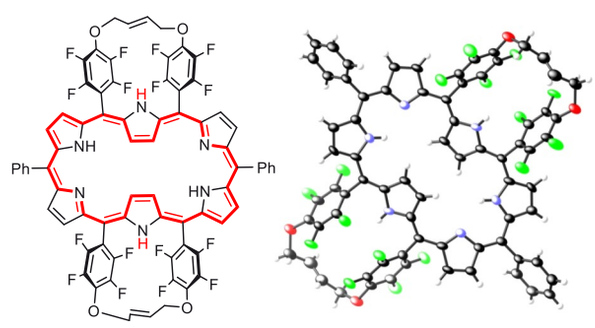
Expanded porphyrins, which have more than five pyrrole units, have been demonstrated to realize versatile electronic states as a consequence of combined characteristics of cyclic conjugated electronic systems and flexible conformations. In particular, [28]hexaphyrin is known to undergo fast conformational dynamics among twisted Möbius aromatic species and a planar Hückel antiaromatic species and displays a moderate diatropic ring current, reflecting the preferential contribution of the former.[1] We have been trying to freeze these structures and a few examples of locked Möbius aromatic systems of [28]hexaphyrins induced by peripheral fablications were already reported. However, on the other hand, metal-free Hückel antiaromatic rectangular [28]hexaphyrins still remain rather limited because of the intrinsic difficulty in locking in planar structures for [28]hexaphyrin without metal coordination.

This time, we show that the conformations of [28]hexaphyrin is fixed by peripheral straps on aryl groups. Using S_NAr-type substitution reaction of 5,20-diphenyl-10,15,25,30-tetrakis(pentafluorophenyl) substituted [26]hexaphyrin with aryl alcohol and subsequent olefin metathesis with Hoveyda-Grubbs catalyst 2nd generation, we obtained a [26]hexaphyrin **1** with peripherally-strapped aryl groups. In the next step, **1** was reduced with $NaBH_4$ to furnish a [28]hexaphyrin **2**.

It is notable that **2** takes on not flexible Möbius-dominated conformations but a rigid rectangular conformation and hence show strong Hückel antiaromaticity. Hückel antiaromatic character of **2** was probed by its X-ray structure, a strong paratropic ring current, characteristic UV/Vis/NIR absorption features, small electrochemical HOMO—LUMO gap, and very fast S_1-decay.



[26]Bridged Hexaphyrin 1
(*Aromatic*)



[28]Bridged Hexaphyrin 2
(*Antiaromatic*)

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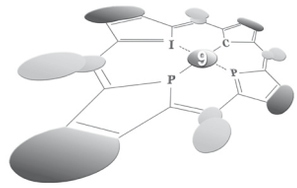

Tetrabenzonorcorrole: a benzo-fused 16π antiaromatic porphyrinoid

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Recently, we have reported a facile synthesis of Ni norcorrole (**Nc**), which is an antiaromatic porphyrinoid with a 16π electron conjugation system (Figure 1a).[1] The simple structure and exceptionally stable character of **Nc** enable design of a variety of novel antiaromatic compounds with unique structures and properties.[2,3]
It is well known that benzo-fusion for peripheries of porphyrinoids greatly influences their properties and electronic structures, as represented by tetrabenzoporphyrin (**TBP**).[4] Thus, in this work we have attempted to synthesize benzo-fused **Nc** "tetrabenzonorcorrole (**TBNc**)", to disclose effects of benzo-fusion on the antiaromatic porphyrinoid core and changes of its properties.
For the synthesis of **TBNc**, we employed the synthetic methodology to obtain **TBP**, in which peripheral benzene rings are formed by retro Diels-Alder reaction of bicyclic skeletons. The precursor norcorrole **1** fused by bicyclic skeletons was prepared in several steps, and **TBNc** could be synthesized by heating a solid sample of **1** (Figure 1b) under the optimized conditions by thermogravimetric (TG) analysis. The ^{1}H NMR spectrum of **TBNc** showed signals that can be assigned to protons attached to benzene rings in the significantly high field region (3.5-0.5 ppm), supporting the strong antiaromaticity of **TBNc**. The structure of **TBNc** was unambiguously elucidated by X-ray crystal analysis (Figure 2). Interestingly, bond alternation of **TBNc** was reduced than that of **Nc** in the crystal structures. DFT calculations suggested that the strong antiaromaticity and the reduced bond alternation of **TBNc** can be attributed to change in the frontier orbitals by benzo-fusion for **Nc**. Spectrochemical and electrochemical studies will be also reported in the presentation.

