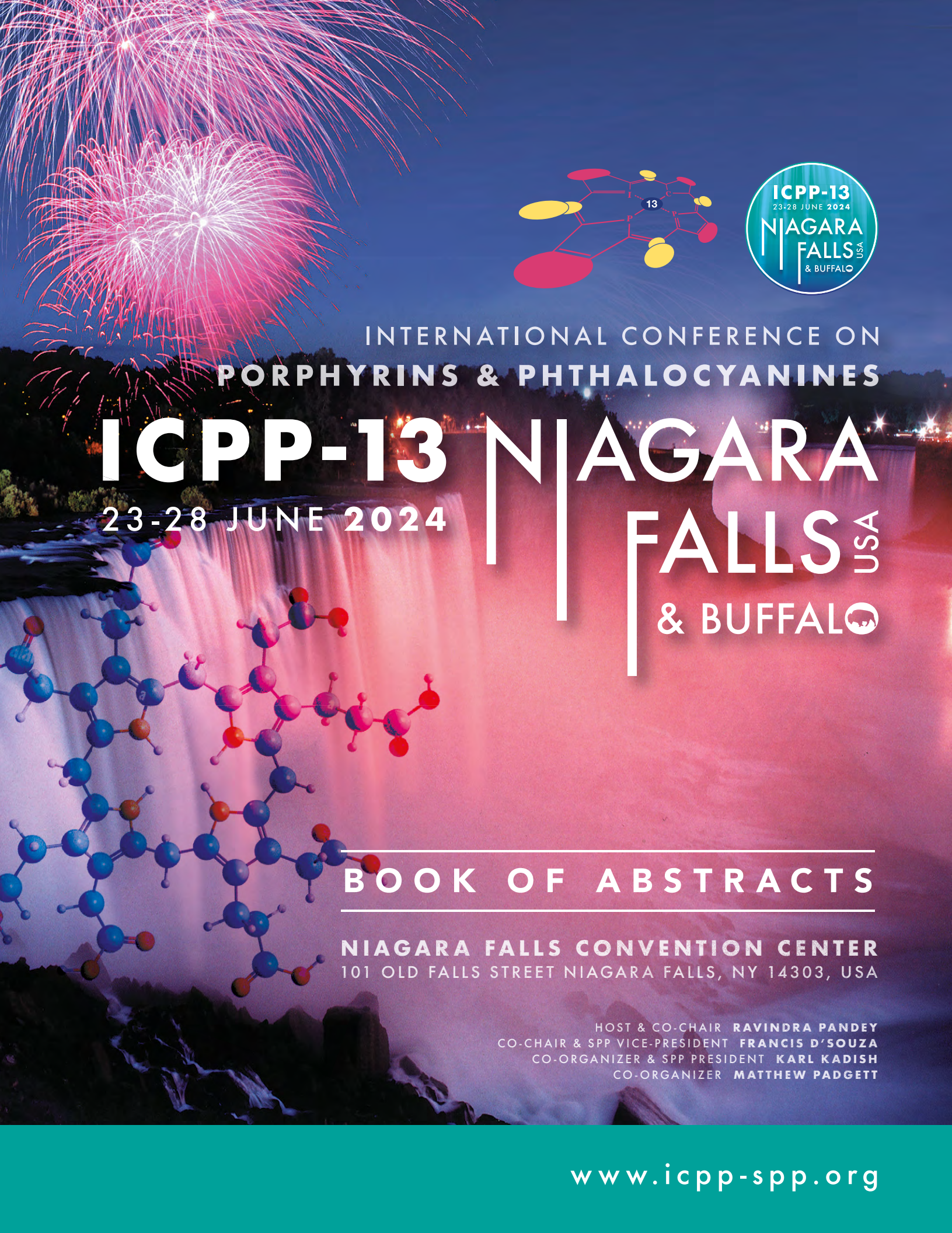

INTERNATIONAL CONFERENCE ON

PORPHYRINS & PHTHALOCYANINES

ICPP-13

23-28 JUNE 2024

NIAGARA FALLS USA & BUFFALO

BOOK OF ABSTRACTS

NIAGARA FALLS CONVENTION CENTER

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Preface

In this book are gathered together all the abstracts of presentations given at the thirteenth International Conference on Porphyrins and Phthalocyanines (ICPP-13) 23-28 June 2024 in Niagara Falls & Buffalo, NY. USA.

The PDF version of this Book of Abstracts is available online on the ICPP website.

441 particpants from 33 different countries have contributed for a total of 461 abstracts.

This book summarizes the most recent activities in porphyrins, phthalocyanines and related macrocycles by members of our society.

The abstracts are divided into three categories as described below:

Award Lectures (7)
Plenary Lecture (1)
Oral Presentations (306)
Poster Presentations (147)

The papers associated with the abstracts are presented in 37 symposia organized by 90 symposium organizers.

The program book, available to each participant is available to download on the ICPP website and contains all the information of each presentation as well as the weekly schedule.

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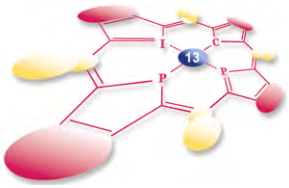

Clinical Photodynamic Therapy: The Evolution of Photodynamic Therapy Treatment of Head and Neck Cancer

Merrill A. Biel

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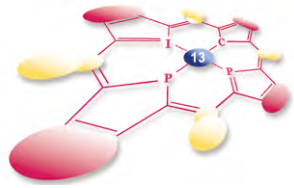
The modern era of photodynamic therapy (PDT) treatment of human cancer began in earnest in 1978, with the publication by Dougherty et al. of the first large series of humans with refractory or recurrent skin cancers successfully treated with PDT using HpD (Photofrin). The first human series of head and neck cancer patients successfully treated with PDT (Photofrin) was published in 1985, by Keller et al. Since that time, numerous clinical investigators around the world have treated thousands of head and neck cancer patients with PDT in clinical trials. These head and neck cancer PDT clinical trials enrolled patients with various stages of disease, and locations of the tumor and were treated using a variety of photosensitizers. Head and neck cancer PDT treatments were performed as the primary treatment with the intent to cure, as a late-stage treatment for palliation of the tumor, or as an adjuvant or neoadjuvant treatment in combination with surgery, radiation, chemotherapy and most recently immunotherapy.

Over the past five decades, head and neck cancer PDT has evolved as newer and more targeted photosensitizers became available for clinical use, as well as advances in laser and fiberoptic technologies allowing for the activating light to be successfully and more easily delivered deep into large invasive tumors. Clinical case studies will be presented to demonstrate the progress that has been achieved in the treatment efficacy of head and neck cancer PDT in various stages of the disease. Potential future clinical developments and applications will be discussed.



AWARDS

Synergistic O_2 and NO Binding to Hemoglobin Matches O_2 Delivery with Metabolic Demand

Ann M English[a]

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Hemoglobin (Hb) *senses* that tissues require O_2 from its O_2 saturation level. To increase blood flow and hence O_2 delivery to tissues, red blood cells (RBCs) export nitric oxide (NO) or a surrogate with NO bioactivity to dilate blood vessels in the microvasculature. How are Hb O_2 desaturation and the export of NO bioactivity coordinated within RBCs? O_2 binding and release from the adult Hb tetramer (HbA) are cooperated and controlled by its R-T quaternary transition. Molecular dynamics simulations [1, 2] reveal transient gas-diffusion tunnels in HbA that are not observed in crystal structures. Tunnel topology remains the same in both the R and T quaternary states, but the O_2 population in the cavities and the preferred O_2 escape portals vary significantly. Notably, most O_2 molecules placed in the b-distal heme pocket escape directly from the b-subunit into HbA's central cavity in the T- but not the R-state, reflecting the lower O_2 affinity of the T-state. Likewise, NO molecules placed in the b-pocket rapidly diffuse from the b-subunit into the central cavity, which contracts in R-state HbA, bringing Cysb93 and NO closer, thereby promoting Cys-SNO formation. In T-state HbA, the Cys-SNO group is solvent-exposed, which enables the export of NO bioactivity from RBCs. Thus, HbA's R-T quaternary transition serves to increase the release of both O_2 and NO bioactivity [3] from RBCs to boost O_2 delivery and blood flow as metabolic demand grows in tissues. Probable reactions of NO with HbA [4, 5, 6] during the respiratory cycle will be further discussed and their essential contributions to RBC function.

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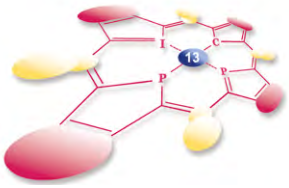

Elucidating Electron Spin Relaxation Mechanisms in Metalloporphyrins and Phthalocyanines for Quantum Information Science

Ryan G. Hadt[a]

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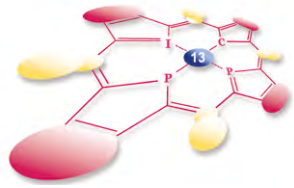
Quantum technologies based on molecules afford unique potential in miniaturization, spatial localization, and tunability through synthetic chemistry. However, many applications within molecular quantum information science hinge on prolonged spin relaxation, a process that effectively leaks quantum information into the environment. This talk will describe the use of synthetically tunable metalloporphyrins and phthalocyanines for the development and application of ligand field spin dynamics, a molecular paradigm to construct spin relaxation structure-function relationships and elucidate the critical bonding, symmetry, and ligand field vibronic excited-state coupling factors enabling room-temperature coherence.

AWARDS



AWARDS

Porphyrins as a key component for photoinduced charge separation, solar cells, and optogenetics

Hiroshi Imahori[a-c]

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Porphyrins are a class of beautiful macrocyclic molecules where four electron-donating pyrroles are connected in a ring by methine carbons, exhibiting an 18π-electron system. They have an intense, allowed Soret band (400–500 nm) and moderate, unallowed Q bands (500–700 nm) in the visible region, with their high molar absorption coefficients (ε~10^4–10^5 M^{-1} cm^{-1}), thus acting as a light-harvesting unit. Typically, zinc, magnesium, and free base porphyrins have a relatively long lifetime of the excited singlet state (1-10 ns). Moreover, they possess suitable electron-donating ability and small reorganization energy of electron transfer, ensuring their use as electron donors in photoinduced charge separation. Synthetically, various substituents can be introduced at the four *meso*- and eight *β*-positions of the porphyrin, resulting in the modulation of electronic, optical, electrochemical, and photophysical properties. For instance, chlorophylls, a family of porphyrins, are widely found in natural plants and photosynthetic bacteria as light-harvesting and/or electron donor components, efficiently converting sunlight into chemical energy. I began my research in porphyrin chemistry when I joined Prof. Yoshiteru Sakata's group at Osaka University as an assistant professor in 1992. I discovered that porphyrin as a donor and C_{60} as an acceptor is an ideal combination for photoinduced CS, leading to the formation of a long-lived charge-separated state with a high quantum yield. After moving from Yoshiteru Sakata's group to Shunichi Fukuzumi's at Osaka University as an associate professor in 1999, I expanded the research to develop self-assembled monolayers and supramolecular solar cells based on porphyrins. Since moving to Kyoto University in 2002 as a full professor, I have directed the research towards versatile organic solar cells including dye-sensitized solar cells, bulk heterojunction solar cells, and perovskite solar cells as well as their model systems, in which porphyrins play an important role. Furthermore, I was involved in the fusion of chemistry and cell biology at the Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, to control cell function by light. In my award talk, I would like to chronologically showcase my past major research achievements associated with porphyrins.

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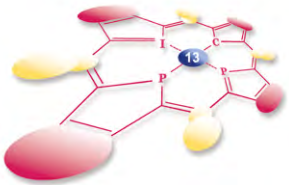

Phthalocyanines as next-generation semiconductors: from high-performance transistors to cannabinoid sensors

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Metal phthalocyanines (MPc) show great promise as semiconductors due to their exceptional optoelectronic properties, high thermal and photochemical stability, and ability to be easily synthesized and functionalized for specific applications. The metal/metalloid ion in the center of the MPc ring can significantly influence the electronic, optical, and magnetic properties of the compound, as well as its solubility and stability. The majority of MPc, such as copper phthalocyanine (CuPc) are used as hole-transport materials (p-type) in organic electronics. Silicon phthalocyanines (R_2-SiPc) are emerging semiconductors that predominantly move electrons and have led to high-performance n-type organic thin-film transistors (OTFTs). Their low synthetic complexity paired with their versatile axial group facilitates the finetuning of their chemical properties, solution properties and processing characteristics without significantly affecting their frontier orbital levels or their absorption properties. The crystal engineering and film-forming characteristics of R_2-SiPc semiconductors can be tuned through appropriate axial group functionalization, therefore facilitating their integration into both OTFTs and OPVs by solution processing or vapor deposition. We have built structure-property relationships between R_2-SiPc structure and thin film processing to enable air-stable and high-performing OTFTs. With a growing international trend of Cannabis legalization, there is a present need for on-the-spot, low-cost, and rapid differentiation of cannabinoids. The two primary cannabinoids, Δ9-tetrahydrocannabinol (THC) and cannabidiol (CBD), obtained from *Cannabis*, elicit very different pharmacological effects necessitating consumer and industry methods for their detection and rapid speciation. Phthalocyanine-based OTFT-based sensors enabled the differentiation of THC and CBD. Device analysis of pre- and post-pyrolyzed rapid plant extract samples was able to predict the THC/CBD ratio with HPLC accuracy. We developed solution-based screening techniques to evaluate the potential of various MPc semiconductors in sensors as well as engineered promising devices and studied the film formation and detection mechanisms of the MPc-based OTFTs. We therefore establish design rules for the development of high-performing cannabinoid sensors.

This conference award presentation will cover our group's recent work on the development of high-performance thin film transistors based on silicon phthalocyanines as well as our design and engineering of cannabinoid sensors based on MPc OTFTs sensors. For more information on our group's research please visit www.benoitlessard.ca

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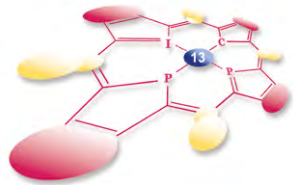


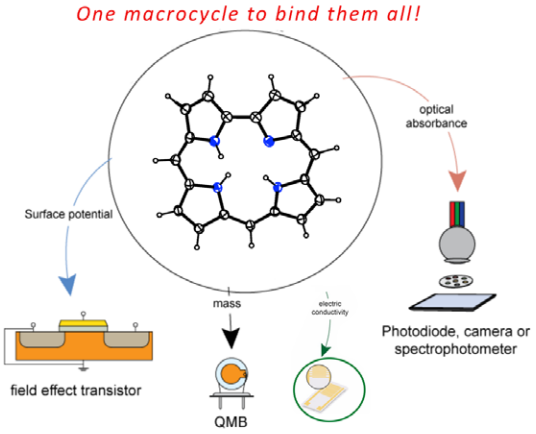
AWARDS

Corrole: The lord of the contracted porphyrinoids!

Roberto Paolesse

Department of Chemical Science and Technologies, University of Rome Tor Vergata, via della Ricerca Scientifica 1, 00133 Rome (Italy)

Corrole, a contracted porphyrin analog previously reported by Johnson as a potential precursor of the corrin ring [1], has assumed a prominent role in the porphyrinoid's scenario. I started my work on this macrocycle when I joined Professor Boschi's group at the University of Rome Tor Vergata, investigating the preparation of metal complexes of β-alkylcorroles. From the beginning, I experienced that corrole chemistry is never boring, because this macrocycle always demonstrated a restless and unpredictable reactivity, making it difficult to correctly characterize the reaction products [2]. At that time, the interest in corrole was quite sparse, but the situation significantly changed when 5,10,15-triarylcorroles appeared in the scene, making this macrocycle a protagonist in the porphyrinoid scenario [3-5]. The synthetic advances of corrole chemistry opened also the way to both the characterization of its reactivity and the exploitation of this macrocycle in different fields, from catalysis to clinical applications [6]. We have been mostly interested in the exploitation of corrole derivatives to develop chemical sensors [7], where they have demonstrated interesting properties. In this presentation, my early work on corrole will be reviewed, and more recent results will be provided.



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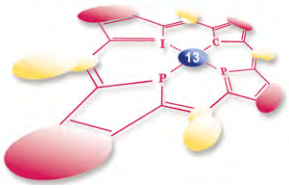


Who would have thought that 4-aza-nitrogens could cause such electronic chaos in a tetrapyrrole?

Martin J. Stillman[a]

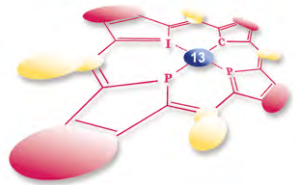
[a]*Department of Chemistry, The University of Western Ontario, London, Ontario, Canada*

Probing the spectral properties of the tetrapyrroles began decades ago because of the connection between structures with large aromatic pi systems and hues extending from dark red to green. I'll pick up the story from the work of Martin Gouterman, a remarkable scientist and his development of the "4-orbital model" to explain porphyrin spectral properties. His rational approach to theoretical analysis by measuring his spectroscopic data meant his data were not only contemporary but the spectroscopic series he planned provided trends that allowed the theoretical approaches to be refined. In this same period, at the University of California, E. Alexander Dratz was working for Melvin Calvin and reported interpretive conversations with Gouterman in his Ph. D. Thesis (1966) in which he described both the MCD spectral properties of a range of porphyrins, hemes and chlorins and theoretical analysis. As Gouterman's group now in Seattle began to exhaust new information from analysis of the absorption and emission spectra of simpler tetrapyrroles, Gouterman began analysis of data from this new technique of MCD spectroscopy. A decade of this work was summarized in his chapter in David Dolphin's 1978 "The Porphyrins". MCD spectral data were also being used by Carl Djerassi's group to great effect and their work also included contributions from Gouterman (and also a young John Dawson). The early MCD spectra of the chlorophylls stand today as model data. Back to 1967 and Andrew Thomson, who at UEA also focused his work on combining spectroscopic data with theoretical analysis on heme proteins as a legacy from his Ph. D. research with R. J. P. Williams. With a new Oxford Instruments superconducting magnet Andrew was keen to answer long-standing questions concerning the dominance of charge transfer transitions in the absorption spectra of iron phthalocyanines and heme protein (specifically, then, myoglobin) using MCD spectral data. Our first papers concerned analysis of the MCD spectra of FePc(L)n using the theoretical results from Stephens, McCaffery, and Schatz to interpret my newly measured excited state angular momentum properties. Between 1972 and 1974 while working with Bryan Hollebone, then at the University of Alberta, I prepared phthalocyanine thin films by sublimation onto quartz plates and we reported on the presence of 2 strong, allowed bands in the 300 nm "Soret" region.

I will, in my talk, continue the story from then, via a return to the FePc spectral properties, which will include our detailed ZnPc data and extensive studies of the pi cations and anions of porphyrins and phthalocyanines using MCD spectral data to guide and anchor assignments. A multi-decade-long collaboration with Nagao Kobayashi led to spectroscopic measurements far from the simple phthalocyanines of my UEA and U of A research. His remarkable compounds provided wonderfully rich spectroscopic data, and with the improvements in computational power, and with John Mack, we were able to bring order to the spectroscopic properties of all tetrapyrroles in an extensive paper in 2005.

My talk will provide a timeline that ties our measurements and analyses beginning in the 1970s through to the development of the reliable theory of today showing that those 4 aza nitrogens do cause electronic chaos for the 18 pi aromatic ring but we understand the origins of that chaos and can tame it!

Acknowledgments: Thank you to the many wonderful students and collaborators who have driven our tetrapyrrole work forward and especially to the many who worked very long hours tending our superconducting magnets. I thank and acknowledge continuous funding since 1975 from the Natural Sciences and Engineering Research Council of Canada (NSERCC) from a range of funding programs.



PLENARY

Porphysome Nanotechnology: From Discovery to Translation and Beyond

Gang Zheng[a,b]

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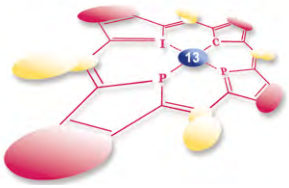
[b]*Department of Medical Biophysics, University of Toronto, Toronto, Canada*

Porphysomes are liposome-like nanoparticles self-assembled from a single porphyrin-lipid building block, which enables their inherent multifunction of photothermal, photoacoustic, photodynamic, fluorescence, PET, MRI, and drug delivery. Since its discovery, we have demonstrated porphysome's high tumor selectivity and multimodal theranostic utilities in diverse tumor models and animal species. We have completed GMP manufacturing, GLP safety studies and clinical trial protocols for its first-in-human use, aka 'beyond lab'. We have also developed a suite of next-generation porphysomes that greatly broadened its theranostic applications from light to sound to radiation. These allow us to pursue new directions of 'beyond local', 'beyond light' and 'beyond cancer'.



Designing fluorinated phthalocyanines as hole selective layer for perovskite solar cell fabrication

Shahzada Ahmad,[a,c] Adrián Hernández,[b] Naveen Harindu Hemasiri,[a] Samrana Kazim,[a,c] Javier Ortiz,[b] Ángela Sastre-Santos[b]

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Perovskite solar cells are promising technology to address sustainability and decreasing emissions. The active layer of perovskite is sandwiched between charge-selective layers, which transport electrons and holes. Arguably, the development of cost-competitive, effective, and stable hole-transporting materials (HTMs) is essential for the future validation of perovskite solar cells. An ideal, HTMs afford the blocking of electrons, promote charge extraction at a perovskite/HTM interface, and transport the holes to the electrode for collection. 2,2′,7,7′-*tetrakis*-(*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-spirobifluorene (Spiro-OMeTAD) is the standard most exploited HTM for n–i–p, type perovskite solar cells fabrication, however, it shows low hole mobility and needs doping with salts. Doping is a trade-off, and aging decreases the performance and accelerates the degradation of perovskite layers due to the migration of hygroscopic dopants and additives from HTMs to perovskite.
Phthalocyanines are porphyrins analogs that deliver effective electrochemical properties and stability, and metal phthalocyanines are being probed as HTMs for perovskite solar cell fabrication. In our quest to investigate new HTMs, we investigated several families of phthalocyanines. Dimers of Zn-phthalocyanines work effectively without the addition of dopants, due to the extended electron delocalization and high charge mobility. Rational use of metals, and peripheral and nonperipheral substituents, also help to adjust the electro-optical properties and solubility. Further, we have developed symmetrically and asymmetrically substituted fluorinated and non-fluorinated-diarylamine with Cu and Zn and incorporated them for solar cell fabrication. These Cu and Zn phthalocyanine-based hole transporting materials were evaluated for their charge mobility, core metal, and substituents roles and we uncovered structure property co-relation. Furthermore, the fluorinated vs non-fluorinated asymmetrically substituted phthalocyanines were evaluated and their role in stability was uncovered. The fluorinated phthalocyanines showed improved stability under multi-stress conditions.