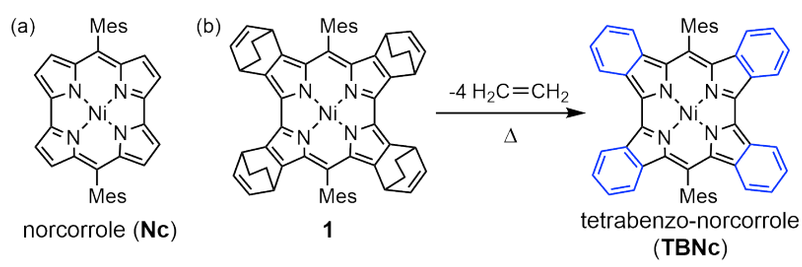

Figure 1. (a) Structure of **Nc** and (b) synthesis of **TBNc**.

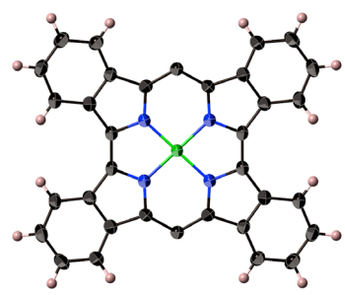

Figure 2. Crystal structure of **TBNc**.

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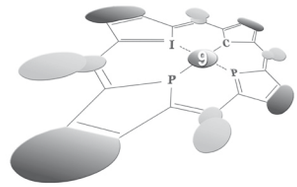

Syntheses and Properties of Novel Linear Tetrapyrroles and Pentapyrroles with Red or Near-Infrared Absorption

Changjiang Yu[a], Qinghua Wu[a], Lijuan Jiao*[a] and Erhong Hao*[a]

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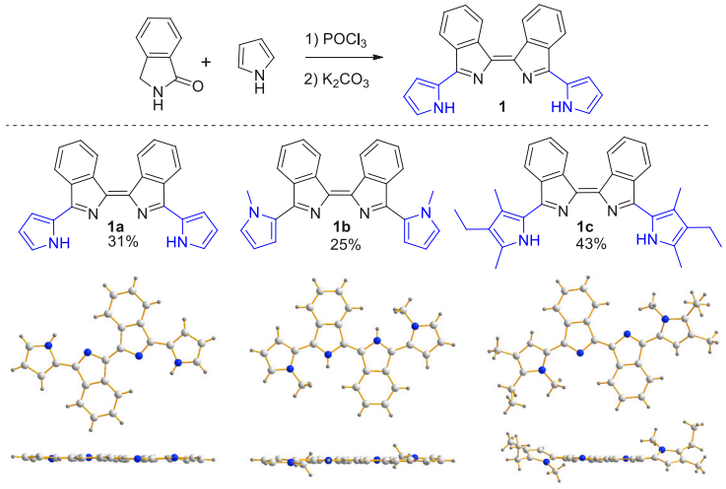
Conjugated oligopyrroles are the core component of many natural products such as tetrapyrrolic porphyrins, expanded porphyrins and prodigiosins.[1] They have attracted considerate research interest currently due to their rich chemical properties and found wide applications in organic synthesis, medicinal chemistry, material science and nanotechnology as near-infrared dyes, anion sensors and photosensitizers.[2] Great efforts have been devoted into developing new synthetic methods for various interesting cyclic and linear oligopyrroles.[3] However, most of the methodologies for them usually require relatively elaborate multistep syntheses, starting from useful pyrrole intermediates.[4]

Herein, we demonstrate the facile syntheses and properties of a novel linear tetrapyrroles and pentapyrroles in relatively decent yields from easily available isoindole-1-one with pyrrole or indole derivatives under mild Lewis acid conditions with no catalyst needed and diversity oriented. The resultant linear tetrapyrroles and pentapyrroles are interesting red and blue pigments with absorption maxima up to 750 nm.



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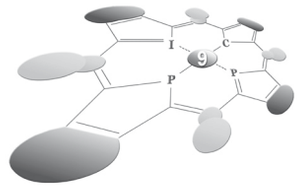

Sonodynamically Induced Apoptosis by 5-Aminolevulinic acid

Nagahiko Yumita[a], Yumiko Iwase[a], Koji Nishi[a], Takahiro Watanabe[a], Junya Fujimori[a], Toshio Fukai, Hiroyuku Kuwahara[a] and Shin-ichiro Umemura[b]

[a] *Yokohama University of Pharmacy, Yokohama*
[b] *Department of Electrical and Communication Engineering, Tohoku University*