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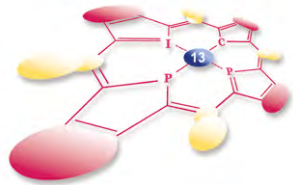

Insight into the efficiency of microalgae lipidic extracts as photosensitizers for aPDT against *Staphylococcus aureus*

Adelaide Almeida[a], Inês Mendonça[a] Daniela Silva[a], Maria Bartolomeu[a], Tiago Conde[b], Rosário Domingues[b]

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Bacterial resistance causes around 1.27 million deaths annually around the globe and has been recognized as a top 3 priority health threat. Antimicrobial photodynamic therapy (aPDT) can be an alternative to conventional antibiotic treatments for bacterial infections. Algae are a promising source of photosensitizers (PSs), as they are known to contain antibacterial compounds, such as lipids, and pigments which can produce long-lasting reactive oxygen species, such as chlorophylls. However, there is a clear gap in the literature about the topic of microalgal lipid extracts' potential as PSs, as there is only one study on this topic. This study aimed to explore the potential of lipid extracts sourced from microalgae of different phyla as PSs in aPDT. The lipid extracts sourced from eleven distinct microalgae, representing various phyla including Cyanobacteria (*Arthrospira platensis*), Ochrophyta (*Nannochloropsis oceanica*), Bacillariophyta (*Skeletonema costatum* and *Phaeodactylum tricornutum*), Haptophyta (*Tisochrysis lutea* and *Pavlova gyrans*), Rhodophyta (*Porphyridium cruentum*) and Chlorophyta (*Dunaliella salina*, *Tetraselmis chuii*, *Scenedesmus obliquus* and *Chlorococcum amblystomatis*) were encapsulated in liposomes and tested against *Staphylococcus aureus* at 1 mg mL^{-1} under white light (100 mW cm^{-2}). All the extracts exhibited an inactivation of *S. aureus* greater than 3 log10 CFU mL^{-1} (between 4 and 8 log10 CFU mL^{-1}), presenting antibacterial activity. The extracts sourced from microalgae belonging to the phyla Bacillariophyta (*P. tricornutum* and *S. costatum*) and Haptophyta (*P. gyrans* and *T. lutea*) exhibited the best inactivation of *S. aureus* (decrease ≈ 8 log10 CFU mL^{-1} after 10-15 minutes of treatment) and were tested at lower concentrations (0.075, 0.0075 and 0.00375 mg mL^{-1}) for *P. tricornutum* and *T. lutea*. All the extracts sourced from *P. tricornutum* and *T. lutea* at these three low concentrations inactivated *S. aureus* by more than 3 log10 CFU mL^{-1} (inactivation similar to chlorin e6 and better than methylene blue), confirming their antibacterial activity when used PSs in aPDT. The bactericidal activity exhibited by the extracts resulted from the photooxidation of polyunsaturated fatty acids (PUFAs) by the singlet oxygen produced by chlorophylls, which eventually led to bacterial lipid peroxidation and cell death. The presence of chlorophyll c, which can absorb a greater amount of energy than chlorophylls a and b; rich content of PUFAs and fucoxanthin, which can also produce singlet oxygen when photo-energized; and a lack of photoprotective carotenoids such as β-carotene, were associated with the algal extracts with higher antimicrobial activity against *S. aureus*. These results reveal that microalgae lipidic extracts can be used as PSs in aPDT as an alternative to conventional antibiotic treatments, and even to conventional PSs, to combat antibacterial resistance.

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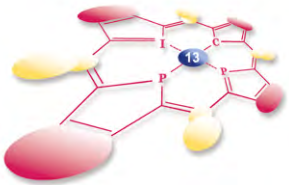

The Beauty of Simplicity: The Smallest Porphyrin Derivatives for Photodynamic Therapy

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The trend towards targeted and multifunctional photosensitizers is leading to increasingly complex molecular structures and sophisticated delivery systems. This trend is known in Medicinal Chemistry to generate "molecular obesity", and is regarded as difficult to reconcile with adequate ADME-Tox properties. The first characteristic of molecular obesity is excessive molecular weight (MW). Porphine (MW = 310 Da) is the simplest porphyrin. It is not adequate for PDT because of its poor solubility and weak absorption in the therapeutic window. Its reduction to the simplest chlorin (MW = 312 Da) or the simplest bacteriochlorin (MW = 314 Da) solves the problem of the electronic absorption in the red/infrared. In this work, we discuss minimal additions to the structures of chlorins and bacteriochlorins that can then make good photosenstizers for PDT while avoiding molecular obesity.

We present a chlorin designed with these principles and, additionally including features that make them adequate for antimicrobial PDT. We show that 5,15-bis(1,3-dimethylimidazol-2-yl)chlorin (MW = 503 Da) is a very efficient photosensitizer to inactivate viruses [1] and bacteria. This is assigned, at least in part, to its ability to cross biological barriers.

We also present a bacteriochlorin designed according to these principles and intended for PDT of solid tumors. We show that 5-methylcarboxamide-10,20-bis(2,6-difluorophenyl)bacteriochlorin (MW = 595 Da) has an intense absorption in the near-infrared ($\varepsilon \approx 100{,}000\ M^{-1}\ cm^{-1}$ at 740 nm), is photostable and is very cytotoxic in vitro. This "small" photosensitizer was successfully employed to treat orthotopic 4T1 mammary tumors in BALB/c mice. This success is due, in part, to the ability of the photosensitizer to infiltrate the tumor mass.

In sum, lean photosensitizers that do not strongly deviate from Lipinski's rule of 5, and may be adequate for oral administration, can be very potent.

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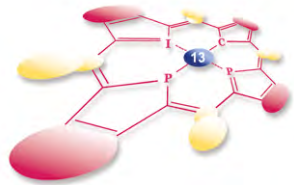

Moving porphyrins and phthalocyanines

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A responsive supramolecular system comprising a bis-imidazolium gelator [1] with a porphyrin and azobenzene photoswitch, both of which are anionic, self-assembles in mixtures of water and ethanol to give a gel that is responsive to light, where the porphyrin moves over micrometer-scale distances when irradiated.[2] The movement is instigated and characterized using total internal reflection fluorescence microscopy. The movement is shown to be a result of both photothermal effects and the trans-cis-trans switching of the azo molecule. In the absence of this switch, no motion occurs, but the system acts as a useful material for the generation of singlet oxygen. [3] More recent results on the movement of molecules in these supramolecular systems will be included, including a phthalocyanine-containing system. The work is aimed at producing responsive supramolecular systems whose dynamics can be modulated using light. Our studies are producing a blueprint for this kind of system.

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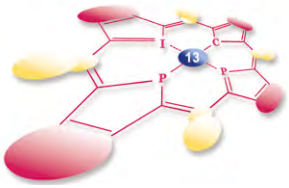

Nonplanar Porphyrins and Carpyridines on Coinage Metals

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Porphyrins and phthalocyanines represent versatile building blocks for self-assembled molecular films, two-dimensional metal-organic coordination networks, and covalent architectures on well-defined surfaces [1]. Hereby, the molecular conformation and shape can play an important role, affecting self-assembly and functionalities. Indeed, nonplanar deformations of porphyrins and related compounds are well-studied in solution chemistry [2].

In my presentation, I will review some of our recent activities comprehensively characterizing nonplanar porphyrins and carpyridines on coinage metal supports in an ultrahigh vacuum environment. Specifically, a family of 2H-tetraphenylporphyrins functionalized with a varying number of ethyl groups, prompting deformations, was explored on Ag(111) and Cu(111) surfaces. Low-temperature scanning tunneling microscopy (XPS) gave insights into the molecular conformation and the resulting supramolecular self-assemblies, whereas X-ray photoelectron spectroscopy was applied to study the temperature-dependence of metalation processes for the differently functionalized porphyrins. Furthermore, intrinsically saddle-shaped 2H-carpyridine molecules [3,4] were explored on Ag(111) and Au(111) surfaces. It was shown that the deformation persists upon adsorption. However, the interaction with the coinage metal support prevents the formation of columnar architectures. Only by combining STM with high-resolution atomic force microscopy (AFM) was it possible to unequivocally determine the adsorption configuration of 2H-carpyridine on the coinage metal supports (see Figure). These experiments provide unprecedented insights into the conformation and adsorption characteristics of nonplanar porphyrins and carpyridines and their functionalities, such as on-surface metalation reactions.

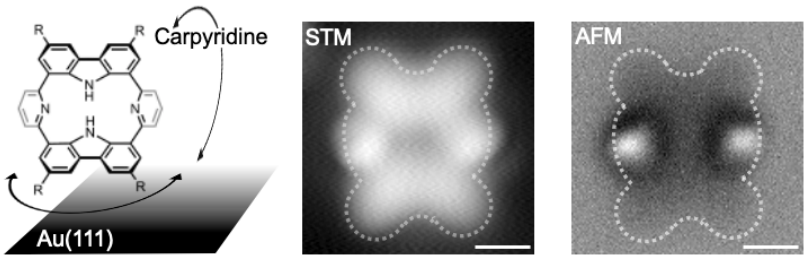

Figure: Left: Scheme of a carpyridine molecule. Middle: STM image of individual carpyridine on Au(111). Right: Corresponding AFM image revealing the nonplanarity and adsorption configuration of the carpyridine. Scale bars: 0.5 nm.

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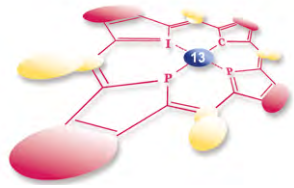

Adsorption of Substituted Zinc Phthalocyanines on Gold: The Role of Molecular Structure, Symmetry and Dimensions on the Interfacial Interactions

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The solution adsorption of perfluorinated zinc phthalocyanines F_xPcZn (x=16, 40, 52, 64), zinc phthalocyanine $H_{16}PcZn$, and tetra-(t-butyl) zinc phthalocyanine $(t\text{-}Bu)_4PcZn$ on gold-coated Si wafers have been investigated. According to XPS, UV-Vis, and Contact Angles, all the phthalocyanines readily adsorbed on gold at room temperature producing uniform hydrophobic monolayer surfaces of phthalocyanine molecules. The strongest adsorption and the highest surface coverage were observed for the non-symmetrical $F_{40}PcZn$ and $F_{52}PcZn$ suggesting a contribution from the molecular dipoles into the interfacial interactions.

A systematic comparison of the phthalocyanines with the increasing number of peripheral substituents demonstrated the strong dependence between the thickness of the phthalocyanine molecules and the charge-transfer interactions with the gold substrate. By XPS, the changes in the core level spectra of Zn2p and N1s due to the adsorption were observed only for $H_{16}PcZn$ and $F_{16}PcZn$, the two planar molecules in the series. In the other phthalocyanines tested, no such changes were observed, arguing that the presence of bulky t-Bu or $i\text{-}C_3F_7$ groups effectively prevents specific interactions with the metal surface.

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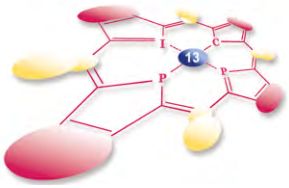

Engineering Fused Ni(II) Porphyrin Polymer Films for Electrocatalytic Oxygen Evolution Reaction

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Metalloporphyrins have been actively investigated for their potential applications as sensors, photosensitizers for solar cells, and catalysts [1]. Inspired by their role in natural photosynthesis, porphyrin-based materials have notably been studied for photo- and electrocatalytic water-splitting reactions [2]. The multiple applications of porphyrins are envisaged by their redox-active nature and interesting optoelectronic properties [3]. Importantly, the optoelectronic properties of metalloporphyrins can be tuned by the incorporation of substituents into one or several of the eight β- and four meso- positions of the porphyrin ring, and/or from the introduction of a cation inside the porphyrin core [4]. Moreover, the direct fusion of metalloporphyrins into highly conjugated oligomers/polymers is an effective way to improve their optoelectronic and catalytic properties [5]. In general, despite their attractive electronic, electrochemical, and optical properties, including an extremely red-shifted absorption up to the infrared, directly fused porphyrin-conjugated polymers struggle to meet the requirements of practical applications due to their very weak solubility and non-reliability [5, 6]. In this context, Oxidative Chemical Vapor Deposition (*o*CVD) has afforded a promising solution to prepare and engineer multiple fused porphyrin-conjugated polymers directly on the desired surface, overcoming the limitation related to solution-based approaches [5, 6].

Herein, we show directly fused nickel(II) porphyrins as heterogeneous single-atom catalysts for the oxygen evolution reaction (OER). The fused porphyrin thin films are kinetically and thermodynamically more active than their non-polymerized counterparts, mainly due to the formation of conjugated structures able to operate via a dinuclear mechanism at low overpotential. More importantly, we demonstrate the role of the porphyrin substituent in the conformation and performance of the conjugated porphyrin polymers as (1) to control the extension of the conjugated system during the oCVD reaction, allowing to retain the valence band deep enough to provide a high thermodynamical water oxidation potential, and (2) to tailor the water interaction with the central metal cation of porphyrin for superior electrocatalytic properties. These findings open the scope for molecular engineering and further integration of directly fused porphyrin-based conjugated polymers as efficient heterogeneous catalysts.

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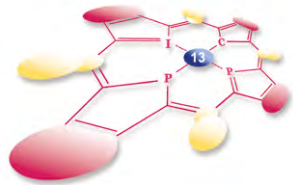

Luminescence studies of nanocrystals decorated with corroles

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The combination of the intrinsic properties of colloidal quantum dots (QDs) and organic dyes in a unique design can afford new systems with advanced photophysical and photochemical properties. In particular, the conjugation of QDs with tetrapyrrolic macrocycles like porphyrins and analogues provides a new class of multifunctional nanostructures with improved features for different applications, namely as theragnostic agents, light emitting devices, sensors and dyes in solar cells.[1,2]
Corroles comprise one of those promising classes of tetrapyrrolic macrocycles with key structural features and tunable physicochemical properties to be used in several areas and where their association with inorganic nanoparticles can bring new functionalities.[3] Herein, we provide novel insights into the *in situ* preparation of nanoassemblies composed of colloidal ZnS/AOT QDs doped and not doped with selected corroles [4]. The synthetic approaches leading to the new nanoassemblies, their structural characterization and the evaluation of the luminescence features will be presented and discussed.

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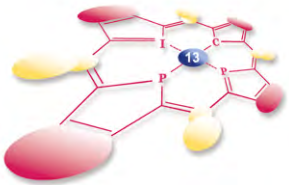

Nanoscale Science with Porphyrins in Relation to On-Surface Chemistry and Metallosupramolecular Engineering of low-D Nanoarchitectures

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On-surface and interfacial coordination chemistry using atomistically well-defined solid supports as anchoring or even construction platforms emphasize the full involvement of the surface atomic lattice in chemical transformations or metal-ligand interactions and coordination spheres. Porphyrins and other tetrapyrrole species are a fascinating family of functional molecules in this fascinating research domain. We examine their surface chemistry and assembly behaviour at the level of individual molecules or even bond characteristics by scanning probe microscopy, frequently combined with complementary space-averaging experimental studies and computational modeling. Basic principles and recent findings in this context are presented and discussed (for example see Refs. [1-7]).

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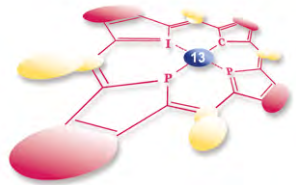

Optoelectronic Processes in Two-Dimensional Covalent Organic Frameworks

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Covalent organic frameworks or COFs can be created by the condensation of molecular building blocks and nodes to form two-dimensional (2D) crystalline architectures. For example, photoactive molecular moieties such as porphyrins and phthalocyanines can be spatially integrated into their crystalline lattice, allowing us to create models for organic bulk heterojunctions, chemical sensors and porous electrodes for photoelectrochemical systems.
Here, we will discuss different strategies aimed at creating electroactive networks capable of light-induced and electrochemical charge transfer. In earlier work, we have developed COF-based heterojunctions containing stacked thienothiophene-based building blocks acting as electron donors with a 3 nm open pore system, which shows light-induced charge transfer to an intercalated fullerene acceptor phase.[1] Contrasting this approach, we have designed a COF-integrated heterojunction consisting of alternating columns of stacked donor and acceptor molecules, promoting the photo-induced generation of mobile charge carriers inside the COF network.[2] Additional synthetic efforts have led to several COFs integrating extended chromophores capable of efficient harvesting of visible and near-infrared light, for example [3]. Heterocyclic regioisomers that can be embedded in the same COF crystal structure allow for fine-tuning of optical absorption and luminescence.[4]
Extending thin film growth methodology to a solvent-stable oriented 2D COF photoabsorber structure, we have established the capability of COF films to serve in photoelectrochemical water-splitting systems.[5] The detailed mechanism of excited state dynamics in light-harvesting conjugated COFs has been revealed through transient absorption spectroscopy,[6] while ongoing work establishes efficient excited state diffusion in 2D COF thin films. Many optoelectronic applications of COFs depend on significant electrical conductivity. Here, Wurster-type structural motifs are attractive building blocks for imparting high conductivity in the corresponding COFs,[7] which also feature tunable optical properties upon integrating donor-acceptor moieties. COF films can also act as ultrafast solvatochromic chemical sensors,[8] as photodetectors,[9] and show very efficient electrochromic response.[10] Ongoing work focuses on the design of ultra-large pore donor-acceptor COFs with extended light-harvesting abilities and optimized charge separation, illustrating their intriguing structural diversity leading to enhanced optoelectronic functionality.

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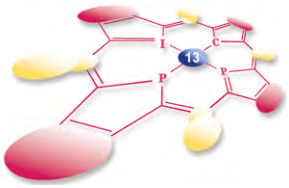

Engineering Peroxygenase Activity into Cytochrome P450 Monooxygenases through Modification of the Oxygen Binding Region

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Cytochrome P450 heme-containing metalloenzymes (CYPs) are monooxygenase biocatalysts for the generation of fine chemicals *via* oxidation reactions that depend on dioxygen. However, the high cost of the required nicotinamide cofactors and their need for additional electron transfer proteins limits their use in larger-scale applications. Here, we investigate whether CYPs can be converted into efficient hydrogen peroxide using peroxygenases through protein engineering of the enzyme's oxygen activation machinery [1]. I will describe improvements in the peroxygenase activity of a CYP enzyme system by modifying selected residues to more closely resemble those of a natural peroxygenase [1,2]. In our CYP system the double mutant in which glutamine and glutamate residues replaced aspartate and threonine, respectively, was found to have significantly higher peroxygenase activity than a single glutamate mutant prototype. Importantly, it functioned better at lower hydrogen peroxide concentrations. Furthermore, all the mutants maintained the regioselectivity and stereoselectivity of the CYP enzyme. The X-ray crystal structures revealed significant structural changes at the oxygen-binding groove providing a rationale for the modified activity. *In crystall*o reactions were undertaken by soaking crystals with hydrogen peroxide before data collection and exhibits electron density corresponding to the expected metabolite [3]. We extended our mutagenesis strategy to other CYP enzymes and generated new peroxygenase biocatalysts for the regio- and stereo-selective hydroxylation of steroids, norisoprenoids and fatty acids at low hydrogen peroxide concentrations [4-6]. When this method is applied to CYP enzymes from thermophilic bacteria these reactions can occur at elevated temperatures enabling enzymatic hydroxylation reactions under non-standard biological conditions [6].

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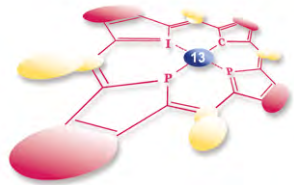

Progression on the Development of Boron Subphthalocyanines, Subnaphthalocyanines and Related Hybrids for their Applications

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For a certain time, our group has been focused on the molecular design, synthesis and applications of boron subphthalocyanines (BsubPcs) and subnaphthalocyanines (BsubNcs), which are macrocycles with a chelated central boron atom.[1] Our focal point continues to be equally balanced between the basic and applied chemistry and their application into organic photovoltaics (OPVs)/organic solar cells (OSCs),[2a] batteries,[2b] and organic light-emitting diodes (OLEDs);[2b] electrochemical[2c] and photophysical properties being critical to these applications.
For this presentation, one focal point will be our progress in the development of BsubNcs. In the past, we have shown that BsubNcs end up being a mixed alloyed composition based on bay-position halogenation that was formed randomly during the reaction of BCl_3 with 2,3-dicyanonaphthalene at temperature to form the BsubNcs. The random bay-position halogenation is impactful in a positive way within OPV devices,[3a] negative within OLED devices[3b] and also has electrochemical variations. However, given it is random halogenation, it is desirable to truly understand its impact systematically. We have therefore in the past developed a valid method to separate the mixed alloyed BsubNcs into mixed bands and acquire data to show the impact of the percentage/number of bay-position halogens, chlorine and bromine included, on electrochemical potentials and photoluminescence.[4a-b] I will also present a new synthetic methodology to avoid the random bay-position halogenation of the BsubNcs. We have also applied a computational model to look at the relative impact of the random bay-position halogenation on the electronics. We have found that the frequency of halogenation has a larger impact on the HOMO/LUMO energy levels than does the random halogen positioning around the bay positions of the BsubNcs. I will also present, that we have also taken into consideration other bay-position substitutions of the BsubNcs to avoid random halogenation and we have also developed BsubNc + BsubPc hybrid materials and there is a way to avoid bay-position halogenation. Once it was avoided, we have the first example of electrochemical and photoluminescence data for the associated BsubNc + BsubPc hybrids. I will also outline our approach to the accelerated development of BsubNcs, BsubPcs and the hybrids whereby their molecular design and synthesis were first justified through a computational model. We are also currently using an AI/ML method to accelerate the BsubNc development. If timing is available, I will also present from an engineering perspective, the fact that BsubPcs can be scaled-up.

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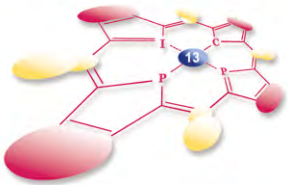

BODIPY-based light-harvesting systems built on the proline scaffold

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Several diverse natural systems use sunlight as their energy source to drive critical chemical reactions and hence harvest photon densities. One enlightening aspect of natural photosynthesis is a ubiquitous model in which the capability of light-harvesting complexes (LHCs) to adapt to stimuli and re-direct photons around a multifaceted network. Based on studies of artificial and natural light-harvesting arrays, it is clear that energy transfer and antenna behavior are most effectively accomplished by assembling ordered networks of chromophores with multiple excitation bands, owing to the precise assembly of chromophores within a protein scaffold. These subunits act as electronic energy transfer (EET) conduits, where each chromophore absorbs at a distinct wavelength and transfers the excited state energy to the terminal low-energy chromophore. During past decades, many imaginative donor-acceptor artificial light-harvesting arrays have been synthesized to mimic certain features of natural photosynthesis machinery by displaying EET processes with the demand to the development of many light-harvesting materials for organic electronics.

In such multi-chromophoric light harvesters, EET can be propagated by two mechanisms, either long distance through-space (Förster) or short distance through-bond (Dexter). Several studies have focused on comprehending EET in natural LHCs, focusing on the parameters which determine the efficiency of EET which include, for example, the donor-acceptor distance, relative orientations of the transition dipoles and the spectral overlap between the relevant absorption and emission bands. Inspired by nature a large number of LHSs have been synthesized mimic the photosynthetic antenna behaviour, based on dendrimers, polymers, MOFs and peptides.

As a scaffold it can be realized that peptides are especially appealing in offering synthetic control both in composition and the relative positioning of the light-absorbing units due to the modular, stepwise approach offered by the solid-phase peptide synthetic (SPPS) technique. Oligoproline is an superlative platform to meet such challenges, as it is rigid and has the advantage of controlling secondary structure with nine or more residues naturally adopting helical structures either proline I, a right-handed helix consisting of local cis-amide bonds favoured in nonpolar solvents, or Proline II adopting a left-handed helical structure in polar solvents with a repeat spacing of 9.4 Å versus 6.3 Å in Pro I.

This talk will cover our recent work towards the construction of BODIPY-based structures using proline as the backbone for positioning the units to propagate EET.[1-3]

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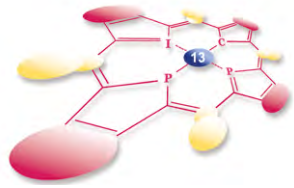

Unusual porphyrin ring conformational distortions in the substituted porphyrin-fullerene cocrystallates

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To examine the influence of fullerene on the macrocyclic ring conformation, single crystal X-ray structures of a series of cocrystals of electron-rich 2,3,5,10,12,13,15,20-octaphenylporphyrin, MTPP(Ph)$_4$ (M = 2H, Co(II), Cu(II)), and 2,312,13-tetramethyl-5,7,8,10,15,17,18,20-octaphenylporphinato copper(II), CuTPP(Ph)$_4$(CH$_3$)$_4$, derivatives [1] and electron-deficient 2,3,12,13-tetra(bromo/2'-thienyl/cyano)-5,10,15,20-tetraphenylporphyrin (M'TPPX$_4$, M' = 2H, Cu(II) or Co(II)) with fullerene, C_{60} or C_{70} were elucidated. All the MTPP(Ph)$_4$•C_{60} (M = 2H, Co(II), Cu(II)) cocrystallates revealed 1:1 stoichiometry with free of lattice solvates but electron deficient (M'TPPX$_4$; X = Br, CN, 2-thienyl; M' = 2H or Cu(II) or Co(II)) showed 1:1 or 1:2 or 3:1 porphyrin/C_{60} stoichiometry in the cocrystallates with varying lattice solvates [2,3]. The macrocyclic rings in MTPP(Ph)$_4$•C_{60} cocrystallates revealed significant distortion with the root-mean-square (r.m.s) value as high as 0.265(2) Å. The porphyrin ring in the solvated H$_2$TPPBr$_4$•(C_{60})$_2$, [(M'TPP(CN)$_4$)$_3$•C_{60}; M' = 2H, Cu(II)] and (H$_2$TPP(CN)$_4$)•C_{70} cocrystallates revealed enhanced distortion (r.m.s. > 0.245(6) Å) than that of their nearly planar parent porphyrins [3]. Interestingly, M'TPP(2'-thienyl)$_4$•C_{60}; (M' = Co(II) or Cu(II)) cocrystallates exhibited switching the parent porphyrin ring conformation from nonplanar (~0.61 Å) to nearly planar conformation (0.08 Å) in the cocrystallates [2]. This is quite opposite to that observed in MTPP(Ph)$_4$•C_{60} cocrystallates. A similar trend is observed in the CuTPP(Ph)$_4$(CH$_3$)$_4$•C_{60} cocrystallate. The porphyrin ring in these cocrystallates was examined by normal-coordinate structural decomposition (NSD) analysis, and they feature major *saddled* distortion with varying degrees of *ruffled* and *domed* or negligible *wave* distortions. The nonplanar distortion in these cocrystallates has been ascribed to intermolecular interactions/crystal packing forces.

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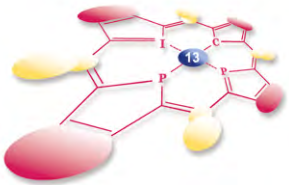

Supramolecular chirogenesis in porphyrin chemistry: Experimental, practical, and theoretical aspects

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Supramolecular chirogenesis is an inevitable part of many natural and artificial systems and deals with various aspects of chirality induction, amplification, and modulation upon non-covalent interactions [1-3]. This phenomenon plays an important role not only in fundamental science but also in different practical fields. Porphyrinoids owing to their appropriate chemical, physico-chemical, and spectral properties, as well as easy handling and versatile modifications, are found to be one of the most effective chromophoric compounds to study supramolecular chirogenesis. Using various porphyrinoids-based supramolecular systems the corresponding chirogenic mechanisms and controlling factors of chirogenesis have comprehensively been investigated [4-8]. Furthermore, smart chirality sensors, hybrid materials, and other chiroptical devices have successfully been designed and developed [9-10].
Recent achievements and further prospects in new practical applications and corresponding theoretical evaluation of chirogenic systems will be discussed.

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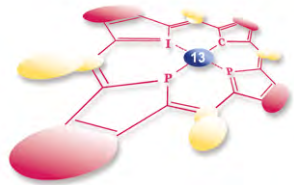

Engineering Porphyrin Conjugated Polymer Thin Films for Heterogeneous Electrocatalysis

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Oxidative chemical vapor deposition (oCVD) was recently demonstrated as a convenient method for the simultaneous synthesis and deposition of porphyrin-conjugated polymers [1]. In oCVD, the monomer and a suitable oxidant are both supplied from the vapor phase to a surface on which oxidative polymerisation and doping occur in a single step [2]. Porphyrins possessing free *meso*-positions [1, 3-4] and porphyrins bearing aminophenyl substituents [5] have both been successfully polymerised using oCVD to yield the formation of formation fused porphyrin tapes and phenazine-bridged porphyrins covalent organic frameworks (COFs), respectively. Importantly in the perspective of practical application, including heterogeneous electrocatalysis, the porphyrin conjugated polymers are readily deposited on virtually any substrate in the form of smooth and thickness-controlled thin films. In addition, porphyrin-conjugated polymers are formed almost independently from their substituents [3-4] and central metal cations [3-5] enabling the engineering of their electrocatalytic properties.

Up-to-date, porphyrin-conjugated polymer thin films prepared by oCVD have been successfully investigated for the electrochemical hydrogen evolution reaction (HER) [3], nitrate reduction reaction (NRR) [5], oxygen reduction reaction [ORR] [5], oxygen evolution reactions (OER) [4-5]. Experimental and theoretical data demonstrate the impact of both the central metal cations [3-5] and substituents [3-4] on the catalytic activities [3-5] and stability [6] of the porphyrin-conjugated polymer thin films. The approach reported in this work, also suitable for the preparation of heterometallic porphyrin conjugated polymer thin films [7], circumvents many limitations of solution-based approaches and pave the way to the facile engineering and integration of efficient electrocatalysts from porphyrins.

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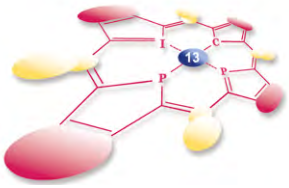

Porphycenes networks, chemosensing properties of 2D and 3D thin films

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Photoactive organic-based molecular materials hold a great deal of potential in many technological and biomedical fields. Porphycenes (H2Po), tetrapyrrole macrocycles constitutional isomers of porphyrins, [1] are 18π electron conjugated chromophores and an intriguing class of molecular materials that can serve as multipurpose scaffolds. They have two H atoms in the inner cavity which are subject to fast tautomerism while, as tetradentate ligands, they can also host almost all the metal ions. Being chemically and thermally stable, their periphery (*meso* and *β* positions) can be functionalized and engineered for specific scopes and applications.
The different pattern of connection of the four pyrrole rings in H2Po, with respect to porphyrins, reflects in the different size of the the inner core while the reduced symmetry of the molecule endows H2Po with unique stability and optical features suitable for the exploitation as ultrafast responsive material. We previously reported the first studies on H2Po continuous and compact 2D/3D vacuum deposited [2,3] thin films with a combination of UV-Vis-NIR optical spectroscopies (absorption, emission, surface differential reflectivity-SDR and reflectance anisotropy spectroscopy-RAS) and surface microscopies (i.e. AFM). We demonstrate a spectacular chromatic change when the film is exposed to acid and weverified the fast reversibility of the process. We now further investigate this behaviour in porphycenes functionalised with *alkyl* and *aryls* substituents in both the *β* pyrrole and *meso* positions as those reported in Figure 1.

Figure 1: a) Chemical structures of the studied porphycenes; b) compararisons of the optical absorptivities of the studied porphycenes in DCM solutions; c) changes in optical absorptions of 9,10-Ph_4H2Po upon addition of 1 and

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Exploring the Chemical Space of Tetracyano-substituted Porphyrinoids: Synthesis, Photophysical Properties, Racemization Features, and Chemical Transformation

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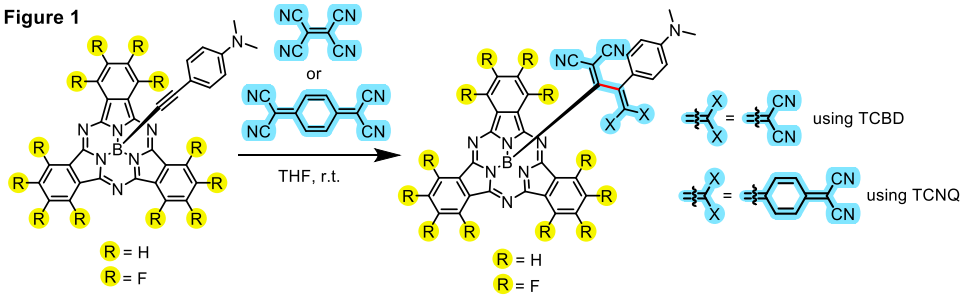
Tetracyanobuta-1,3-diene (TCBD) is a powerful electron-acceptor unit that can be easily incorporated in molecular systems containing activated alkynes through a [2+2] cycloaddition-retroelectrocyclization (CA-RE) reaction [1]. In the last few years, we have successfully employed this synthetic strategy to prepare several TCBD-based phthalocyanines [2a], subporphyrin (SubPor) [2b], and subphthalocyanine (SubPc) [2c-f] photo- and electroactive conjugates, compounds which have shown interesting physicochemical properties.
In order to expand the chemical space of tetracyano-substituted porphyrinoids, we have now synthesized some novel derivatives *via* a CA-RE reaction of ethynyl-substituted SubPcs with tetracyanoquinodimethane (TCNQ), an electron acceptor stronger than TCBD (Figure 1). Interestingly, the resulting TCNQ-based SubPcs, which are obtained as a racemic mixture of the S_a and R_a atropisomers due to the presence of a chiral axis within the molecule (highlighted in red in Figure 1), show physicochemical properties significantly different from that of their TCBD-based SubPc and SubPor analogues, in particular, strikingly different racemization features. A wide range of spectroscopic and electrochemical techniques as well as theoretical calculations have been employed to rationalize such unexpected behaviour.

Figure 1



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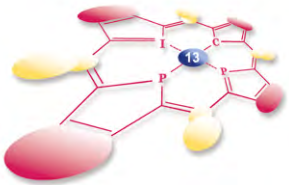

π-Extended porphyrin-phthalocyanine heterojunction devices exhibiting high ammonia sensitivity with a remarkable light effect

Marcel Bouvet*,[a] Sujithkumar Ganesh Moorthy,[a] Jacob Arvidson,[b] Rita Meunier-Prest,[a] Hong Wang*[b]

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π-Extended porphyrins represent an attractive class of organic compounds because of their unique photophysical, optoelectronic and physicochemical properties. Herein, a cross-conjugated (Ace-PQ-Ni) and a linear-conjugated (AM6) porphyrins are used to build double-layer heterojunction devices by combining with lutetium bisphthalocyanine complex ($LuPc_2$) (Fig. 1). The heterojunction effect at the porphyrin-phthalocyanine interface plays a key role in their charge transport properties. Both devices exhibit exceptionally high ammonia sensitivity at RT and under ambient relative humidity, with a limit of detection as good as 156 and 115 ppb for Ace-PQ-Ni/$LuPc_2$ and AM6/$LuPc_2$ sensors, respectively. Interestingly, Ace-PQ-Ni/$LuPc_2$ and AM6/$LuPc_2$ sensors display opposite effects upon light illumination. While the former shows largely decreased ammonia sensitivity under light illumination, the current variation of the latter under ammonia is remarkably enhanced with a multiplication factor of 13 and a LOD as good as 83 ppb. Their striking difference in sensing properties upon light illumination is attributed to their different p-conjugation pathways (cross-conjugation versus linear-conjugation).

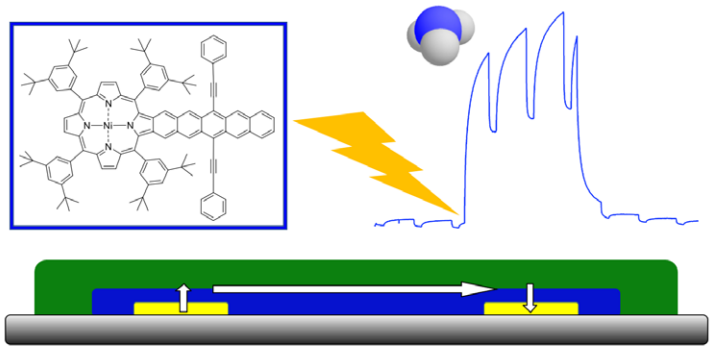

Fig. 1: Scheme of the heterojunction device, the porphyrin AM6 and the light effect on ammonia sensing.

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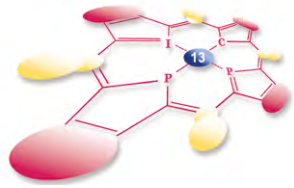

Morpholine modified porphyrinoids for anticancer and antimicrobial treatment

Jonathan Britton[a], Azole Sindelo[a], Pinar Sen[a,b], N. Bridged Magaela[a] , Refilwe Matshitse[a] , Balaji Babu[a] , Muthumuni Managa[a] , Lindokuhle Cindy Nene[a], Khanyisile Buthelezi[c], Aviwe Magadla[a], Earl Prinsloo[c], Tebello Nyokong[a]

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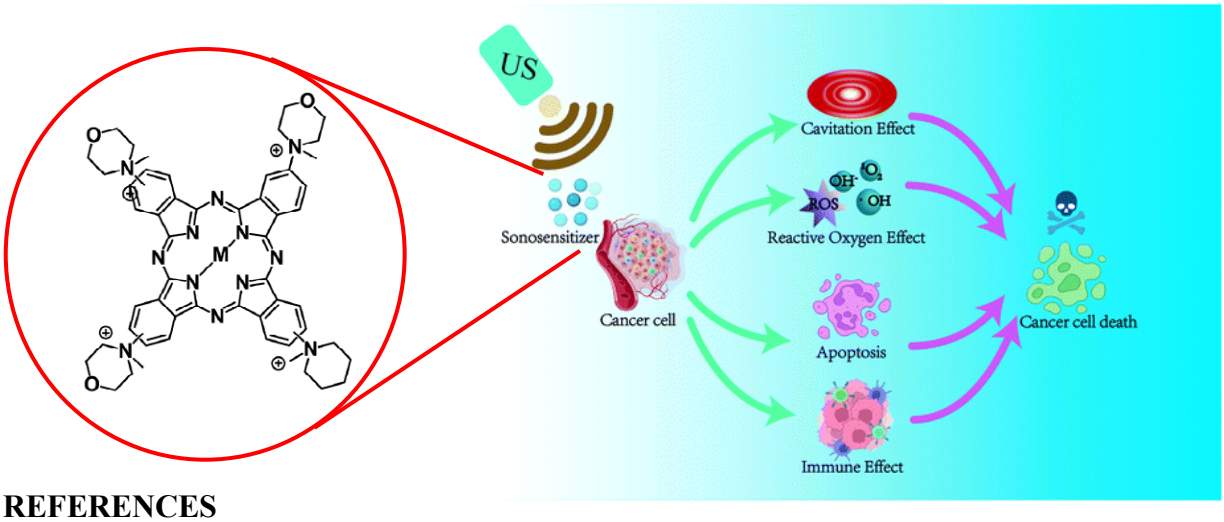
Morpholine has diverse biological applications, such as anti-inflammatory, anti-cancer and antimicrobial activities. Morpholine-substituted phthalocyanines have been shown to have improve solubility and more re-shifted absorbance peaks[1,2]. Photodynamic therapy has shown promising results as an alternative anticancer modality, but the penetrability of the light used is limited to up to 10 mm past the epidermis. Ultrasound has since been developed as a supplementary, and sometimes alternative to light for sensitizer activation, as it has improved tissue penetrability[3-5].
In this presentation we'll be reporting on the synthesis and use of morpholine-modified phorphyins and phthalocyanines, along with the use of ultrasound, for the elimination of bacteria and cancerous tissue[1-5].



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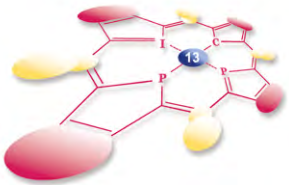

Pushing the Limits of Oxidation-based Pyrrole-modifications of Porphyrins

Nivedita Chaudhri,[a] Dinusha Damunupola,[a] Nisansala Hewage,[a] Li, Ruoshi,[a] Matthew J. Guberman-Pfeffer,[a] Matthias Zeller[b] , Christian Brückner[a]

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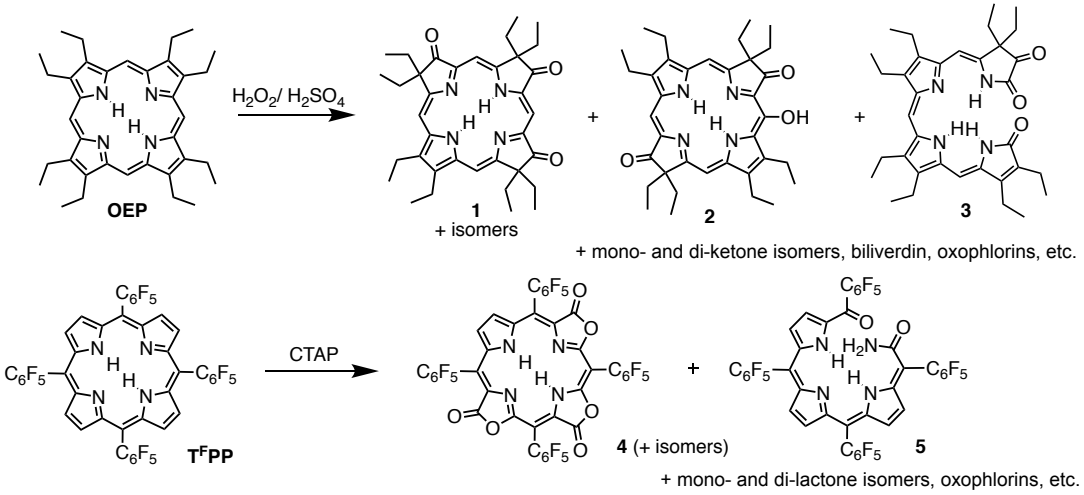
The direct oxidation of octaethylporphyrin **OEP** to generate oxochlorins is long-known. We expanded on these findings with detailed investigations of the aromaticity of the triketones [1]. Pushing the oxidation of **OEP** using longer reaction times, temperatures, or peroxide concentrations, generates, *inter alia,* the novel *meso*-hydroxydiketone **2** [2] and known trioxobiliverdin **3** [3]. We will report on the reactivity of **2**.



Similarly well investigated, oxidative conversion of *meso*-arylporphyrin **T^FPP** generates porpholactones and all isomers of the dilactones. Recently, we prepared multiple isomers of the trilactones **4** using several stepwise oxidations of porphyrin **1** [4]. We will report on the reinvestigation of some direct (and forceful) **T^FPP**-to-porpholactone conversions that each produced unique product mixtures [5]. Importantly, we identified in the mixtures a unique tripyrrolic, open-chain compound **5** derived from the degradation of a porpholactone oxazolone moiety. This distinguishes the formation and structure of this compound from all previous biological or nearly all other non-biological biliverdin-like linear porphyrinoid degradation products that are derived from ring cleavages between the pyrrolic building blocks.