Background: Sonodynamic therapy of cancer is based on preferential uptake and/or retention of a sonosensitizing drug (sonosensitizer) in tumor tissues and subsequent activation of the drug by ultrasound irradiation. Recently, we found that photochemically active porphyrins such as hematoporphyrin, protoporphyrin, Porfimer Sodium and a gallium porphyrin complex can induce significant antitumor effect when activated by ultrasound. 5-aminolevulinic acid (5ALA) has been reported to induce protoporphyrin. In this study, we investigated sonodynamically induced apoptosis in HL-60 cells by.
Methods: Cells were incubated for 4 h with 5ALA and then exposed to 2 MHz ultrasound in the presence or absence of 5ALA. Apoptosis was assessed according to cell morphology, DNA fragmentation, and the measurement of caspase–3 activity. Pprotoporphyrin was also measured using fluorescence spectrometry.
Results: Cells treated with TS and ultrasound clearly showed apoptosis associated with morphological change, DNA ladder formation and caspase–3 activation. On the other hands, significant morphologic changes, DNA ladder formation and caspase–3 activation were not observed in cells exposed to either ultrasound or 5ALA alone. Sonodynamically induced apoptosis and caspase–3 activation, were significantly suppressed by histidine, a scavenger of reactive oxygen species.
Conclusion: In this study, we demonstrated sonodynamically induced apoptosis in HL–60 cells, as evidenced by morphological changes and caspase–3 activation. 5ALA induced protoporphyrin was measured after 4 h incubation using fluorescence spectrometry. The significant reduction by histidine in the number of sonodynamically induced apoptotic cells and caspase–3 activation suggests that ultrasonically generated singlet oxygen is an important mediator of sonodynamically induced apoptosis. The results reported in this study may be preliminary, but they significantly support the possibility of in vivo induction of apoptosis by sonodynamic treatment using 5ALA.

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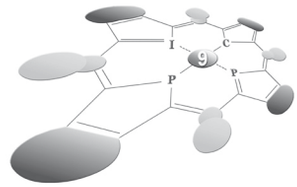

Preparation and characterization of photodynamic antimicrobial P(MMA-co-MAA)/MMT electrospun nanofibers for wound dressing

Quan Zhang[a], Yaxuan Dai, Jiancheng Dong, Qingqing Wang*

[a] *Key Laboratory of Science and Technology of Eco-Textile, Ministry of Education , Jiangnan University, Wuxi, Jiangsu 214122, China*

Chronic wound requires longer time to heal completely, so it may easily cause infection, posing a great threat to people health. Thus a new type of wound dressing material with favorable antimicrobial properties becomes particularly important. In this topic, photosensitizers were immobilized within and also onto the surface of electrospun P(MMA-co-MAA)/MMT nanofibers, by which the nanofibers were endowed with photodynamic antimicrobial properties. Solution intercalation followed by electrospinning technique was employed in this process to prepare P(MMA-co-MAA)/MMT composite nanofibers, the carboxyl groups and montmorillonite（MMT）of which were used to adsorb cationic photosensitizers to fabricate photodynamic antimicrobial nanofibrous membrane, and the fibrous structure and their diameter distribution were optimized[1]. The biocompatibility and antimicrobial behavior of the as-prepared material were evaluated. The results indicated that the addition of MMT decreased the diameter of the nanofibers, and the electrospun P(MMA-co-MAA)/MMT nanofibrous membrane showed good adsorption capacity of photosensitizers. P (MMA-co-MAA)/MMT composite nanofibers showed good biocompatibility[2], and after immobilization of the [meso-tetrakis (N-methylpyridinium-4-yl) porphyrin] Zn(Ⅱ) (Zn-Por), the antibacterial effect against *Staph. Aureus* can reach 99.95%. The latest results on the application of these materials immobilized with other photosensitizers against *Staph. Aureus* and *Escherichia coli* will also be presented.

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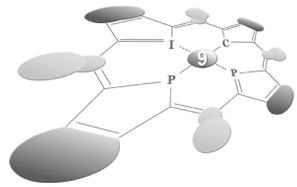

Chromophorylation of subunits A and B of allophycocyanin from *Chroococcidiopsis thermalis* sp. PCC7203

Qian-Zhao Xu[a], Bao-Qing Zhao[a], Lu Lu[a], Pan-Pan Peng[a], Dan Miao[a], Wen-Long Ding[a], Ming Zhou[a], Hugo Scheer[b], Kai-Hong Zhao[a]