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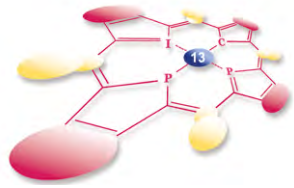

Radioluminescence: An elegant yet complex strategy to combine deep-tissue photodynamic therapy and radiotherapy

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Photodynamic therapy (PDT) is intrinsically restricted by the shallow penetration of light in tissue and can therefore not be induced in deep tissue without invasive strategies [1]. An elegant non-invasive approach to overcome this limitation consists of conjugating the photosensitizers to radioluminescent nanomaterials also called nanoscintillators, which behave as localized light sources remotely activated by the X-rays used in radiotherapy.

Upon X-ray irradiation, nanoscintillators emit UV/visible light that can excite nearby photosensitizer and induce PDT [2]. As X-rays penetrate deeply in tissues, radioluminescence can activate PDT non-invasively at depth and without being restricted by large tumor volumes and optical shielding by blood vessels. The feasibility of exciting photosensitizers using nanoscintillators has been demonstrated by us and others [3, 4, 5]. However, there is a mismatch between a low theoretically expected efficacy of radioluminescence-induced PDT and the much higher experimentally measured efficacy. Thus, it appears critical to understand the origin of the observed effect that may stem from several therapeutic contributions. Contributions that may have been overlooked include the increased radiation dose that can be induced by the heavy atoms of the nanoscintillators, [6] but also a potential beneficial interaction between low-dose PDT and radiotherapy [7].

This presentation will focus on the different radiotherapeutic effects that can be induced by nanoscintillators used to activate PDT in deep tissue during radiotherapy. Since these effects may play a major role in overall treatment efficacy, they need to be thoroughly considered when designing future nanomaterials for X-ray-induced PDT.

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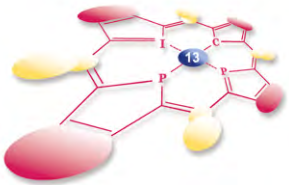

Modality Following Mechanism: Informing Best Practice in Combination Therapies that Incorporate PDT

Theresa M. Busch[a]

[a]*University of Pennsylvania, Perelman School of Medicine, Department of Radiation Oncology, Philadelphia, USA*

Photodynamic therapy (PDT) lends itself to cancer treatment in the combinational setting. It is very versatile because PDT exhibits multiple mechanisms of therapeutic action (Figure 1), accompanied by nonoverlapping toxicities with other modalities of cancer treatment. Consequently, PDT can readily be incorporated with numerous other types of therapy, including surgery, chemotherapy, molecular therapy, immunotherapy, or radiotherapy. Benefits of PDT in the combinational setting include its self-limiting depth of effect that can facilitate delivery to margins or residual disease after surgery without damage to deeper underlying structure (a concern in radiotherapy applications). Moreover, PDT can generate anti-tumor immunity, characterized by a productive inflammatory response and release of damage-associated molecular patterns (DAMPs), cumulating in the recruitment and activation of T-cells. Thus, PDT can be combined with drugs or radiotherapy to promote the complimentary activation of immune or cell death pathways, alongside the mitigation of resistance pathways, producing synergy in treatment outcomes. The integration of PDT in a multimodality approach can be guided by therapy-induced changes in the characteristics of a tumor, such as its microenvironment or molecular signature. For example, the effects of neoadjuvant or concurrent treatment with radiotherapy, surgery, and molecular targeting drugs on responses to PDT can be studied in terms of physiological attributes (e.g., oxygenation) of the tumor environment, its immune characteristics and survival signaling. We discuss several combined modality approaches to PDT that are studied preclinically and clinically from the perspective of how they exploit PDT dependencies and effects on the tumor microenvironment.

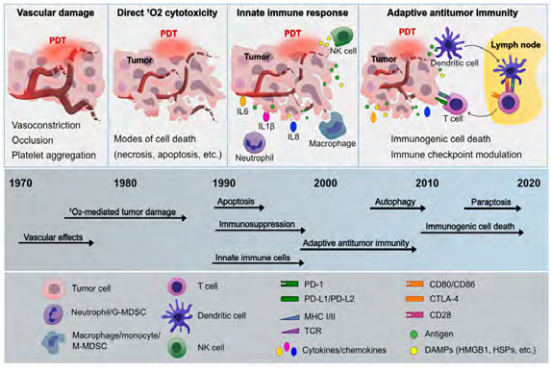

Figure 1. The therapeutic effects of PDT are mediated through varied mechanisms of action. This provides opportunities for its incorporation in numerous multimodality settings. Reprinted with permission from: Cramer GM, Cengel KA, Busch TM. *Forging Forward in Photodynamic Therapy*. Cancer Res. 2022 Feb 15;82(4):534-536. doi: 10.1158/0008-5472.CAN-21-4122. PMID: 35180305.

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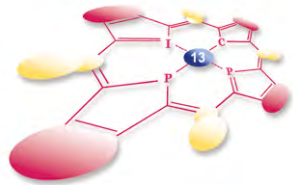

Synthesis of new symmetrical and unsymmetrical Aza-DPM and Aza-BODIPY analogues

Andrew N. Cammidge[a], **Budur N. Alanazi, Ahad O. Alsahli, David L. Hughes, Isabelle Chambrier, Jacob Gretton, Ala Alturk**

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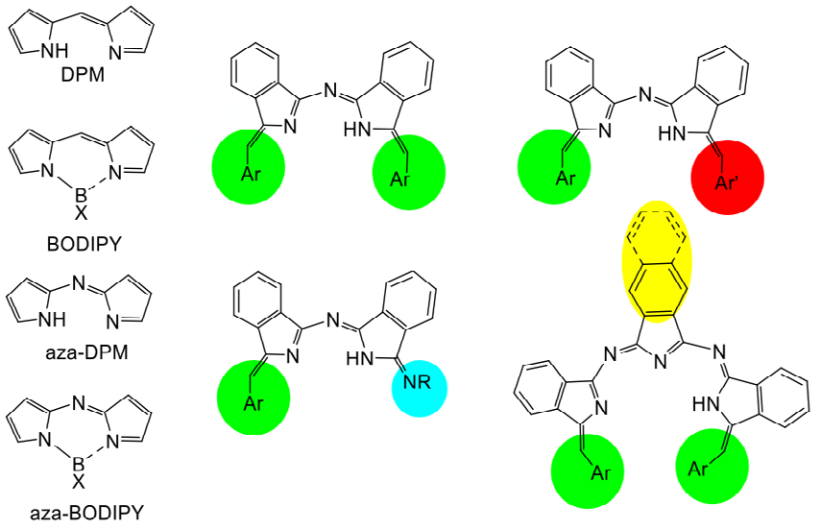

Aza-dipyrromethenes (aza-DPMs) and their boron complexes (aza-BODIPYs) are an increasingly studied class of chromophores that can be viewed as aza-porphyrinoid fragments. We previously prepared benzo-fused analogues of aza-DPMs and aza-BODIPYs, initially as side-products in porphyrin-phthalocyanine hybrid syntheses [1-3] but also exclusively [4].

The benzo fusion results in a different electronic configuration compared to normal (aza) DPMs/BODIPYs that preserve the benzenoid aromaticity [4].

Here we describe a more detailed investigation of these analogues, particularly focusing on synthesis strategies to access unsymmetrical systems. Boron (and other metal) complexes are described along with higher-order trimeric structures.

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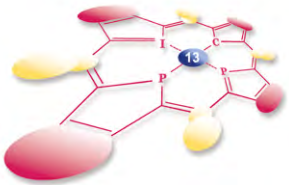

Meso-Perfluoro-alkyl Corroles as precursors of functionalized corroles

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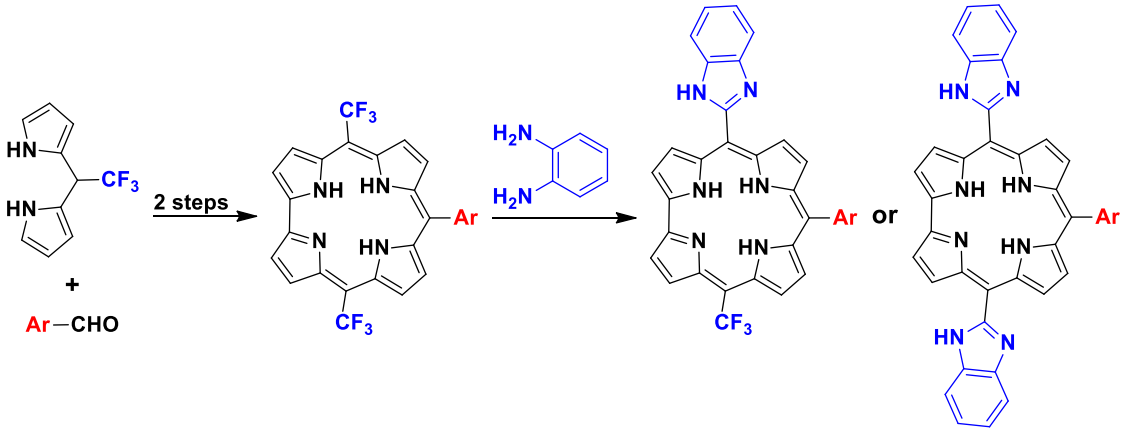
Corroles-bearing *meso*-aryl groups are now quite easily prepared from commercially available reagents, and their post-functionalization is now well documented [1]. On the contrary, when other *meso*-substituents are considered, such as alkyl chains, functional groups or heterocycles, only few examples of such macrocycles can be found in the literature [1]. We have recently described the two steps preparation of corroles bearing two *meso*-perfluoroalkyl chains [2]. In addition to their strong electron-withdrawing character, these groups are of particular interest because of their reactivity with various nucleophiles. For example, when macrocycles bearing two long heptafluoropropyl or pentadecafluoroheptyl chains were involved in basic and controlled hydrolysis, ABC corroles having a *meso*-acyl groups were obtained [2]. After a few reminders of these previous results, this presentation will focus on the access to corroles bearing *meso*-heterocyclic substituents and/or unprecedented *meso*-functional groups from the condensation of a bis-*meso*-CF_3 corrole with various amines or polyamines.



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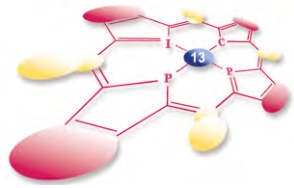

Examining the Role of Conjugated Porphyrin Polymer Thin Films in Oxygen Evolution Reaction Electrocatalysis.

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Porphyrins are actively investigated as oxygen evolution reaction (OER) catalysts. However, only a few studies refer to their integration into electrode devices as heterogeneous catalysts [1-2], mainly due to processability constraints. Recently, our group developed a methodology allowing the straightforward preparation of fused metalloporphyrins conjugated polymers thin films over various substrates based on oxidative chemical vapor deposition (oCVD) [3]. In this way, a new venue for studying the electrocatalytic activity of fused metalloporphyrin conjugated polymers bearing different metal centers and substituents is open.

We studied the electrocatalytic activity of fused metalloporphyrins conjugated polymers on conductive substrates towards the OER, finding a significant influence of the nature of the metal cation and the substituents and the polymerization reaction on the catalytic performance. For instance, directly fused Ni(II) porphyrin conjugated polymers were found to be more kinetically and thermodynamically active than their non-polymerized counterparts due to the formation of conjugated structures enabling a dinuclear radical oxo-coupling (ROC) mechanism affording lower overpotential.[4] The combination of experimental and theoretical studies unveiled the role of the porphyrin substituent in the conformation and performance of the conjugated polymers. Specifically, using (4-methoxycarbonyl)phenyl groups enabled the control of the extension of the conjugated system during the oCVD reaction, allowing the retention of the valence band deep enough to provide a high thermodynamic water oxidation potential. Using such a substituent also provided a flexible molecular geometry facilitating O_2 formation from the interaction between the Ni–O sites, a weakened π-bond of the *Ni–O sites for enhanced radical character, and an optimized water interaction with the central metal cation of the porphyrin resulting in superior electrocatalytic properties.

Conversely, for directly fused Co(II) porphyrin-conjugated polymers, it was found that the electrocatalytic activity originates from a polymer-derived, highly transparent $Co(Fe)O_x$ species formed under operational alkaline conditions. [5] Although the newly formed active catalyst greatly benefited from both the polymeric conformation and the inclusion of the iron-based species originating from the oCVD reaction, these observations highlight the importance of thorough investigations on the stability and true catalytically active sites identification after the operational function of porphyrin-based electrodes.

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Novel optical sensor for PFOA detection in water using different low-cost materials for corrole deposition

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Nowadays great interest has been devoted to optical sensors intended for environmental monitoring, thanks to their properties: fast response, good sensitivity, low-cost equipment, portable instrument, and easy signal acquisition. This work reports the development of an optical sensor based on the color variation and quenching emission of different silicon and aluminum corrole, upon interaction with a specific emerging pollutant belonging to the PFAS family in water samples: the perfluorooctanoic acid (*PFOA*). We have developed innovative protocols to make hybrid materials by the deposition of metal complexes of corrole and based on different low-cost materials as solid support (nanocellulose, agarose gel and Colour Catcher®) [1, 2, 3]. The hybrid materials were utilized in optical measurements using a novel PT-like instrument setup made by the 3D printer and implied by a peristaltic pump (illustrated in figures below), able to record the colorimetric and emission variations upon the specific interaction between metal corrole receptor and PFOA. In the mechanism for PFOA sensing, the metal complex corrole coordinates axially with the carboxyl group of the perfluoroalkyl chain, which causes the start of the aggregation process through the F-F interactions between the different units of PFOA axially coordinated to the receptor. The aggregation process led to a colorimetric variation proportionally to analyte concentration which is then digitalized by a novel PT-like instrument setup [4]. This study allows the realization of an optical portable platform, composed of low-cost electronic devices, such as a LED as a light source and a web-cam as a detector, obtaining a convenient sensor device able to perform analysis in situ of water samples with good reproducibility, high sensitivity and a very low LOD.

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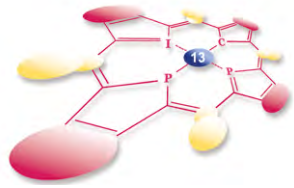

Kinetic Investigations on the Chiral Induction in $TPPS_4$ J-Aggregates

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Chirality in supramolecular chemistry is a highly investigated topic. From a fundamental point of view, it is important to understand the mechanism of chirality transfer or propagation from a chiral monomeric building block to a complex supramolecular architecture. More intriguing is the case when chirality occurs upon supramolecular assembling processes starting from achiral building blocks, in the presence of a proper chiral bias. In this context, the tetra-anionic water soluble 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin ($TPPS_4$) has been extensively investigated since, under strongly acidic conditions, it self-assembles into J-aggregates whose complex hierarchical structure is mainly controlled by the kinetic of growth, mixing protocols and a variety of added templating reagents.[1] The mechanism that has been proposed is based on the rate-determining formation of an m-mer of porphyrins able to auto-catalyze the subsequent growth of the final structure. These latter exhibit chirality as a consequence of spontaneous symmetry breaking [2] or by transfer induced with external chiral species.[3] Counter-anions [4, 5] and mixing protocols [6] can largely affect the kinetics of aggregation and the final observed dissymmetry g factor. We have shown that some amino acids are more effective in influencing the spontaneous symmetry breaking occurring in these systems, leading to an enhancement of the induced CD signals. The exact role of each amino acid along the aggregation pathway is still elusive since a complex interplay of factors operates among the components of these supramolecular building blocks.[7] Moreover, a series of divalent metal ion derivatives of $TPPS_4$, such as Cu(II), Pt(II), Ni(II), Zn(II) and Co(II) have been selected to study the progressive impact of the coordination geometry imposed by the metal ion on the interaction with some aromatic amino acids. Besides hampering the formation of J-aggregates, the absence/presence of axial ligands bound to the metal and generating steric hindrance on the porphyrin plane has a deep effect on the degree of interaction, as measured by the modification of the electronic absorption properties and the binding constants. The results are in line with the extent of hydrophobicity and the size of the aromatic region of the amino acids.[8]

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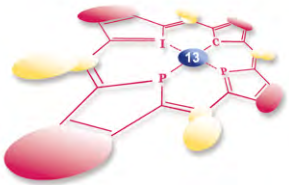

Tailored hybrid nanomaterials functionalized with polysaccharides and porphyrins for biomedical applications

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The study of new potential photosensitizers has become a significant challenge in recent years in response to the search for drugs for anti-cancer therapies. One such method, now being intensively studied, is photodynamic therapy (PDT), which involves delivering photosensitive compounds to cancer cells and irradiating them with UV-Vis in the presence of oxygen, thereby inducing apoptotic or necrotic cell death. The use of photosensitive compounds in combination with appropriately selected biopolymers can increase the efficiency of photosensitizers and improve their application possibilities. In addition, an interesting approach seems to be using 3-in-1 materials based on magnetic nanoparticles coated with biopolymers with embedded photosensitizers. Magnetic nanoparticles are widely used in biomedical research due to their specific properties, such as small size, biocompatibility, broad chemical affinity, non-toxicity, and a wide range of potential modifications that further enhance their desired functionality [1].

Therefore, the present work focuses on preparing and characterizing polysaccharide materials in combination with porphyrins and their combination with magnetic nanoparticles. The structure and morphology of the materials were studied with the Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR), Scanning and Transmission Electron Microscopy (SEM, TEM), X-ray powder diffraction (XRD), and thermogravimetric analysis-differential thermal analysis (TGA-DTA) methods. The size of nanomaterials was studied using the TEM and Dynamic Light Scattering (DLS) methods [2].

An essential goal of our research was to test the potential usefulness of the polysaccharide as a new carrier for porphyrazine-type photosensitizers and to determine whether this polysaccharide would effectively stop unwanted photodegradation of macrocycles [3].

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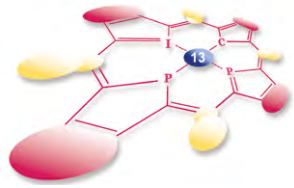

The derivatives of bilirubin have great potential as a medical drug

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Bilirubin, a distinctive yellow pigment originating from the degradation of heme in erythrocytes, occupies a pivotal role in the physiological processes of vertebrates. It is a crucial component of Bovis Calculus (Bezoar), highly esteemed and frequently utilized in traditional East Asian medicine. Studies on bezoar have shown that bilirubin forms complexes with calcium (bilirubin calcium), taurine, bile acids, and other substances like sugars, lipids, and inorganic salts, which is integral to its pharmacological properties.

Experimental outcomes, particularly from mouse toxicology comparative tests, have provided insightful data. These tests included samples of bezoar with a bilirubin concentration of 35%, and a 99% pure bilirubin (both synthetic and extracted from pig bile), across three distinct samples. Remarkably, all samples demonstrated an absence of toxicity. Furthermore, bezoar, bilirubin, and various bilirubin conjugates (such as bilirubin calcium, bilirubin taurine, and bilirubin bile acid) have shown efficacy in anti-inflammatory actions, enhancement of skin wound healing, and protection of cardiovascular and cerebrovascular systems.

The classification of bilirubin complexes, differentiating between monomeric bilirubin and bilirubin binders, represents an innovative stride in identifying new biologically active substances. This classification heralds the potential for groundbreaking developments in medical research and therapeutic applications.

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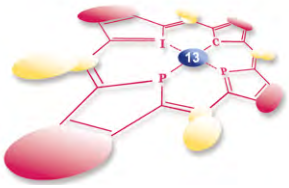

New Total Synthesis of Biliverdin and Bilirubin IXα

Fapu Chen, Yage Chen, Zhang Luo, Feng Pan, Xiliang Zhao, Jun Zhou, Moris S. Eisen, Rui Chen, and Zhi Li

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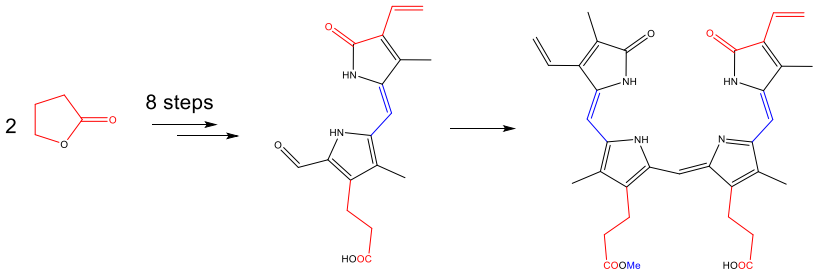
Bilirubin, a yellow pigment formed during the heme breakdown in the red blood cells, plays a central role in the physiological processes of vertebrates. It is the main component of Bovis Calculus (Bezoar), which is one of the most valuable and often-used medicinal materials in East Asia. Its association with jaundice and its potential as a biomarker for various pathological conditions have sparked immense interest among scientists and clinicians. Although the significance of bilirubin in human health has been extensively studied, its chemical synthesis has remained a challenging endeavor. We present an innovative chemical synthesis of biliverdin and bilirubin on a 30 g scale in a minimum number of steps from very inexpensive starting materials under very mild conditions. The scalable convergent synthesis overcomes existing limitations such as difficult chromatographic separation, high toxicity of selenium compounds and isomerization, enabling a deeper understanding of its structure-function relationship and opening doors to applications in diagnostics, therapeutics, and material science. The key intermediates, rings B and D were prepared on a kilogram scale beginning with the very economical butyrolactone. The methine bridge configuration in the ring system AB and CD was assigned as a Z-syn-periplanar conformer as corroborated by single-crystal X-ray studies.



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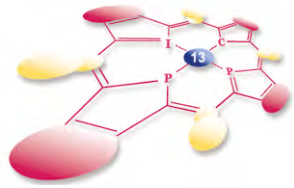

Biomimetic Porphyrin Nanoparticles

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The biomimetic nanoparticle represents a pioneering drug delivery platform inspired by natural biological features, aiming to enhance both the biocompatibility and specificity of nanotechnology in delivering drugs to targeted diseases. Here, we present multiple porphyrin biomimetic systems designed to mimic natural biological attributes for theranostic applications.