[a]*State Key Laboratory of Agricultural Microbiology, Huazhong Agricultural University, Wuhan 430070, P.R. China*
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Biliproteins are photoreceptors with linear tetrapyrrole (bilin) chromophores. They are divided into two groups: light-harvesting phycobiliproteins, and photosensors of the phytochrome family. Phycobiliproteins harvest light and then transfer the excitation energy to photoactive reaction centers. In cyanobacteria and red algae, phycobiliproteins are organized into heterohexamers, $(\alpha\beta)_3$, which are then assembled to phycobilisomes, highly ordered light-harvesting complexes. Phycobilisomes consist of a core and several rods. The core comprises several allophycocyanin (APC) subunits (ApcA, ApcB, ApcD, ApcE and ApcF), which are chromophorylated with phycocyanobilin (PCB). *Chroococcidiopsis thermalis* sp. PCC7203 is capable of growing under near-infrared light (NIR). Acclimated cells contain phycobilisomes with extremely red-shifted components absorbing >700 nm [1]. Under these conditions, a set of genes is expressed that code for several alternative APC subunits (ApcA2, ApcA3, ApcB2 and ApcB3) that do not exist in white-light grown cells. We expressed these genes in *E. coli* capable of synthesizing PCB. ApcA2, ApcA3, ApcB2 and ApcB3 could covalently bind PCB under the catalysis of CpcS1 from *Chroococcidiopsis thermalis* sp. PCC7203. The chromophorylated subunits, PCB-ApcA2, -ApcA3, -ApcB2 and –ApcB3 absorbed maximally around 610 nm, and fluoresced maximally around 640 nm, which is similar to subunits A and B of conventional APC. Only ApcB2 could also bind PCB smoothly in the absence of CpcS1; the autocatalytic product is the same as that generated in the CpcS1-catalyzed reaction. In the absence of CpcS1, chromophorylation of ApcA2 did scarcely take place, that of ApcA3 generated traces of an autocatalytic product (λ_{Amax} = 615 nm, λ_{Fmax} ~ 642 nm), and that of ApcB3 resulted in spontaneous formation of a red-shifted product (λ_{Amax} = 635 nm, λ_{Fmax} ~ 660 nm).

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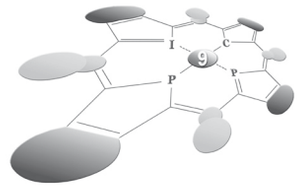
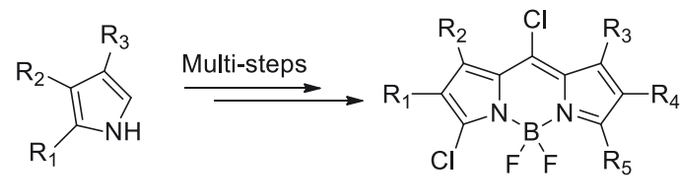


Synthesis and reactivity of 2,8-dichloro- and 2,3,5,6,8-pentachloro-BODIPYs and investigation of the regioselectivities of the reactions

Ning Zhao, Sunting Xuan, Frank R. Fronczek, Kevin M. Smith, M. Graça H. Vicente

Louisiana State University, Baton Rouge, LA 70803



1:R_1=COOBn, R_2=R_3=Me; **3**:R_1=R_2=R_3=R_5=Me; R_4=Et
2:R_1=R_2=R_3=H; **4**:R_1=R_4=R_5=Cl; R_2=R_3=H

The asymmetric and symmetric polychlorinated BODIPYs (4,4-difluoro-4-bora-3a,4a-diaza-s-indacenes), platforms 3 and 4 were synthesized from dipyrroketones which were obtained from pyrroles 1 and 2, respectively, in multi steps synthesis. BODIPYs 3 and 4 both contain one chloro group at the 8-position, and additional chloros at the 3 or 2,3,5,6-positions. Pd(0)-catalyzed Stille and Suzuki cross-coupling reactions using several organostannanes or boronic acids, as well as nucleophilic substitution reactions with N-, O-, and S-centered nucleophiles, were used to study the reactivity and selectivity of the different chloro groups. The most reactive was the 8- chloro group, followed by the 3,5-dichloro groups, and the 2,6-dichloros were the least reactive. On the other hand, the reactivity of the 5-methyl group of BODIPY 3 was investigated by using a Knoevenagel condensation and a oxidation reaction with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). These reactions successfully converted the 5-methyl to a styryl group and a 5-formyl group, respectively. The photophysical and structural properties of the new generated BODIPYs were studied and will be discussed.

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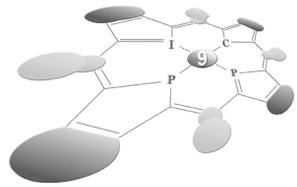
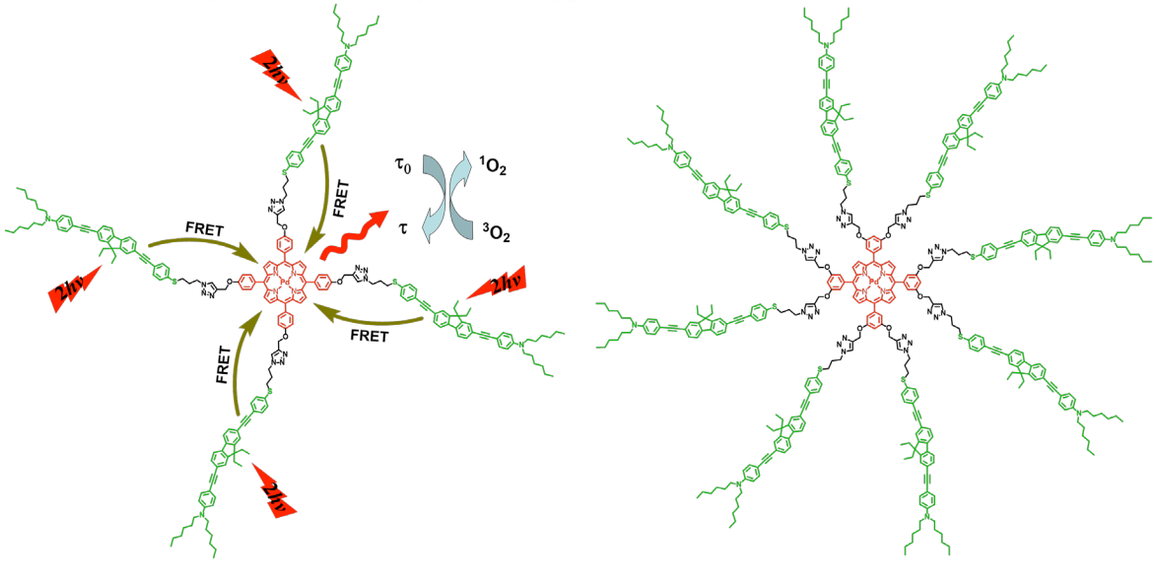


Design of Two-Photon Absorbing Probes for the In-Vivo Monitoring of Oxygen Pressure

Zheng Zheng[a], **Yann Bretonnière**[a], **Chantal Andraud**[a]

[a]*Laboratoire de Chimie de l'Ecole Normale Supérieure de Lyon, 46 allée d'Italie, 69007 Lyon, France*

Oxygen-dependent quenching of phosphorescence is a widely used method for imaging of oxygen in biological systems. Recently, the synergy of phosphorescence quenching with two-photon microscopy has emerged because two-photon excitation can greatly improve the penetration depth and spatial resolution for both imaging and therapy. The most interesting phosphorescent probes are palladium complexes of porphyrins. Unfortunately, direct coupling of phosphorescence with two-photon microscopy is hampered by the extremely low two-photon absorption cross-sections (10-50 GM) of palladium porphyrins complexes. In order to solve this problem, Vinogradov and Prasad have developed an original approach consisting in grafting efficient two-photon chromophores on the central porphyrin complexes to efficiently enhance the cross-section *via* an antenna effect.[1, 2] In our study, four new fluorene-based two-photon absorbing (TPA) chromophores have been synthesized and their one- and two-photon photophysical properties have been investigated. An optimum chromophore was successfully attached covalently to a central palladium porphyrin complex *via* click reaction. Compounds **1** and **2** demonstrate that the incorporation of a suitable donor chromophore can enhance the effective TPA cross section of the system, allowing efficient sensitivity towards oxygen at 800 nm.



1 **2**

FRET = 98.9 % 98.3 %

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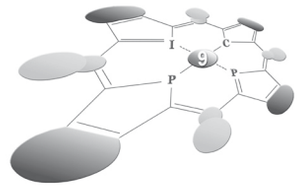

Development of Novel Near-infrared Fluorescent Probes for Subcellular Imaging

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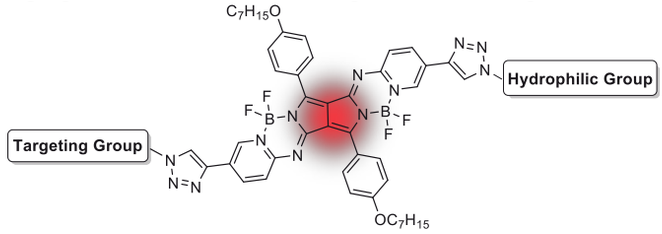
[b] *Department of Biomedical Sciences, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China Email: dkpn@cuhk.edu.hk*