The porphyrin-based ultra-small nanostructure, known as PLP, mimics natural lipoproteins and inherently combines positron emission tomography, fluorescence, and photodynamic therapy functions for theranostic purposes[1-2]. PLP's biomimetic nature exhibits favorable pharmacokinetics without requiring PEGylation. Its rapid tumor intracellular trafficking enables nanostructure dissociation upon tumor accumulation, releasing monomeric porphyrins for low-background near-infrared fluorescence imaging and activatable photodynamic therapy.

To address the challenges in glioblastoma treatment, such as penetrating the blood-brain barrier (BBB) and achieving precise tumor targeting, we utilized the properties of endogenous apolipoprotein E3 (apoE3). Acting as a natural apolipoprotein, apoE3 facilitated the transcytosis of nanoparticles across the BBB and established strong interactions with glioblastoma cells that overexpress the low-density lipoprotein receptor. This strategic approach resulted in the development of glioblastoma-targeted porphyrin-lipid apoE3 lipid nanoparticles with inherent theranostic properties [3].

Furthermore, we engineered a nanoagent with a dual-biomimetic system: (1) mimicking efficient light-harvesting organelles found in nature, chlorosomes, with unique dye supramolecular assemblies and tunable photonic properties, and (2) mimicking high-density lipoproteins to stabilize intact dye assemblies and impart favorable in vivo behaviour [4]. This dual-biomimetic system enables precise control over particle size and optical properties, facilitating tunable mouse bioimaging (photoacoustic/fluorescence imaging) and phototherapies (photothermal /photodynamic therapies).

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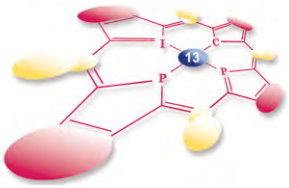

Toward Digital Discovery of Zr Porphyrinic Metal-Organic Frameworks

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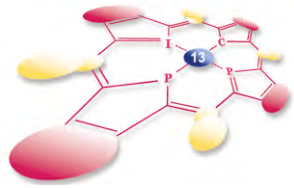
Zirconicum-based porphyrinic metal-organic frameworks (Zr-PMOFs) have garnered considerable attention owing to their exceptional chemical stability, tunability, and diverse functionalities. Recently research has explored the utilization of various elongated and functionalized porphyrin linkers in Zr-PMOF synthesis to create isoreticular structures with a range of functionalities. However, synthesis efforts have predominantly yielded frameworks with a single type of structure, attributed to the similarity in synthetic conditions across most Zr-PMOFs, posing challenges in achieving desired target structures.

In this work, we introduce a novel synthetic approach, the merged-net approach, which is designed to construct targeted Zr-PMOF structures using various porphyrin linkers. Through the merged-net approach, we successfully synthesize a new series of Zr-PMOFs, demonstrating their practical applicability, such as catalysis and water adsorption.

Encouraged by the success of rational methodologies such as the merged-net approach, we have integrated chemical insight into the material discovery process, developing the Up-Down Approach (UDA). This method combines the best elements of both top-down and bottom-up approaches and has proven effective in identifying new PMOFs. These rational approaches significantly expand the chemical space of PMOFs, focusing on advanced functionalities.



Trifluoromethylation and Annulation Reactions for Further Postfunctionalization Possibilities with Polypyrrole Systems

Jong-Keol An[a], Donghyeon Kim[a], Sudesh T. Manjare[a], David G. Churchill[a,b]

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In this research presentation, we will underscore three important "main group" chemistry-related compound types and potentially overlapping themes that we have come across through either independent or collaborative research endeavors (Cowork with X. Zhan; Z. Gross laboratories) with polypyrrole synthetic chemistry. We shall present many examples stemming from beta-CF_3 group incorporation into corroles. [1, 2] We shall discuss P corrroles and porphyrins and will emphasize certain results among the more than a few papers on the CF_3 group containing corroles published recently. [1] Additionally, we would like to introduce the Se containing annulation product that we obtained and reported on in 2014 (Figure 1, *right*) and how this might be an interesting dimension to pursue with corrole and porphyrins (less so perhaps with phthalocyanines). [3] This annulation reaction, which might be developed further in the context of *chiroptical-switchable* materials, comes in fact from the BODIPY literature; it is relatively important however to mention this strategy at this ICPP conference in the context of main group chemistry. In the future, we hope that these synthetic strategies can coalesce; new main group chemistry containing materials can thus be generated to meet various applications, especially emergent applications involving therapeutics and medicine.

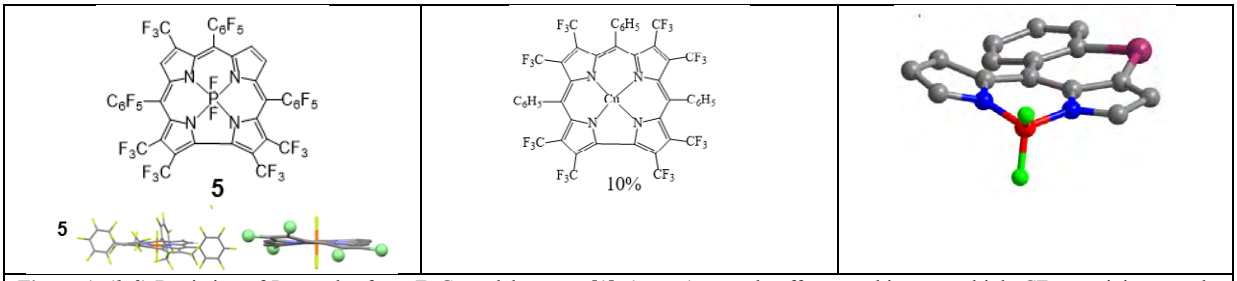

Figure 1. (*left*) Depiction of P corroles from Z. Gross laboratory [1], (*center*) an early effort to achieve a multiple CF_3-containing corrole product via *postfunctionalization* [2], and (*right*) Se BODIPY annulation reaction product that could be more broadly explored in the future in, e.g. corrole research.[3]

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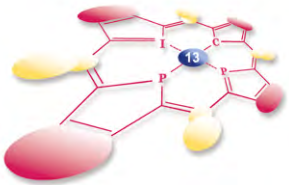

Wave Distortion in Au(II) Porphyrins

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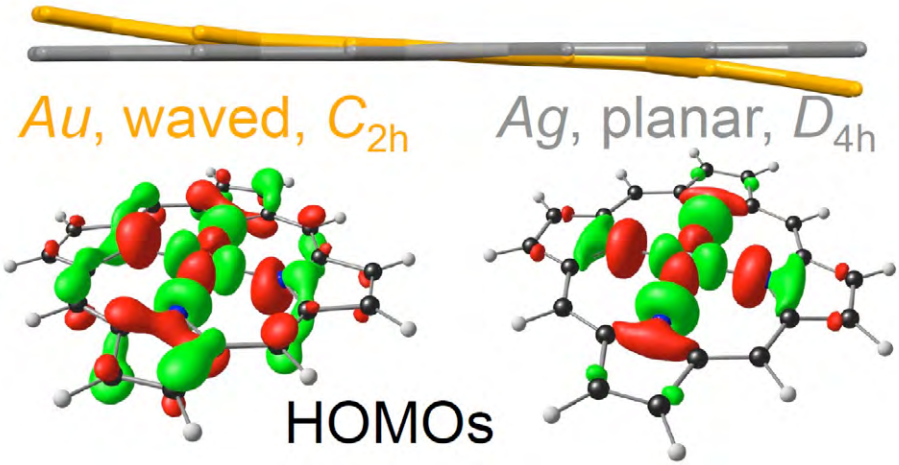
A detailed density functional theory (DFT) study of gold(II) porphyrins has shown that relativistic effects result in a lowering of the first ionization potential by approximately 1 eV, relative to analogous silver(II) systems, explaining the rarity and high reactivity of the Au(II) species [1]. The calculations also successfully reproduce the experimentally observed wave-shaped distortion of Au(II) porphyrins [2]. The electronic imperative of the Au(II) center to assume a pseudo-d^{10} configuration leads to a nonplanar wave distortion that allows for an Au(d_{x2-y2})-porphyrin(a_{2u}) orbital interaction. One consequence of the distortion is the delocalization of a significant fraction of the spin density on to the porphyrin ring. The wave distortion also drives a lateral distortion of the porphyrin, which results in unequal pairs of opposite Au-N bond distances. These results ascribe a substantially more subtle electronic structure to Au(II) porphyrins relative to that previously assumed.



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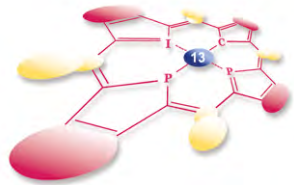

Coordination-Driven Self-Assembly of Multi-Porphyrin Architectures for Small Molecule Activations

Timothy R. Cook[a], Daoyang Zhang[a], Matthew R. Crawley[a]

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The use of metal-ligand bonding as a driving force for self-assembly reactions enables the construction of polynuclear architectures. Depending on the building blocks used, the resulting assemblies may be discrete molecules or extended frameworks. The Cook Group explores coordination-driven self-assembly with an emphasis on functional designs[1]. By exploiting the presence of multiple metal centers and rigid organic building blocks, it is possible to design metal-organic architectures that are capable of catalysis, electrochemical energy storage, and separation chemistry. This talk will introduce fundamental aspects of coordination-driven self-assembly and then will highlight our advances in the area of oxygen reduction electrocatalysis and other processes of relevance to renewable energy based on assembling two or more porphyrin units together to form cofacial prisms, cubes, and related structures.

The self-assembled cages may be characterized by a variety of techniques including mass spectrometry, NMR, EPR and X-ray crystallography to assess the stoichiometries of formation and to better understand how their structures govern reactivity. The kinetics and selectivity of the Oxygen Reduction Reaction (ORR) are highly sensitive to changes to the cofacial cleft, which may be tuned by changing the length of the molecular clip building blocks used to bridge the two porphyrins. We have used these designs primarily to carry out ORR[2-4] and have more recently been exploring their use as electrocatalysts for CO_2 reduction.

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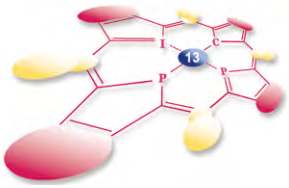

The pigments of life: A continuous source of inspiration for medical applications

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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, energy transfer, 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] A variety of applications from solar cells, and hydrogen production to medicine were reported.

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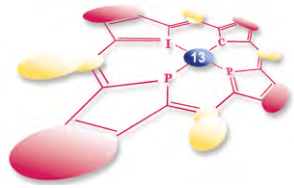

Combining helicenes and porphyrins

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Chirality describes an object that can exist as a pair of non-superimposable mirror-images. One of the most intriguing properties of chiral molecules is their ability to interact specifically with left- and right-handed circularly polarized light either in absorption (Electronic Circular Dichroism, ECD) or in emission (Circularly Polarized Luminescence, CPL) [1]. In 2021, we reported the synthesis of the first enantiopure helicene-porphyrin conjugates molecules. Their unpolarized and polarized optical properties were investigated and they reveal an intense bisignate Exciton Coupling (EC) signal and Δε values up to 680 M^{-1} cm^{-1} for the Soret band along with a CPL in the (far-)red region, where examples of chiral luminophores are limited[2]. Since then, other examples combining helicenes and porphyrins have been developed[3,4], notably for applications in host-guest supramolecular chemistry[4], or for Chiral-Induced Spin Selectivity (CISS effects).

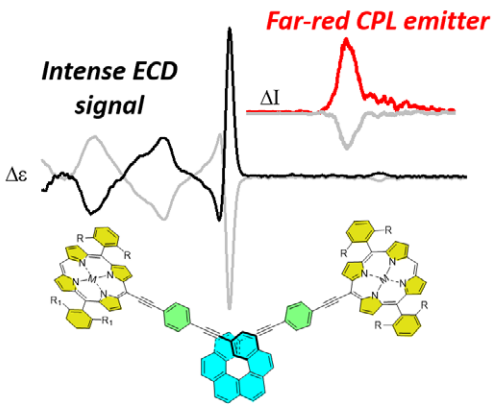

Figure 1: Chemical structure and Chiroptical (ECD and CPL) activities of helicene-porphyrin derivatives

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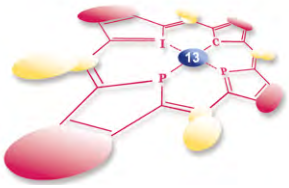

Far-Red and Near-IR Capturing BODIPYs for Modulating Light-Induced Charge Separation

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Supramolecular nanostructured hybrid nanomaterials decorated with photosensitizers designed for light energy conversion and storage, optoelectronics, and chemical and biochemical sensing provide outstanding opportunities for innovative low-cost nanotechnologies[1-3]. Functional carbon nanomaterials, for example, fullerenes, nanotubes, and graphene coupled with wide-band capturing photosensitizers play pivotal roles in such applications. Both covalent bonding and self-assembly motifs with complimentary binding have been successfully employed in such studies, and have been used in the fabrication of devices for light-to-electricity and light-to-fuel conversion[1-3]. The presentation from recent work covers topics including (i) symmetry-breaking charge transfer in far-red capturing BODIPY dimers[4], (ii) design concepts and syntheses of multi-modular donor-acceptor conjugates for charge stabilization upon interactions with single-wall carbon nanotubes,[5] and (iii) broad-band light capturing, and high-potential charge-separated states in molecularly engineered donor-acceptor systems and supramolecular nano-assemblies[2]. The design principles of these multi-modular systems and key outcomes will be summarized.

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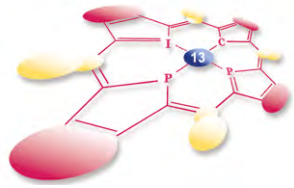

Interactions between achiral porphyrins and miRNA

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MicroRNAs (miRNAs) are a class of highly conserved, short (18-24 nucleotides) and non-coding RNAs that regulate gene expression by base-pairing to one or more mRNA targets, causing either target degradation or translational repression.[1] Dysregulation of miRNAs contributes to the initiation and development of human diseases like cancer.[2] Recent insight into the roles of miRNAs has made them attractive tools and targets for novel therapeutic approaches.[3] Since the relevant roles of miRNAs in biological processes are connected with cancer, the mature miRNAs stabilization or destabilization by small molecule ligands could be used as a selective, novel, anti-cancer therapeutic strategy. In addition, recent discoveries have revealed that mature miRNAs could form highly ordered structures similar to aptamers, suggesting diverse functions beyond mRNA recognition and degradation.[4] This study focuses on understanding the secondary structures of human miR-26b-5p (UUCAAGUAAUUCAGGAUAGGU) using circular dichroism (CD) and chiroptical probes, in particular four achiral porphyrins were utilized to both act as chiroptical probes and influence miRNA thermodynamic stability.[5] Various spectroscopic techniques, including UV-Vis, Fluorescence, Resonance Light Scattering (RLS), Electronic Circular Dichroism (ECD), and CD-melting, were employed to study their interactions. UV-Vis titration revealed that meso-tetrakis(4-Nmethylpyridyl) porphyrin (H2T4) and meso-tetrakis(4-carboxyphenylspermine) porphyrin (H2TCPPSpm4) formed complexes with distinct binding stoichiometries up to the ratio 6:1 and 3:1, respectively and these results were supported by RLS and fluorescence, while the zinc (II) derivative porphyrin ZnT4 exhibited a weaker interaction. ZnTCPPSpm4 formed aggregates in PBS, with higher organization in the presence of miRNA. CD titrations displayed an induced CD signal in the Soret region for every porphyrin investigated, indicating that they can be used as chiroptical probes for the miR-26b-5p. Lastly, CD-melting experiments revealed that, at a 1:1 ratio, porphyrins did not significantly affect miRNA stability, except for H2TCPPSpm4. However, at a 3:1 ratio, all porphyrins, except ZnTCPPSpm4, exhibited a strong destabilizing effect on miRNA secondary structures. These findings shed light on the structural versatility of miR-26b-5p and highlight the potential of porphyrins as chiroptical probes and modulators of miRNA stability.

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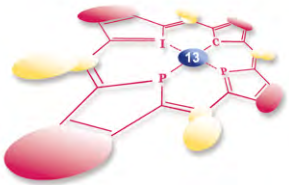

Functionalized fluorinated bacteriochlorins for photoimmunotherapy

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Innovative approaches for combating resistant cancers through the stimulation of the immune system show great potential. One notable example of such therapeutic strategies is photodynamic therapy (PDT), which operates on the principles of photochemistry. PDT not only exerts direct effects on cancer cells but also disrupts tumor vasculature and activates the host immune system. However, to achieve successful therapeutic outcomes, including the eradication of primary tumors and distant metastases, the design of appropriate photosensitizers (PSs) with desired optical and photophysical properties is imperative. These properties enable efficient generation of reactive oxygen species (ROS) under tumor microenvironmental (TME) conditions, particularly hypoxia. [1-2]
This work places particular emphasis on the photochemical characteristics of bacteriochlorin-based photosensitizers, with a focus on their intense NIR absorption and sufficiently long-lived triplet states that enable ROS generation. [3-4] ROS not only initiates an inflammatory reaction but also induces the expression of heat-shock proteins, promotes immune cell infiltration, and establishes long-term immune memory. The distinctive features of PDT open up new possibilities for combining PDT with agents that stimulate the immune response, as well as with immunotherapy, specifically those based on PD-1/PD-L1 blockade. Furthermore, this work provides an overview of our recent findings regarding the synthesis of TEM-targeted conjugates possessing desired spectroscopic and photochemical properties, as well as enhanced selectivity and biological activity confirmed in various advanced cellular and animal models. Bacteriochlorin-based PDT *in vivo* led to a strong and long-term antitumor immune response. Optimized PDT regressed the growth of not only primary but also distant tumors examined in bilateral syngeneic and pseudo-metastatic mouse models. Our data provide evidence for the role of PDT for local immune modulation, and that the combination with PD-1/PD-L1 checkpoint inhibitors is a promising strategy in the therapy of highly resistant and difficult-to-treat cancers such as colorectal cancer and melanoma.

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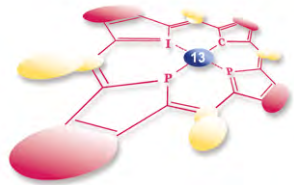

Structural Versatility of Metalloporphyrins for Photovoltaic Applications

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The optical and electrochemical properties of porphyrins can be tailored through molecular design and functionalization at the β or meso positions of the porphyrin ring, as well as by introducing various central metal ions. The selection of the centrally coordinated metal cation within the porphyrin core plays a crucial role in influencing electronic properties, enabling the modulation of frontier orbital levels. Consequently, porphyrin-based molecules can be tailored as either donor or acceptor components in photovoltaic devices.

We have designed and synthesized metalloporphyrins with significant electronic properties to be used in organic solar cells, showing efficiencies up to 15%. Ni-porphyrin derivatives, characterized by a deeper HOMO energy level, have demonstrated the potential to achieve high power conversion efficiency (PCE) values in solar devices. Additionally, we employed an Au(III) porphyrin core for the first time, serving as a non-fullerene acceptor for organic solar cells (OSCs) and resulting in a remarkable PCE of 9.24%. Furthermore, we investigated A-π-D-π-A small molecules based on Cu(II) porphyrin, a component rarely used in efficient OSCs, revealing an ambipolar behavior.

Our research also delved into the impact of functionalizing the porphyrin core at the β positions relative to meso-substituted porphyrins on electronic properties. In this presentation, I will highlight our recent work on the design, synthesis, and application of various porphyrin-based small molecules incorporating diverse structural modifications. These modifications aim to enhance the electronic properties of these systems, ultimately contributing to the development of highly efficient OSCs.

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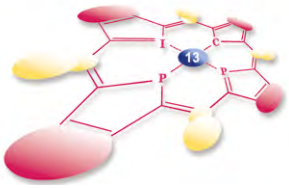

Metallosupramolecular subphthalocyanine cages: molecular containers for reactions on guest fullerenes

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Over the last years, the use of metallo-organic cages to perform chemical transformations over fullerenes has become a hot topic since these compounds are key components in state-of-the-art technologies. In previously reported examples, reactions were carried out in organic solvents [1], and crucially, they required stoichiometric amounts of the cage [1,2]. Herein we report a subphthalocyanine (SubPc) supramolecular cage that works as a catalytic molecular reactor to perform transformations over fullerenes in water [3]. Taking into account the ability of metallo-organic Pd(II)-SubPc capsules to form stable host:guest complexes with fullerenes, we have prepared a water-soluble cage (**SubPc-cage**, Figure 1a) that provides a hydrophobic environment for conducting cycloadditions over encapsulated C_{60}, namely, Diels-Alder reactions with anthracene. The presence of catalytic amounts of **SubPc-cage** promotes co-encapsulation of insoluble C_{60} and anthracene substrates, allowing the reaction to occur inside the cavity under mild conditions. The lower stability of the host:guest complex with the resulting C_{60}-anthracene cycloadduct facilitates its displacement by pristine C_{60}, which grants catalytic turnover. Bis-addition compounds are also regioselectively formed inside the cage when using excess anthracene. Last, we have broadened the scope for the outstanding **SubPc-cage** catalyzed Diels-Alder reaction in water media to other 9-substituted anthracene derivatives, and the cavity-promoted reactivity of the larger homologue C_{70} has been also explored. The results have been rationalized using theoretical calculations at the GFN2-xTB level (Figure 1b).

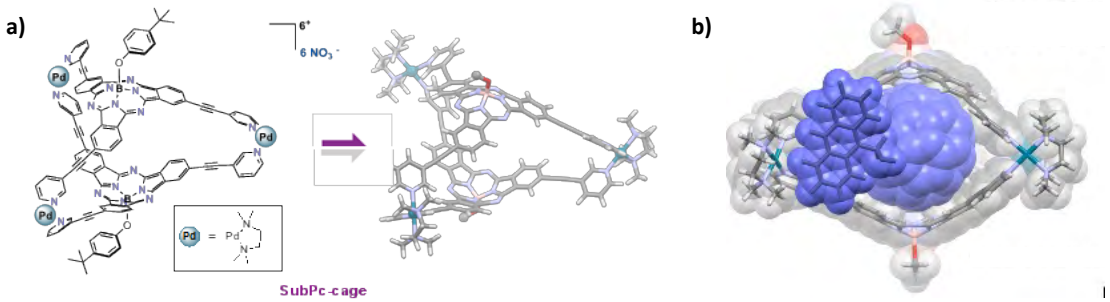

Figure 1. a) Structure of **SubPc-cage**; b) Minimum-energy structures of the pre-organized complex between **SubPc-cage** and a 9-functionalized anthracene.

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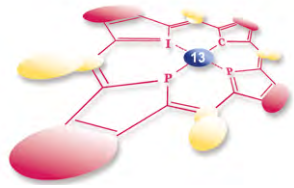

Interaction of BODIPY with cucurbit[7]uril and its influence on PDT

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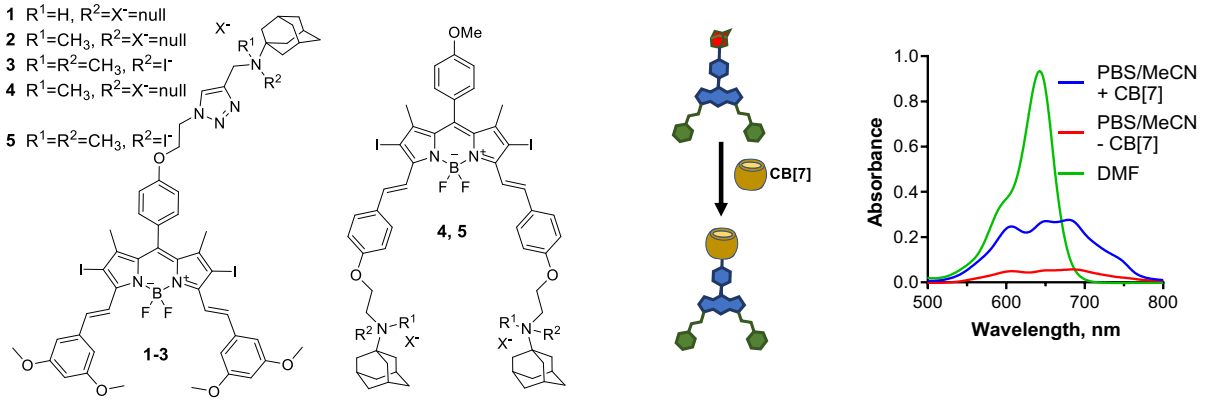
Compounds based on the structural skeleton of boron-dipyrromethene (4,4-difluoro-4-borata-3a-azonia-4a-aza-*s*-indacene; abbreviated as BODIPY) have high molar absorption coefficient and related to this they have interesting photophysical properties – such as high quantum yields of fluorescence and singlet oxygen. For these properties, BODIPY found usage as fluorescence probes or photosensitizers in photodynamic therapy [1, 2]. However, the lipophilic BODIPY core is not ideal for use in a water environment, such as distribution through the bloodstream. That is the reason why we decided to introduce cucurbit[7]uril (CB[7]) moiety. Cucurbiturils are condensed from glycolurils monomer, and based on the number of monomer subunits, and they have different cavity sizes. Guest-host interaction was chosen to connect CB[7] to BODIPY. Thus, BODIPY with suitable guest moiety had to be synthesized. Adamantylamine moiety was selected for this purpose because the interaction between CB[7] and adamantylamine is strong [3]. Five different BODIPY compounds were synthesized with varying numbers of adamantylamine units – the first approach had one adamantylamine unit in the *meso* position, and the second approach had two adamantylamines on styryls. A biological evaluation of the photodynamic activity of BODIPY was performed on HeLa cells.



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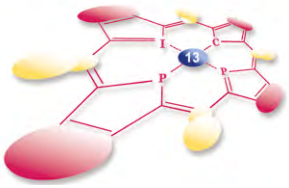

Triplet dynamics in porphyrin-based metal–organic frameworks

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High quantum yield triplet generation from the initial singlets is desired for photon-to-chemical energy conversions in solid working compositions. Unlike natural photosynthesis apparatus that built elegant strategies to avoid triplets (for oxidative degradation), artificial systems like porous metal–organic frameworks (MOFs) can afford an inert operation if long-lived triplets can be efficiently prepared and harvested. The premise of high-yield and long-lived triplets may not be transformative photophysics of what is known as a single molecular system with high singlet-triplet intersystem crossing (ISC). We have discovered that—like in the chlorophyll assembly in a light-harvesting complex—a large disparity in the distribution of the excitonic center of mass inhibits the ISC in the chromophore assemblies in MOF.[1, 2] Such phenomenon, observed in MOFs built out of heavy metal-based nodes (e.g., carboxy-coordinated zirconium ion) suggests ineffective spin-orbit coupling impact on the linkers. In the quest for routes that can facilitate (or cease) triplet generation, singlet fission (SF) was found effective.[2] However, SF involves CT-based intermediate (not ISC) and can be modulated by the linker density dictated by the topology of the frameworks.[3] To understand the origin of the disparity in the distribution of the excitonic center of mass and improve the spin-orbit coupling, we studied a series of porphyrin-based MOFs with varying metal cores. This study will not only shed light on some basic photophysical and energetic criteria but also will shed light on the fate of the triplets, if formed, in these elegantly organized systems.

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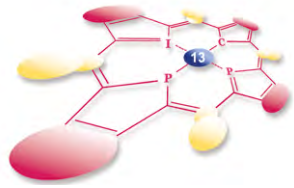

Ultra-high irradiation of corroles and porphyrins for short antimicrobial treatments

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In recent years antibiotic resistance has rapidly spread around the world, posing a critical threat to public health. Methicillin-resistant S. aureus (MRSA) was clinically identified in 1960 and over several decades new strains have emerged, leading to a global catastrophe that continues today.[1] For antifungals, resistance to azoles is one of the biggest challenges to clinical success.[2] More recently, the yeast Candida auris has been recognized as a serious health threat due to its innate and acquired resistance to antifungal drugs. An increasing number of new cases of Candida auris with resistance to standard antifungal treatments, including azoles, echinocandins, and polyenes, have been reported.[3] To address this emerging public health problem, it is important to develop non-invasive, non-toxic, and new antimicrobial techniques that are more effective and faster than current antibiotics. Herein, we will report the synthesis and evaluation of porphyrins and corroles bearing either one, two, or three of four carboxylic acid groups as antibacterial efficacy against Staphylococcus aureus (methicillin-resistant or methicillin-sensitive strains) and antifungal activity against the yeast Candida albicans and the filamentous fungi Aspergillus fumigatus.[4] We will also demonstrate that it is possible to enhance antimicrobial activity using very short ultra-high irradiation.

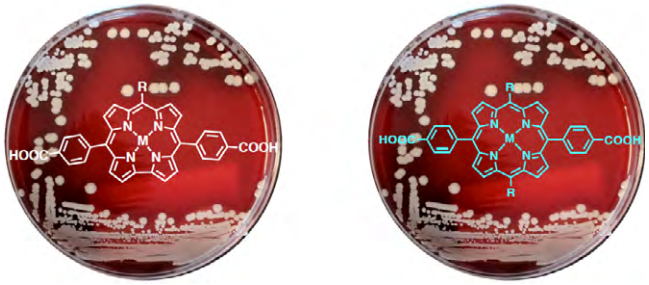

Figure 1: corroles *versus* porphyrins

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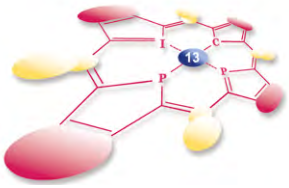

Oxidative C-N fusion of pyri(mi)dinyl-based porphyrins

F. Akhssas, N. Amiri, M. Berthelot, A. Bousfiha, A. K. D. Dimé, D. Lucas, H. Cattey, J. Roger, P. Fleurat-Lessard, C. H. Devillers

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Extending the π-conjugation of aromatic molecules, in particular porphyrinoids, via C-C or C-N coupling(s) with peripheral aromatic fragment(s) has been the focus of numerous research over the last two decades [1]. Indeed, C-C/C-N fusion of one are several hydrocarbon(s) or aromatic heterocycle(s) onto the porphyrin periphery forces the porphyrin core and the substituent to be coplanar, which enhances the electronic communication between both fragments. π-extended porphyrins display important changes in their optical and electrochemical properties such as a decrease of the HOMO/LUMO gap, bathochromic shift in their absorption/emission spectra, large absorption and fluorescence in the NIR range [2]. Nowadays, π-extended C-C/C-N linked porphyrins are commonly obtained using toxic and/or expensive chemicals, often under harsh conditions. Due to the extension of the conjugation path, the oxidation potential decreases which may lead to over-oxidation during the fusion process.

In this work, the (electro)chemical oxidation of original pyri(mi)dinyl-porphyrins will be presented affording the C-N fused (bis)pyri(mi)dinium derivatives in a stepwise manner [3a,b]. The resulting pyridinium derivatives exhibit important changes in their physico-chemical properties (NMR, UV-vis., CV) as compared to their initial unfused precursors. The mono- and bis-pyrimidinium-porphyrins are not stable and evolve towards the original *meso,β*-fused thiazinamine-porphyrins [3c].

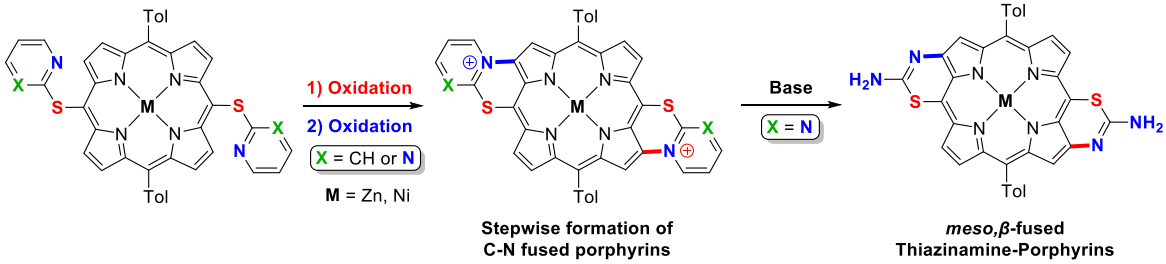

Figure: *Oxidative C-N fusion of meso-Pyri(mi)din-2-ylthio-Porphyrins.*

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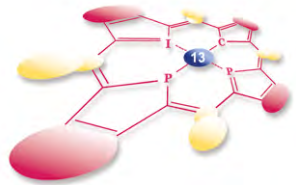

Porphyrinoids based sensors for Volatilomics Applications

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Metabolomics is the systematic study of the distinct chemical signatures left by specific cellular and physiological processes. It involves a range of analytical methods to identify low molecular weight metabolites in biological samples associated with specific health or disease conditions. The primary goal of metabolomics studies is to identify alterations in the metabolic profile due to specific conditions or diverse pathologies, ranging from cancer to infectious diseases.
Volatilomics, a subset of metabolomics, focuses on small metabolites that are volatile or semi-volatile. The human volatilome can be examined in various samples such as breath, skin, urine, saliva, and feces [1].
The study of volatile compounds holds significance in analytical chemistry. However, analytical machines are often bulky, expensive and require specialized personnel for operation and data interpretation. Volatilomics is particularly intrigued by the prospect of replacing these analytical machines with sensors, which are small devices directly connectable to electronic platforms.
In sensors, the separation stage in analytical instruments is replaced by the sensor's affinity for the molecules in the sample. Sensors produce signals related to the total molecules they encounter. Sensors can be selective, prioritizing one molecular species over others, or non-selective when affinities are comparable. In principle, to replace a gas chromatograph (GC), an array of sensors, each selective to a different species, is necessary.
However, the development of sensors for volatilomics draws inspiration from nature, specifically olfaction [2]. Olfaction's ability to sense various odors with a limited set of receptors has led to the concept of combinatorial selectivity. Porphyrinoids, with their modular structure comprising a central metal atom, aromatic ring, and peripheral motifs, offer a wide variety of sensitivity patterns suitable for electronic nose designs.
Porphyrins have been extensively used in volatilomics, initially as the functional layer of quartz microbalances. In 2003, an array of porphyrins and corroles demonstrated the diagnosis of lung cancer through breath analysis [3]. Subsequent applications targeted tuberculosis from breath, lung and kidney cancers from urine, and COVID-19 from serum. These sensors were also utilized in studying malaria and stem cell proliferation in murine models. Recently, quartz microbalance sensors faced competition from porphyrins-based impedance sensors, expected to reduce production costs and result in simpler, more widely usable devices. For instance, a capacitive sensor array made of porphyrinoid-coated silica particles detected COVID-19 from volatile organic compounds (VOCs) in serum. Porphyrins-doped PEDOT was implemented in facemasks for diagnosing chronic kidney diseases.
In the presentation, the rationale behind these developments will be elucidated, and notable case studies will be discussed.

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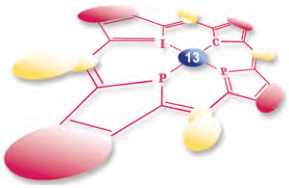

Peptide corrination in drug development

Robert P. Doyle[a,b]

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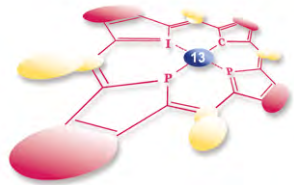
Corrination is the conjugation of a corrin ring-containing molecule, such as vitamin B12 (B12) or B12 biosynthetic precursor dicyanocobinamide (Cbi), to small molecules, peptides, or proteins with the goal of modifying pharmacology. The benefits of corrination over other conjugation modes lie in the ability to specifically target select corrin-binding proteins such as intrinsic factor, transcobalamin, or haptocorrin for use in targeting or to affect pharmaco-kinetics, modify solubility, and alter drug localization, all without having to reverse the process to allow for maintained drug function (pending suitable design). In this talk, I will discuss the use of corrination to mitigate side-effects profiles of novel obesity medications from GLP-receptor agonists to oxytocin analogs. Also noted will be the use of corrin rings to produce peptide disulfide bonds in a regioselective manner, and a possible role for corrination in peptide stability and formulation.



Anodic Oxidation of a Zinc Porphyrin Layer on an Aqueous Surface

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The properties of porphene, a conjugated two-dimensional polymer composed of fully fused porphyrin rings, are readily tunable by the insertion of various metal ions into its binding sites, suggesting possible uses in nanoelectronics. However, the original preparation by oxidative polymerization of a layer of porphine on an aqueous surface by the action of a chemical oxidant contained in the subphase [1] proceeds through a large number of seeds and yields uncomfortably small single-crystalline domains (~100 nm). One way to reduce the number of polymerization seeds and increase the domain size would be to use anodic oxidation at a small tip. We have constructed a Langmuir-Blodgett trough with such a tip and a circular counter-electrode (Figure 1) and are examining this possibility (Figure 2). Initial tests on a layer of 1,1´-dicarbooctadecyloxyferrocene were successful [2].

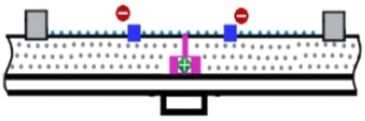

Figure 1. Side view: the solution, barriers, working electrode, and counter-electrode.

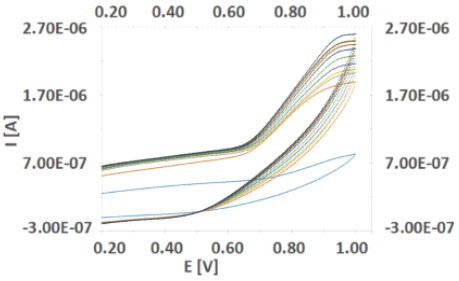

Figure 2. Cyclic voltammograms were obtained upon a gradual approach of the tip up to and beyond an aqueous surface coated with a bilayer of zinc porphyrin. Bottom curve: tip far below the surface.

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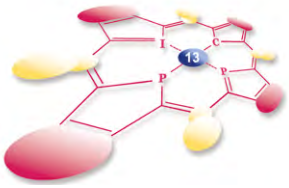

Nano-encapsulating phthalocyanines into polymeric materials

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Nanomedicine has raised the promises of the Enhanced Permeation and Retention (EPR) effect stipulating that nanoparticles will target tumour tissues because of the specific extravasation of nano-sized items through the defects of the tumour neovasculature. Even if the EPR effect has many limitations, the use of nanoparticles especially polymeric nanoparticles has other advantages such as increasing drug loading and delivery and improving their biocompatibility.

The several encapsulation strategies we have explored over the last years in the context of multiple collaborations to encapsulate and deliver phthalocyanines to tumour cells and tissues will be presented. Many different polymeric materials have been used, such as triblock Pluronic polymers,[1] polyvinylpyrrolidone and other surfactants,[2, 3] poly-L-glutamic acid,[4] silsesquioxane,[5, 6] as well as polycaprolactone, poly(benzylmalate) and methacrylate polymers.

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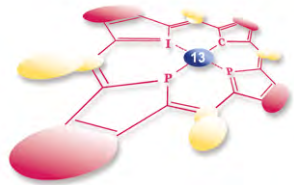

Engineering open-shell porphyrin nanoarchitectures on surfaces

David Écija[a]

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The emergence of pi-magnetism in carbon-based nanomaterials synthesized by on-surface synthesis has revolutionized our understanding of the interactions between spins [1, 2]. In this talk, I will revise our recent works regarding the on-surface synthesis of open-shell porphyrinoids and their supramolecular and covalent assembly.

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Synergistic Effect of Copper Corrole and Iron Porphyrin in Porphyrrole Aerogel for the Electrocatalysis of Oxygen Reduction Reaction

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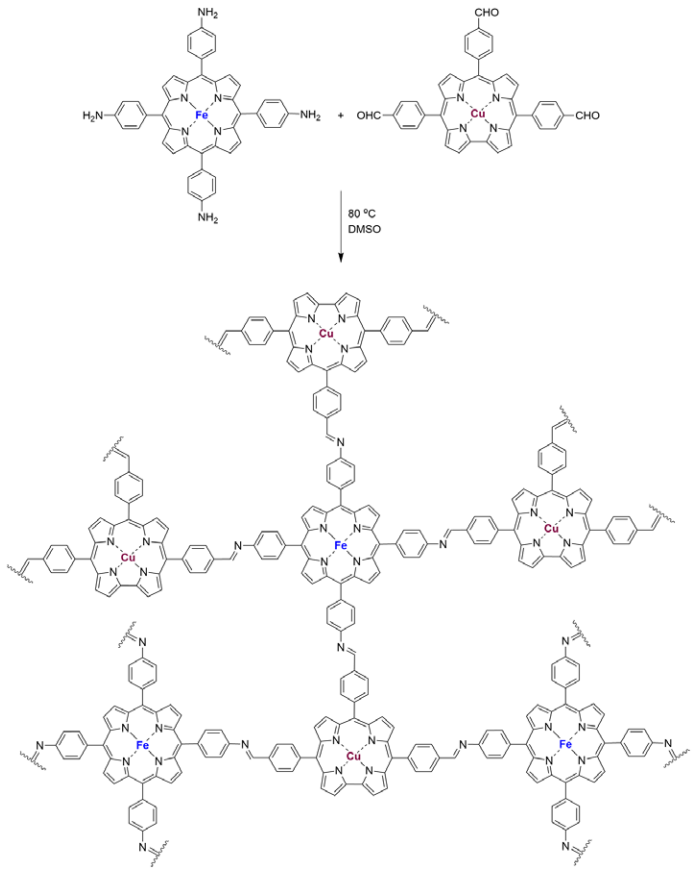

The development of bio-inspired catalysts for oxygen reduction reactions is one of the most prominent pathways in the search for active materials to replace Pt-based catalysts in fuel cells. Herein, we report a new bio-inspired catalyst using a directed synthetic pathway to create adjacent Cu and Fe sites. This new catalyst is composed of a covalent three-dimensional framework in an aerogel form (**Scheme 1**). Aerogels are high surface area and porous hierarchical structures, that can allow the formation of ultra-high active site density and optimized mass transport of reactants and products to and from the catalytic sites. The new aerogel-based catalyst exhibits excellent performance in half-cell in 0.1 M KOH, with an onset potential of 0.94 V vs. RHE and half-wave potential of $E_{1/2}$ = 0.80 V vs. RHE, high selectivity towards the 4-electron reduction of oxygen to hydroxide anions, and very good durability. These results are translated very well in anion exchange membrane fuel cell (AEMFC), reaching an open circuit potential of 0.97 V and iR-corrected peak power density of 0.51 W cm^{-2}. Based on density functional theory calculations, the improved activity relative to the Fe-porphyrin and Cu-corrole is ascribed to the effect of the extended carbon network and the proximity of the metal sites.

Scheme 1. Illustration of FeCu porphyrrole gel synthesis and basic structure.

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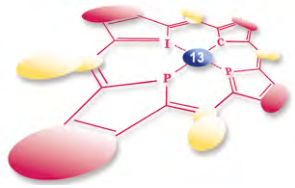

STM studies of metal porphyrin reactivity at solid-liquid interfaces

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ORALS

Many chemical reactions are catalyzed by metal porphyrins, and insight into their reaction mechanisms is of fundamental importance for the design of new chemical processes. A wealth of conventional spectroscopic techniques is available to study reaction mechanisms at the ensemble level, but with the emergence of single molecule microscopies it has become possible to obtain unique information about reactivity at sub-nanometer scale. Using a dedicated Scanning Tunneling Microscope (STM) setup, we have been investigating the reactivity of manganese(III) porphyrins at the chemically relevant interfaces of atomically flat surfaces and apolar organic liquids, at room temperature under atmospheric pressure [1-4]. When self-assembled monolayers of these porphyrins are exposed to an oxygen atmosphere, STM revealed that a variety of reactions can occur which are expressed as clear changes in porphyrin signature in the STM images. Different redox states of the porphyrins can be identified [3, 5], and the dynamics of the reactivity are monitored in real time. I will demonstrate that the STM setup can be used as an active tool to control the redox chemistry of the metal porphyrins, and that specific choices of surface (graphite or gold) and organic liquid can have a significant influence on metal porphyrin reactivity.