There has been considerable interest in the development of near-infrared (NIR) absorbing and emitting dyes due to their many promising applications. In particular, these materials are widely used in bioimaging owing to their advantageous properties that allow reduced auto-fluorescence and deeper light penetration into biological tissues.[1] Recently, pyrrolopyrrole aza boron dipyrromethenes (PABDPs) have been prepared by treating diketopyrrolopyrrole with hetero-aromatic amines in the presence of titanium tetrachloride.[2] These compounds exhibit intense absorption and fluorescence in the NIR region, as well as a relatively high photostability. These properties suggest that they are promising candidates for potential applications in molecular optoelectronics and biomedicine.

Recently, we have prepared two PABDP derivatives that can be used for subcellular imaging (see the general structure as below). A deeper understanding of the role of and processes in each subcellular organelle is a basic issue for exploration of pathologies of various diseases and for discovery of more potent medicines.[3] Mitochondria and lysosomes are important organelles. The former are the principal energy-producing compartments in most cells, playing an important part in numerous vital cellular processes.[4] The latter are the hinge in regulating cellular metabolic capabilities, which involve accepting intracellular cargo from each autophagy.[5] Consequently, mitochondrion-staining and lysosome-staining reagents and techniques are important in biomedical research and diagnostic applications. Although a number of fluorescent dyes are commercially available for this usage, only a few are in the long-wavelength range. In this presentation, we will report the synthesis and spectroscopic properties of these fluorescent probes and their performance in subcellular imaging.



The general structure of PABDP-based subcellular imaging agents

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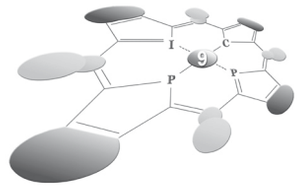
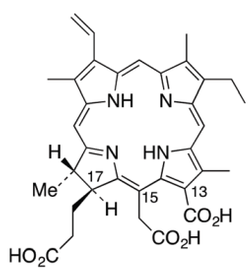


Cellular uptake and cytotoxicity of di-aspartate and aspartate-lysine chlorin e_6 conjugates

Zehua Zhou, R. G. Waruna Jinadasa, M. Graça H. Vicente and Kevin M. Smith

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA

Chlorin e_6 is a degradation product of chlorophyll a. Four chlorin e_6 di(amino acid) conjugates were synthesized containing two aspartate groups at the 13^1,17^3- position, 15^2,17^3-positions, or at the 13^1, 15^2 positions, or two different amino acids, lysine at 13^1 and an aspartate at 15^2 positions.[1] The cell uptake and cytotoxicity of four di(amino acid) chlorin e_6 conjugates were studied in human HEp_2 cells, and compared with chlorin e_6. The cells were quantified using the CyQuant Cell Proliferation Assay. The Cell Titer Blue Assay was used to determine its toxicity[2]. The zwitterionic 13^1, 15^2-disubstituted chlorin e_6 conjugates had higher cell uptake, and were more cytotoxic than chlorin e_6, with phototoxicity IC_{50} 9 to 11 μM using light dose approximately 1.5 J/cm^2. In contrast, the anionic 13^1, 17^3- and 15^2, 17^3-di-aspartyl chlorin e_6 conjugates had lower cell uptake, and were less cytotoxic than chlorin e_6, with phototoxicity IC_{50} 26 to 35 μM at 1.5 J/cm^2. These conjugates were mostly localized in the Lysosome and Golgi apparatus, with smaller amounts in the ER.[1,2]



chlorin e_6

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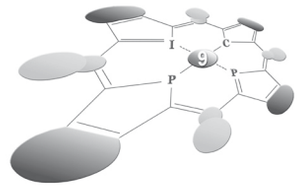

Synergistic Coupling of Fluorescent "Turn-Off" with Spectral Overlap Modulated FRET for Ratiometric Ag^+ Sensor

Mengliang Zhu[a], **Yabin Zhou**[b], **Liguo Yang**[a], **Lin Li**[a], **Dongdong Qi**[a], **Ming Bai**[c], **Yuting Chen**[d], **Hongwu Du***[b], **and Yongzhong Bian***[a]

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A useful strategy for ratiometric fluorescent detecting of Ag^+ is demonstrated. Upon selective binding of Ag^+ to a BODIPY-porphyrin dyad (**1**), the synergistic coupling of two functions, namely the suppressing of FRET from BODIPY donor to porphyrin acceptor and the fluorescence quenching of porphyrin acceptor, leads to exceptionally large changes in the intensity ratio of two distinct emissions (F_{513}/F_{654}) which allow for the ratiometric detecting of Ag^+ with excellent sensitivity in solution and living cells.

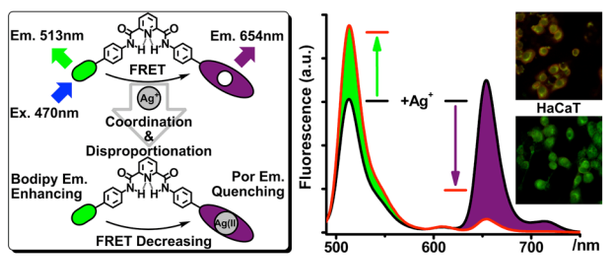

Figure 1. Ratiometric fluorescent detection of Ag^+ by FRET-based BODIPY-porphyrin dyad (**1**).

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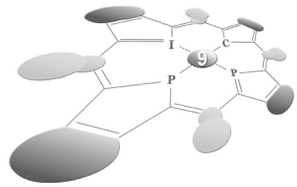

Synthesis and Electronic Structure of Zinc(II) Porphyin Dimers with a Bridging Amide-Bonded Xanthene Moiety

Xu Liang[a], Minzhi Li[a], John Mack[b], Nagao Kobayashi[c] and Weihua Zhu[a,*]

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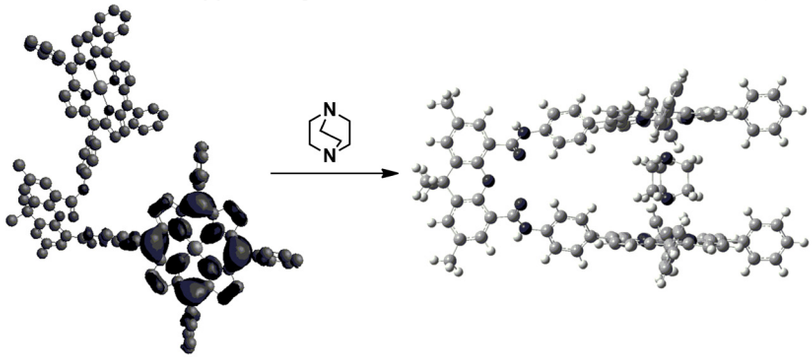
Porphyrin oligomers with macrocyclic rings that are covalently linked in a cofacial configuration have received considerable attention in recent years due to their unique electronic structures and novel optical properties. Several types of conjugated porphyrin oligomers have been reported such as, doubly- or triply-fused co-planar porphyrins, alkyne-bridged porphyrin strands, and p-phenylene-bridged twisted/planar porphyrin dimers. Interest of porphyrin dimers with linking moieties, especially those that adopt a face-to-face manner has been increasing in recent years. Porphyrin dimers with face-toface conformations exhibit an increased ability to bind two metals ions in a suitable geometry, opening up the possibility of mimicking the activity of heme and nonheme iron and copper-binding bioproteins such as oxidase, oxygenase, and oxygen transport proteins, which have binuclear active sites. In this Poster presentation, A free base porphyrin dimer bridged by a flexible amide-bonded xanthene moiety and its binuclear zinc(II) complex zinc(II) complex were synthesized and characterized. Electronic structure of these two compounds were well characterized by spectroscopy, electrochemistry and theoretical calculations[1].

In addition, an in-depth study of the electronic structure of a 1,4-diazabicyclo[2.2.2]octane (DABCO) induced molecular self-assembled xanthene-bridged and amide-bonded porphyrin dimer is also reported[2]. Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations are used to identify trends in the optical spectroscopic properties. B3LYP geometry optimization predicts the formation of an almost perfectly eclipsed structure with respect to the two porphyrin rings with the analogous pyrrole nitrogens separated by 7.7–8.1 Å

Acknowledgments: This work was supported by the Natural Science Foundation of China (No. 21171076).