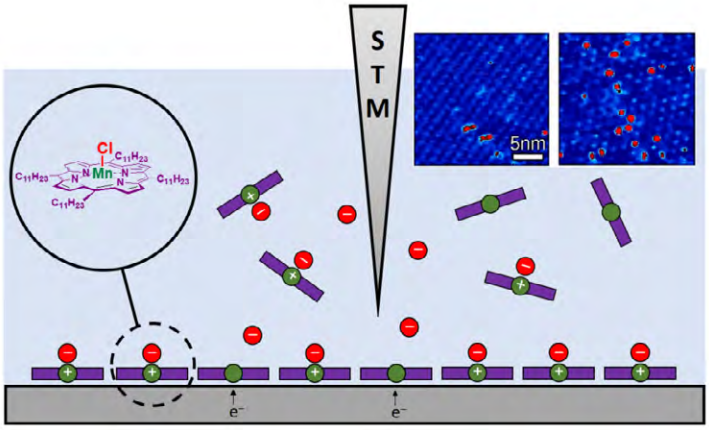

Figure 1: *schematic representation of the study of the reactivity of Mn(III) porphyrins at a solid-liquid interface with STM. On the top right two STM images are shown of self-assembled monolayers of these porphyrins (dim spots) and manganese-oxo reaction products (bright spots) after exposure to* O_2.

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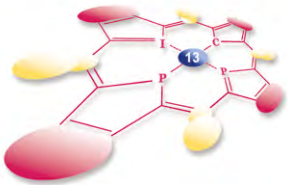

Exploring Aromaticity and UV-Vis Absorption Correlations in Phthalocyanines and Subphthalocyanines

Sílvia Escayola[a,b], Jorge Labella[c], Dariusz W. Szczepanik[d], Albert Poater[a], Tomas Torres[c], Miquel Solà[a], Eduard Matito[b]

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Phthalocyanines (Pcs) and subphthalocyanines (SubPcs) are critical in various applications, including solar cells and photonics, due to their unique π-conjugated systems and optical properties [1]. Understanding the relationship between their structure, aromaticity, and electronic properties is essential for targeted molecular design. Our study integrates spectroscopic analysis and advanced computational methods, including Time-Dependent Density Functional Theory (TD-DFT) and various aromaticity indices [2], to investigate the structural, electronic, and optical properties of a series of Pcs and SubPcs (Figure 1). We demonstrate that *meso* and *β* substitutions significantly influence the aromaticity and UV-Vis absorption properties of these compounds. Our results reveal distinct trends in Q and B band shifts in response to structural changes, suggesting a relationship between the aromatic character of specific molecular pathways and the absorption energies. The study provides a nuanced understanding of the role of frontier orbitals in determining optical properties, extending beyond the traditional Gouterman model. Additionally, we highlight the importance of considering both global and local aromaticity in these systems, offering insights into electron delocalization pathways. The findings underscore the potential of using aromaticity as a predictive tool for tuning the optical properties of these compounds, providing a robust framework for future research and molecular engineering in this field.

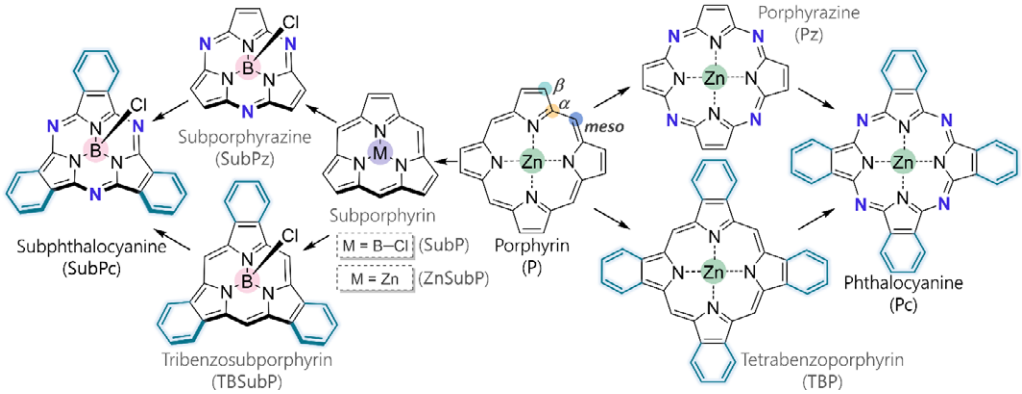

Figure 1. Metallo or B−X coordinated (sub)porphyrins and (sub)phthalocyanines

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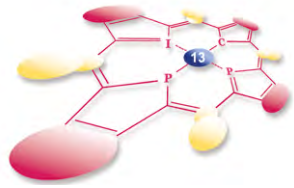

Porphyrins for antimicrobial environmental applications

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ORALS

Porphyrin derivatives have garnered significant attention as photosensitizers in photodynamic therapy (PDT) and, more recently, in antimicrobial applications [1]. These versatile compounds possess inherent photoactive properties that can be harnessed to address microbial contamination in different environmental contexts. Their capacity to generate high levels of reactive oxygen species (ROS) contributes to their potent antimicrobial activity. Whether in their free form or immobilized on various supports, porphyrin derivatives have demonstrated their ability to effectively target and eliminate a wide range of microorganisms, including bacteria, viruses, and fungi, under various environmental conditions [1,2]. Nowadays, the applications of porphyrin-based photodynamic antimicrobial treatment (aPDT) extend to areas such as water and wastewater treatment, as well as surface disinfection, among other environmental applications [3-5]. In this communication, recent advances in the use of porphyrin derivatives as photosensitizing agents for environmental applications will be discussed.

Acknowledgments & Funding
Thanks are due to the University of Aveiro and FCT/MCTES for the financial support to LAQV-Requimte (UIDB/50006/2020 and UIDP/50006/2020), CESAM (UID/AMB/50017/2019 and UIDB/50017/2020 + UIDP/50017/2020) and the FCT project PORP2PS (EXPL/QUI-QOR/0586/2021) through national funds and when applicable co-financed by the FEDER, within the PT2020 Partnership Agreement and "Compete" 2020. Thanks, are also due to the Portuguese NMR and Mass Networks. C.V. thanks FCT for their doctoral grants SFRH/BD/150358/2019. NMM Moura thanks FCT for his funding through program DL 57/2016 – Norma transitória (CDL-CTTRI-048-88-ARH/2018).

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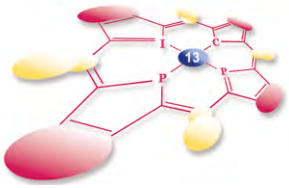


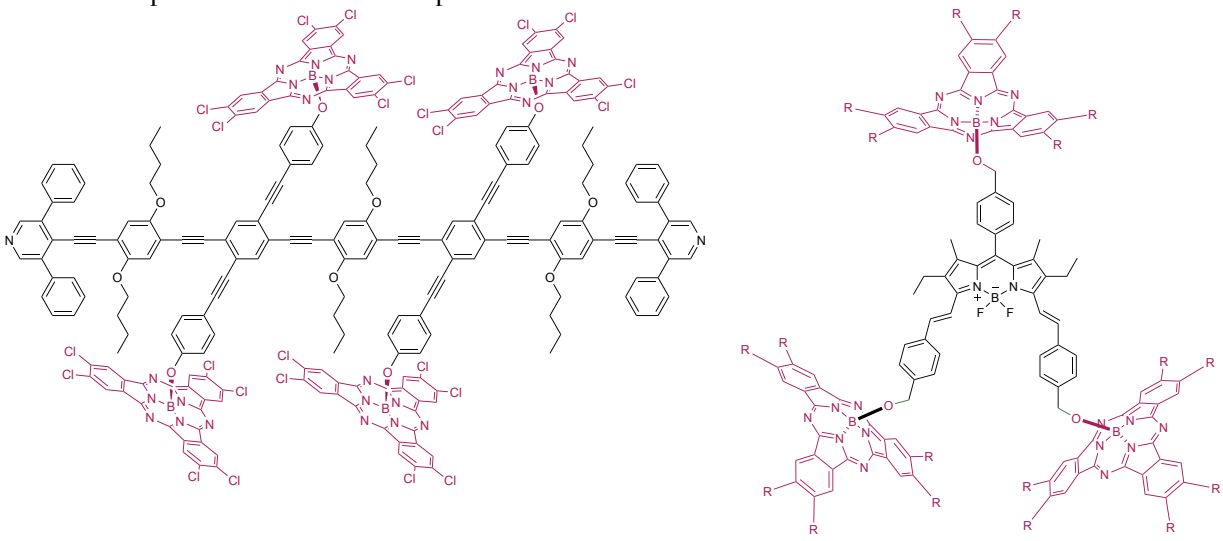
Energy Shuttling with SubPc-Arrays

Rüdiger Faust, Gero Grunewald, Denise Täubert, and Lorena Vogt

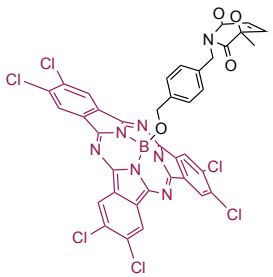
University of Kassel, Institute for Chemistry and CINSaT – Center for Interdisciplinary Nanostructure Science and Technology, Heinrich-Plett-Str. 40, 34132 Kassel, Germany, r.faust@uni-kassel.de

The cone-shaped subphthalocyanines (SubPcs) have emerged as promising functional chromophores with an intriguingly broad application profile that is driven by their synthetic accessibility and their relative ease of handling in combination with impressive solar light harvesting and/or photooxidative properties.

We have previously exploited the base-induced ring-opening of the SubPcs for the design of desymmetrized A3B-phthalocyanines and porphyrazines. This experience has now prompted us to explore in further detail the use of SubPcs in multi-chromophore ensembles around rigid aromatic and alkynyl scaffolds (see Figure below). Of particular interest in this respect is our venture into photoexcitable molecular wires. Furthermore, the presentation will also highlight SubPc-scaffolding using photophysically active bringing units such as porphyrins and BODIPYs. Synthetic details along with preliminary results of the photophysical investigations of the prepared multi-chromophore ensembles will be reported.



In a second line of research we are currently investigating SubPc as a scaffold for singlet oxygen catch-and-release units. Initial designs rely on the singlet oxygen capture of pyridones covalently attached to the SubPc core (see Figure to the right). This research will be extended to supramolecular binding motives to provide for the dynamic and reversible attachment of the carrier unit. Progress of this ongoing research will be reported.



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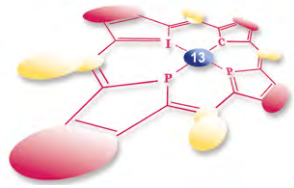

Early prediction of sepsis based on fluorescent biomarkers of bacterial metabolism

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Background: Early detection of bacterial sepsis is critical for effective patient treatment [1,2]. Even a low bacterial load of just 10 colony-forming units (CFU)/ml of blood can trigger sepsis. While blood culture-based tests are standard for diagnosis, they are labor-intensive and time-consuming, requiring skilled personnel [3]. To address this, we developed a proof-of-concept method that exploits fluorescent biomarkers of bacterial survival mechanisms to detect sepsis more efficiently. **Method:** We created an in vitro model to mimic sepsis using pathogenic E. coli and S. aureus, two common bacteria in sepsis. We injected 1 ml of healthy donor whole blood with these bacteria at low (10^2 CFU/ml), medium (10^4 CFU/ml), and high (10^8 CFU/ml) concentrations to simulate different stages of sepsis development. We monitored two fluorescent biomarkers of bacterial metabolism—protoporphyrin, indicating bacterial ALA metabolism, and β-LEAF, indicating enzyme activity involved in processing antibiotics—over 48 hours. For practical application of this early sepsis diagnosis method at the point of care, we developed a smartphone-based platform using components like linear polarizers, a Moto G5 Android smartphone, an LED driver, a rechargeable battery, a smartphone case, and custom mobile app software. **Results:** With the ALA approach, the initial protoporphyrin fluorescence appeared just one hour after ALA incubation for both E. coli and S. aureus. The signals continued to rise, reaching a plateau after 24 hours, regardless of the initial bacterial concentration (ranging from 10^2 to 10^8 CFU/ml). As for the β-LEAF method, in blood with high bacterial counts, detection of bacterial presence occurred immediately for E. coli (a strong β-lactamase producer) but took 24 hours for S. aureus (a weak β-lactamase producer). With low bacterial loads, β-lactamase activity was detected between 12 and 48 hours for E. coli and only after 48 hours for S. aureus. Notably, these biomarkers complement each other in bacterial sepsis detection: β-LEAF identifies gram-negative strains like E. coli 1-4 hours earlier than protoporphyrin, while protoporphyrin detects gram-positive strains like S. aureus more than 10 hours earlier than β-LEAF. Thus, by combining these two biomarkers, sepsis can be detected within 2 hours of infection with both types of bacteria. When using the smartphone platform, protoporphyrin signals could be detected as early as 2 hours for S. aureus and 4 hours for E. coli, in blood with clinically relevant pathogen loads (10^4 CFU/ml). **Conclusion:** Our data suggest a potential strategy to diagnose bacterial sepsis much earlier than existing methods. This strategy is built on the functional biochemistry of bacteria and ultimately can lead to a portable platform for the prediction, triage, and diagnosis of sepsis at the point of care.

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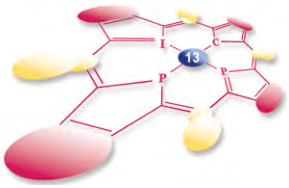

Synthesis and Comparative Photophysical Study of (Perylenediimide-Azobenzene)$_2$Silicon Phthalocyanine Pentads

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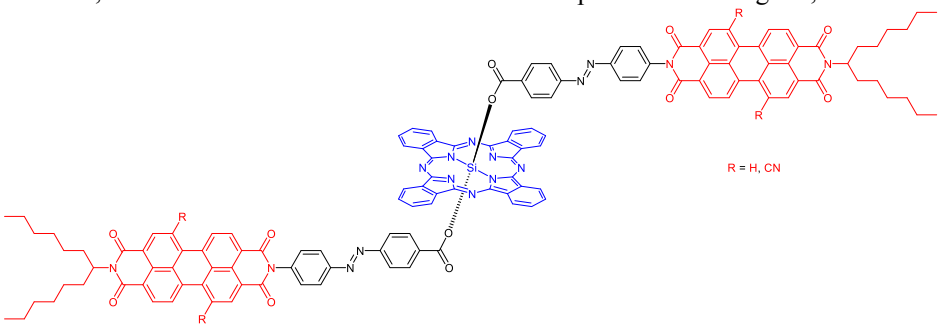
Organic photovoltaics is based on a photoinduced electron transfer process, the latter receiving then great scientific attention. We are interested in the study of the generated charge-separated states, and thus we have combined phthalocyanines (Pcs) [1] and perylenediimides (PDIs) [2] in different stoichiometries and geometries, to generate long-lived charge-separated states [3]. More recently, we have started to investigate PDI-azobenzene systems [4], achieving exciting results. Herein, we will show the extension of these studies to pentads containing Pcs, azobenzene and PDIs.



Acknowledgment: This research was supported by the European Regional Development Fund "A way to make Europe" and the Spanish Ministerio de Ciencia, Innovación y Universidades/AEI (PID2022-140315NB-I00 to FF-L) and by the US-National Science Foundation (2000988 to FD). The computational work was completed at the Holland Computing Center of the University of Nebraska, which receives support from the Nebraska Research Initiative.

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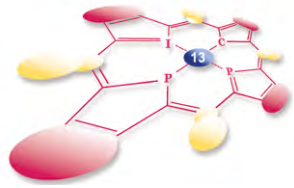
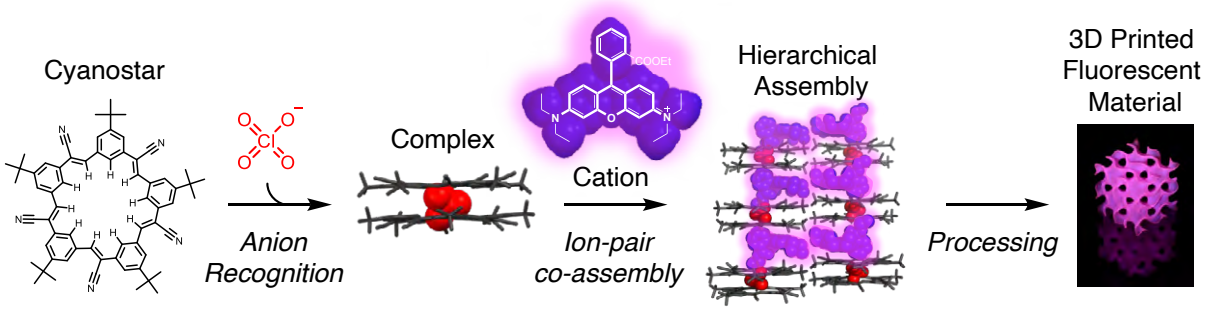


Optical Materials from Fluorescent Dyes and Macrocycles by Hierarchical Design

Amar H Flood

Indiana University. USA

Fluorescence is critical to applications in optical materials including bioimaging, photonics, and solar energy harvesting. While fluorescent dyes are potential key components of these materials, electronic coupling between them in the solid state quenches their emission, preventing their reliable translation to applications. We recently discovered a universal solution to this long-standing problem with the creation of a class of materials called small-molecule ionic isolation lattices (SMILES). These SMILES materials perfectly transfer the optical properties of dyes to solids, are simple to make by mixing cationic dyes with anion-binding cyanostar macrocycles (see figure), and work with major classes of commercial dyes: xanthenes, oxazines, styryls, cyanines, trianguleniums. Dyes are decoupled spatially and electronically in the crystalline lattice by using cyanostar (see hierarchical assembly in the figure). SMILES crystals have the highest known brightness per volume and solve concentration quenching to impart fluorescence to commercial polymers (see 3D printing in figure). SMILES materials enable predictable fluorophore crystallization to lay a basis for plug-and-play optical materials. We will present progress on understanding the energy transfer, crystal engineering, and development of a design framework for programming the SMILES materials with extensions to porphyrin and BODIPY dyes.



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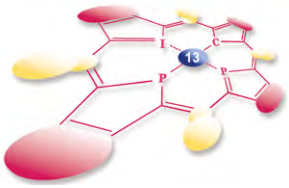

α-Helix Rich Heme Binding Peptide Assemblies

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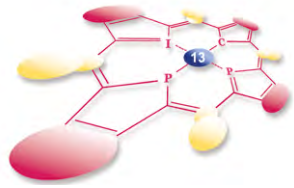
Peptide materials and their ability to self-assemble into nanoscale architectures have shown great promise in health related fields such as drug delivery and regenerative medicine. Inspired by the many energetic process that occur in supramolecular protein arrangements in naturally occurring systems like light harvesting and long range electron transport, these same peptide material design principles used in medicine can be adopted and applied towards energy related materials. The larger class of peptide materials, however, is dominated by β-sheet rich assemblies. Many examples of metalloporphryin binding peptide assemblies rich in β-sheet structures exist and have demonstrated photodynamic and catalytic properties that are highly dependent on the self-assembled structure. However, a majority of heme binding sites in naturally occurring proteins occur in α-helix rich environments. Here, we present our design strategy for developing α-helix rich peptide assemblies. We probe the influence of the assembly, on the binding kinetics of carbon monoxide (CO) by employing classic transient absorption spectroscopic methods. The results do not resemble typical CO recombination kinetics with heme proteins. We offer a few implications that these results may have on the utility of these peptide assemblies as catalytic materials.



Electron-Transfer coupled Bond Formation Mechanism in the Sulfoxidation Reactions of Compound I

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The sulfoxidation reaction is one of the well-known oxygenation reactions catalyzed by metalloenzymes in biological metabolic processes. Heme enzymes such as cytochrome P450 and peroxidases used oxoiron(IV) porphyrin π-cation radical species (Compound I) as reactive intermediates. Previous kinetic studies proposed the participation of the electron transfer (ET) process from sulfide to Compound I in the sulfoxidation reaction. However, recent studies on the electrochemistry of Compound I suggest that the ET process is endergonic and it never occurs solely. To clarify the reaction mechanism of the sulfoxidation reaction, we carried out a Marcus plot analysis for the sulfoxidation reaction of Compound I. The Marcus plots for the variation of the redox potential of Compound I could be simulated with a linear function. The slopes of the lines were large enough to propose the ET process in the rate-limiting step. Moreover, the slope of the line increased with a decrease in the driving force of the ET. The variation of the slope is expected from Marcus's theory. These results indicate the participation of the ET process in the sulfoxidation. The Marcus plot for the variation of the redox potential of the *p*-substituted thioanisole could also be simulated with a linear function. However, the slope of the line was smaller than that for the variation of the redox potential of Compound I. Furthermore, the slope of the Marcus plot was also varied by the steric effect of the sulfide. As the sulfide is bulkier, the reaction becomes slower and the gradient of the Marcus plot becomes smaller. These results indicate the involvement of the O–S bond formation process in the rate-limiting step of the sulfoxidation reaction. To explain all results in this study, we propose the electron transfer coupled bond formation (ETBF) mechanism, in which the endergonic ET process is coupled with the exergonic bond formation process in the rate-limiting step of the sulfoxidation reaction.