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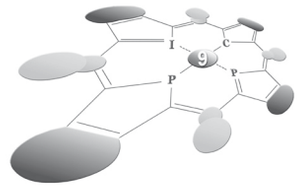

Synthesis and Properties of Xanthene Bridged Amide-Bonded Maganese(III)Porphyrin Dimers

Weihua Zhu*, Minzhi Li, Li Xu and Xu Liang*

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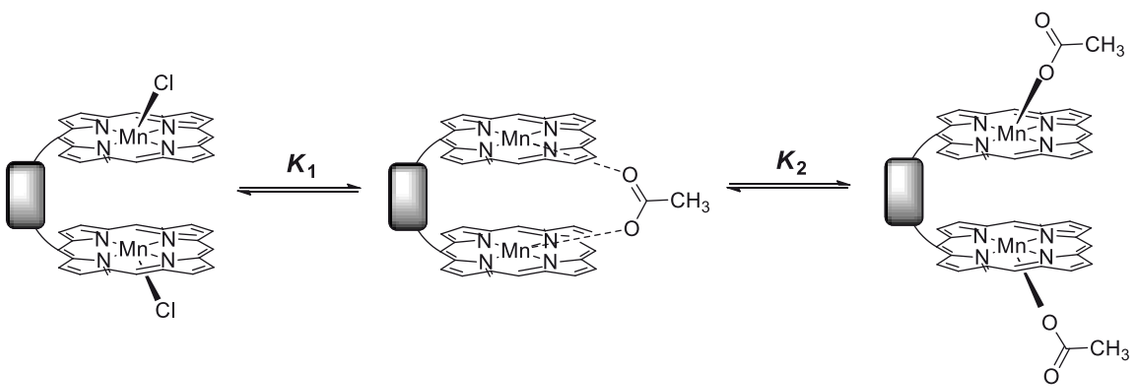
Research interests of porphyrin dimers with linking moieties, especially those that adopt a face-to-face manner has been increasing in recent years. Porphyrin dimers with face-toface conformations exhibit an increased ability to bind two metals ions in a suitable geometry, opening up the possibility of mimicking the activity of heme and nonheme iron and copper-binding bioproteins such as oxidase, oxygenase, and oxygen transport proteins, which have binuclear active sites. Xanthenes, have found widespread use as synthetic dyes in a wide range of applications, and their spectroscopic properties have been extensively studied. Xanthene moieties have usually been introduced to porphyrin arrays through direct C–C bonds at the meso-positions and the electronic structures, and optical and magnetic properties of these compounds have been studied in depth. In contrast, porphyrin xanthenes with flexible bridges such as alkyl chains and amines have received considerably less attention, and their spectroscopic properties and electrochemical properties have not been reported. Our own interests here are focused on the xanthene bridged amide-bonded porphyrin dimer containing manganese(III)Cl metal center, and we will explain how anion and solvent binding will affect redox potentials and axial ligation of this flexible Mn(III)porphyrin dimer and now turn our attention to the spectroscopy, electrochemistry, spectroelectrochemistry, and ligand binding properties.

Acknowledgments: This work was supported by the Natural Science Foundation of China (No. 21171076).



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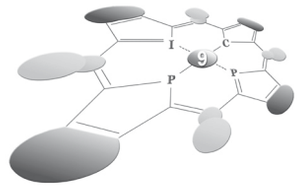

Application of Iron polyphthalocyanine as a highly oxygen reduction reaction catalyst in fuel cell

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Metal-phthalocyanine (MPc) macrocyclic have been perceived as promising alternatives to Pt and Pt-based catalysts for oxygen reduction reaction (ORR). Particularly, iron phthalocyanine (FePc) exhibits excellent ORR activity in comparison with other central MPc complexes. However, the application of FePc is hampered by its instability during ORR and low ectric conducticity. Therefore, the larger conjugate structure of iron polyphthalocyanine (FePPc) is synthesized, and mixed with multi-walled carbon nanotubes (MWCNTs), which facilitate electron transfer through π-π interaction to improve the conductivity of the composite material (FePPc/MWCNTs). Then, the composite material is pyrolyzed at 800°C in a Ar atmosphere to improve the catalytic activity and stability. The morphology of the synthesized FePPc/MWCNTs-800 is observed by high resolution transmission electron microscopy (HRTEM), and the results show that the FePPc forms a uniform coating on the surface of MWCNTs. The electrocatalytic activity is measured using a rotating disk electrode (RDE) technique, the FePPc/MWCNTs-800 exhibits a four-electron transfer process, the best ORR activity (E_{ORR} = 0.79V vs. RHE) and remarkably stability (current loss = 13% after 55h). X-ray photoelectron spectroscopy (XPS) indicates that the pyridine-type nitrogen in FePPc/MWCNTs-800 plays an important role in the ORR activity. X-ray absorption fine structure spectroscopy (XAFS) reveals that the structure of phthalocyanine ring is destroyed through heat-treatment, but the coordination geometry around Fe is closer to the square planar Fe-N_4 structure, which demonstrates the active sites in the catalyst should be Fe-N_4.

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