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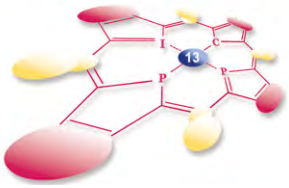

Electronic and magnetic interactions between N-confused porphyrin dimers

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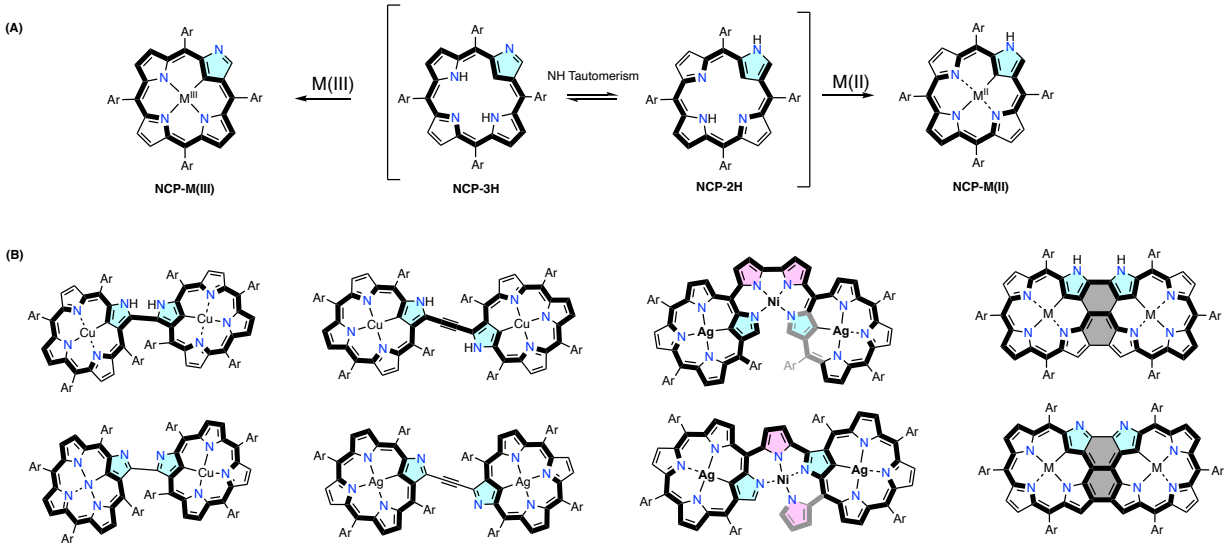
The aromaticity of the planar porphyrinoids is usually controlled by the number of electrons in the p-conjugated circuits and is readily altered by modulating the p-circuits upon oxidation, reduction, ring-fusion, ring expansion, etc. In the N-confused porphyrin case, the p-conjugation pathways can be modulated by NH tautomerism (**NCP-3H** and **NCP-2H**).[1] The circuits can be controlled by metalation (e.g., **NCP-Ag** and **NCP-Ni**). The a-position of the confused pyrrole ring could serve as a turnout point of the p-conjugation pathways, and the outward-pointing N atom serves as the coordination site.[2] In this presentation, the peculiar role of the N-confused pyrrole ring for electron and magnetic interactions between two porphyrin rings using several dimeric N-confused porphyrin systems.[3]



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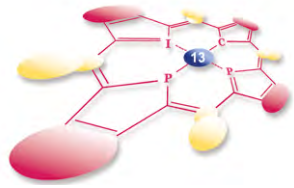

Functional integration of near-infrared-light-absorbing ball-shaped metal complexes

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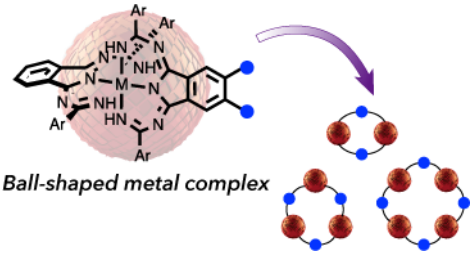

In recent years, near-infrared (NIR) light (specifically 700-1000 nm) has garnered significant attention. Even though 52% of solar energy is infrared light, the utilization of energy in this region remains an area for improvement because most current natural and artificial materials do not interact with it. Porphyrinoids can be readily derivatized to tailor their structural and physical properties. Porphyrinoid-based NIR materials are good candidates for NIR-harvesting. Although porphyrinoids can interact with NIR light with appropriate derivatization,[1] the synthesis of such materials that can achieve both intense absorption of NIR light and controlled physical properties is still challenging, requiring a complex and time-consuming synthesis route. Therefore, novel NIR chromophores with simple synthetic procedures are an essential topic in utilizing NIR light.

Previously, we have successfully developed a novel porphyrinoid-based NIR dye called a "ball-shaped metal complex".[2] These complexes are constituted by two unique tridentate ligands with pyrrole moieties. Such complexes are synthesized by simply a one-step mixing of diiminoisoindoline, benzonitrile, and template metal ions. Despite their non-cyclic structure, the backbone of complexes can strongly interact with NIR light. Seamless functional integration is attainable through the utilization of diverse functionalized precursors. This presentation will expound upon our recent research, elucidating the novelty of ball-shaped metal complexes as a porphyrinoid-based NIR chromophore in the next generation.

Similar to the methodology employed for phthalocyanines, a low-symmetry complex can be synthesized by utilizing two distinct precursors. Our prior research has demonstrated the synthesis of low-symmetry complexes through mixed condensation reactions of two cyanoaryl derivatives.[3] We extended to synthesizing low-symmetry complexes using two diiminoisoindoline derivatives and obtained alkyne-substituted low-symmetry complexes. The cyclic oligomers were synthesized through the oxidative dimerization of alkyne moieties. Dimer or trimer can be selectively obtained by arranging reaction conditions. The optical properties of oligomers revealed the influence of the number of monomer units and the molecular symmetry on the NIR properties. Furthermore, low-symmetry complexes incorporating dye precursors were designed, and their cyclization led to the fabrication of composite materials that can utilize a wide range of NIR light.

In summary, integrating suitable organic synthesis techniques with ball-shaped metal complexes has facilitated tailoring their structural and NIR-optical properties. The unique three-dimensional structure of complexes expects to realize novel three-dimensional structures that are difficult to achieve with conventional planar porphyrinoids. Our research endeavors focus on developing novel materials, capitalizing on the distinctive three-dimensional properties.

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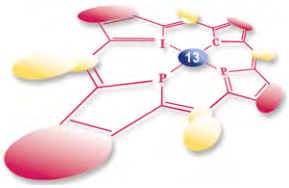

Fabrication and characterization of photoactive (nano)materials for water disinfection

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The increasing population in urban areas, the non-stop rise of global CO_2 emissions with its consequences for climate change, and the growing demand for efficient utilization of renewable energy sources make it urgent to develop novel technologies. Current water disinfection methods are associated with high energy and resource consumption, which poses a challenge to the implementation of the United Nations Sustainable Development Goals. Residue-free and energy-efficient solutions, relying on advanced oxidation methods, can offer a solution to the issue when based on renewable energy-powered systems. The use of materials capable of photochemically generating reactive oxygen species (ROS) stands as one of the most promising approaches to more effectively harness solar energy.[1] While at the molecular level, PS activity could be efficiently adjusted, in heterogeneous systems, this poses a challenge as it is difficult to study and comprehend the factors that determine the activity of the material.

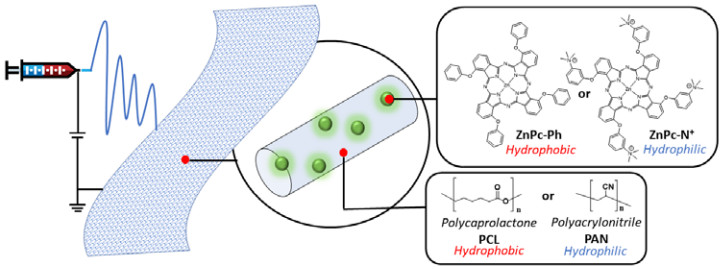

***Fig. 1**. Schematic view of nanofabrication of photoactive materials containing different components.*

With tunable structures, remarkable photophysical properties, and the ability to produce ROS under red light irradiation, phthalocyanine derivatives have been investigated for many years as photosensitizers for antimicrobial PDT[2]. In combination with different carrier polymers, we employ electrospinning for the fabrication of micro and nano-scale materials (fiber diameter ranges from 150 to 1500 nm). The antimicrobial effectiveness of such materials relies not only on the properties of the photosensitizer but also significantly on the characteristics of the polymer carrier. The design and synthesis of photoactive compounds that can be used as structural components of nanoscale materials and the structure-activity relationship of such systems will be presented.[3]

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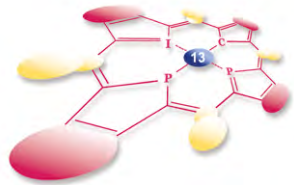

Subphthalocyanine Derivatives for Cell Staining

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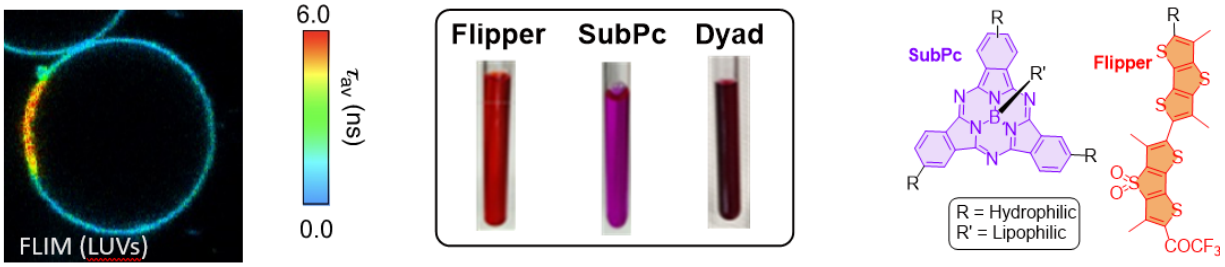

Fluorescent molecules are of high interest for chemical biology. In this regard, SubPcs have a remarkable performance in optical imaging and for photodynamic therapy[1, 2] and fluorescent Flippers, dithienothiophene dimers (DTT-DTTO$_2$), possess a donor/acceptor duality that has been widely studied.[3] Here, we designed, synthesized, and evaluated a water-soluble amphiphilic dyad combining both subphthalocyanine + flipper (SubPc-Flipper) as an amphiphilic dyad.[4] The dyad not only retains the mechanosensitivity of flippers but also demonstrates high selectivity and emission in different kinds of lipidic membranes. Overall, the results of this study represent a significant advancement in the applications of SubPcs, flippers and dyads in fluorescence microscopy.

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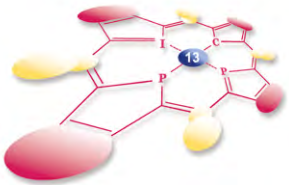

Self-assembled Multifunctional Ferroelectric Materials

Miguel García-Iglesias,[a] Nicolás M. Casellas,[b] Victor Rodríguez, Martijn Kemerink,[c] Tomás Torres.[b]

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Recent progress in self-assembly and supramolecular chemistry has paved the way to achieving control over the structure and function of organic materials elegantly and effectively. This bottom-up strategy, ubiquitous in biology, leads to dynamic and ordered materials with highly desirable unconventional properties.
In this context, we have designed and synthesized a new class of disc-like organic molecules [1] that (i) are semiconducting, (ii) possess dipolar side groups and (iii) can be organized into columnar morphologies that support both ferroelectric coupling and quasi-1D charge transport (Figure 1). In such materials, the ferroelectric polarization is strongly coupled to the bulk conductivity, giving rise to switchable and rectifying current-voltage characteristics. [2]

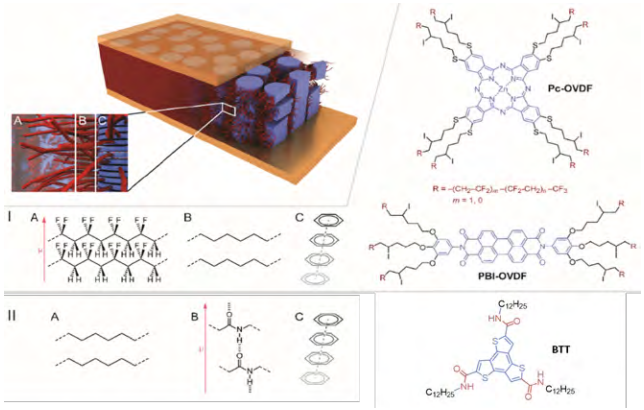

Figure 1. A cartoon of the devices studied and the chemical structure of some of the investigated compounds and their supramolecular organization.

Furthermore, making use of the previous design, we are currently studying the preparation of the next-generation of macro- and nanostructured organic photovoltaic devices (OPVs) using self-assembled donor-acceptor conjugates that demonstrate both a permanent dipole moment and light-harvesting properties. [3]

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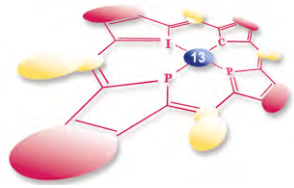

Probing Hemeprotein Active Sites with Hyperfine Spectroscopy

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Heme proteins are a very important class of metalloproteins that perform not only different kinds of catalysis but a wide range of other biological functions, including oxygen transport and storage, electron transfer and regulation [1]. The key to such a diversity of functions and catalyzed reactions essentially resides in the ability of the protein to modulate the properties of the heme prosthetic group. Depending on the environment, the heme ion can adopt different oxidation and spin states, some of which are paramagnetic. For those states of the protein, EPR spectroscopy is suitable to provide valuable information on the architecture of the modulating active site pocket, where the heme moiety is located.

Heme enzymes can be found in various oxidation states, among which Fe^{2+}, Fe^{3+} and Fe^{4+} are the most relevant. These states can exist in two different spin configurations, defined as high-spin and low-spin (even intermediate), depending on the distribution of the electrons in the *d* orbitals. Coordination by the porphyrin ring places the iron d-orbitals close to the high-spin low-spin transition so the spin state depends essentially on the nature of the 5th and 6th ligands. Strong ligands will cause a big energetic splitting of the e_g and t_{2g} orbitals so that only the lower energy t_{2g} orbitals will be occupied leading to a low-spin configuration. Instead, weak ligands will have an opposite effect allowing the occupancy of the e_g orbitals, thus determining a high-spin configuration. The distribution of the various iron unpaired electrons in the different orbitals determines the CW-EPR signature of every oxidation and spin state [2]. Additionally, in the catalytic species, compound I, the iron magnetically interacts with a free radical yielding the magnetic behaviour and the CW-EPR spectrum even more diverse [3].

CW-ENDOR and Pulse EPR experiments allow for the study of weak hyperfine interactions of the ferric heme electron spin and magnetic nuclei in its surroundings, mainly nitrogen and hydrogen nuclei from the porphyrin and axial substituents. Examples of how the study of hyperfine interactions can provide evidence of ligand binding, the structural arrangement of the heme pocket and the orientation of orbital geometry will be provided [4].

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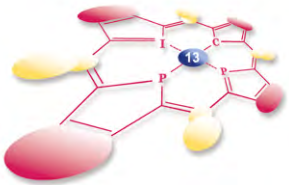
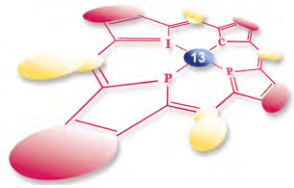


Therapeutic potential of photoactivable nanoparticles

Magali Gary-Bobo

IBMM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

Currently, the development of *in vitro* and *in vivo* models according to the 3Rs (reduction, replacement, refinement) is of great importance. Indeed, research activities need these robust and easy-to-use techniques to demonstrate the imaging and therapeutic potential of innovative nanoparticles. Among several effective organic or inorganic nanoparticles, we are focusing on tunable nanoparticles offering several advantages in terms of drug or genetic material loading capabilities, photoactivatable properties for imaging or photodynamic therapy, and personalization for targeting. In our team, the biological effects of these nanoparticles are studied first on human cancer cell lines in culture and then on zebrafish embryos. The robustness of these models enables us to provide rapid and reliable proof-of-concept for biocompatible and therapeutic nanoparticles.



Photodynamic Materials as an Antimicrobial Strategy for Infection Prevention

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Efforts to control hospital-acquired infections (HAIs) have been hampered by the emergence of drug-resistant pathogens, necessitating the pursuit of advanced functional materials that are capable of the self-disinfection of such microbes in hospital environments. To that end, we have explored antimicrobial photodynamic inactivation (aPDI) as an approach for pathogen control and infection prevention. *In vitro* aPDI studies were performed against bacteria and viruses employing photosensitizer-embedded or conjugated nano-fibrillated cellulose, polyacrylonitrile or nylon nanofibers, dual-dyed wool/acrylic or cotton/PET blended fibers, olefinic block copolymers, and spray coatings. For natural polymer scaffolds [1], cellulose-porphyrin conjugates (nanocrystals, nanofibers, or paper sheets) were found to be highly effective against a broad spectrum of pathogens: our best results demonstrated that *S. aureus*, *A. baumannii*, *P. aeruginosa* and *K. pneumoniae* all exhibited photodynamic 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, non-covalent approaches to photodynamic materials using artificial polymers were also explored: i) using electrospinning, cationic porphyrin and BODIPY photosensitizers were embedded into polyacrylonitrile and nylon nanofibers, and the resultant nonwoven materials possessed both antibacterial and antiviral activities; ii) using melt-pressing [2], we developed a photosensitizer-embedded olefinic block copolymer that exhibited excellent antimicrobial properties against a range of microbes, including Gram-positive and Gram-negative drug-resistant bacteria, as well as against enveloped and non-enveloped viruses; and iii) we have explored photodynamic coatings on polymer microfibers for pathogen inactivation [3,4], and have demonstrated population reductions of >99.9999 and 99.6% for *S. aureus* and antibiotic-resistant *E. coli*, respectively, after exposure to visible light for 1 h. In response to the current COVID-19 pandemic, we also confirmed that these coated fibers can inactivate a human common cold coronavirus serving as a surrogate for the SARS-CoV-2 virus. We have further explored photodynamic antimicrobial polyethylene terephthalate/cotton (TC) blended fabrics, comprised of thionine-conjugated cotton fibers and polyethylene terephthalate (PET) fibers dyed with disperse dyes, as potent self-disinfecting textiles [5], and demonstrated a photodynamic inactivation of 99.985% against Gram-positive *S. aureus*, 99.99% against Gram-negative *E. coli*, and ~99.99% inactivation of enveloped human coronavirus 229E, all after 1 hr of visible light illumination. More recently, we have developed dual-coated fabrics employing photosensitizer-luminous powder using silk-screen printing and demonstrated that this strategy can produce antimicrobial materials that function even when illumination ceases. Together, these results demonstrate that such materials may have widespread applicability for non-specific pathogen disinfection, and further research may lead to their application in hospitals and healthcare-related industries where novel materials with the capability of reducing the rates of transmission of a wide range of bacteria, viruses, and fungi, particularly of antibiotic-resistant strains, are desired.

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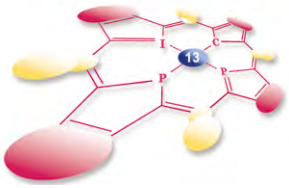

Metallocorrole dimers and sandwiches

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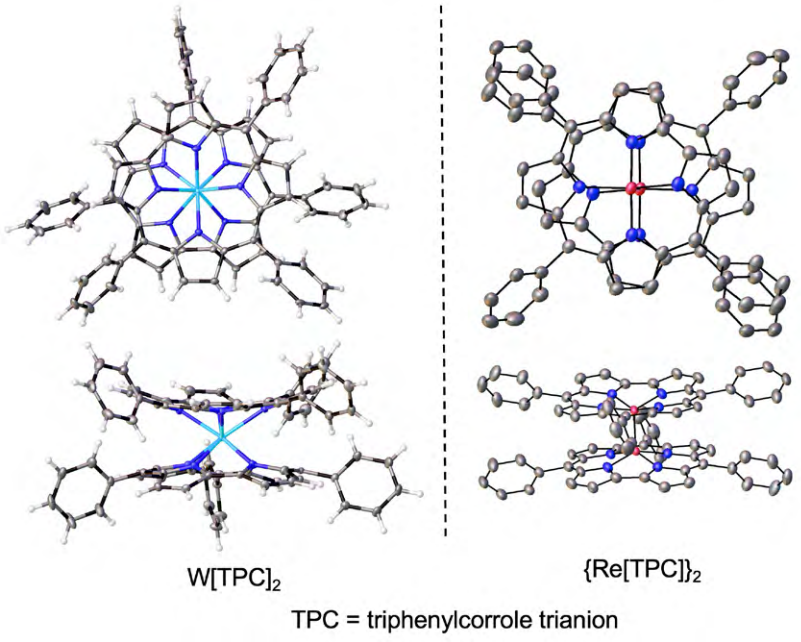
This talk will focus on recent developments in "exotic" metalloporphyrins and metallocorroles involving 4d and 5d transition metals,[1] with emphasis on metal-metal multiple-bonded systems[2] and sandwich compounds.[3,4]



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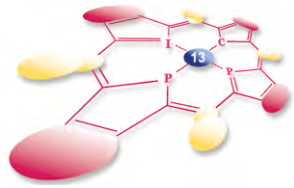

Synthesis and biological evaluation of porphyrin-peptide conjugates targeting triple-negative breast cancer cells

Francesca Giuntini[a], Miryam Chiara Malacarne[b], Marzia Bruna Gariboldi[b], Manuela Marras[b], Paolo Dognini[a], Alan Simm[c], Enrico Caruso[b]

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Breast cancer is the most common cause of cancer among women, both in developed and developing countries, and the leading cause of cancer death among women worldwide [1]. 10%-15% of total breast cancer is defined as triple-negative breast cancer (TNBC) [2], a subtype characterised by the lack of expression of estrogen receptor, progesterone receptor and human epidermal growth factor receptor [3]. TNBC is highly aggressive, it gives metastases in the lungs, liver, and central nervous system, and responds poorly to current treatments [4]; thus, finding new therapeutic options for TNBC is paramount.
Photodynamic therapy (PDT), is a therapeutic approach combining light and photosensitizers (PSs) to generate cytotoxic reactive-oxygen species. The intrinsic selectivity of PDT, due to the negligible cytotoxicity of PS in the absence of light and oxygen, makes it a particularly appealing anticancer approach and prompted efforts to identify strategies to further enhance the selectivity of PS for cancer cells. Thus, PSs were conjugated with nanoparticles, antibodies, peptides/proteins and many other species to maximize the accumulation of PSs in the target cells [5]. In particular, the conjugation of porphyrins to peptides attracted particular attention because it allows directing the PSs to the target cells, while at the same time helping to circumvent some unfavorable behaviors, such as poor hydrophilicity or aggregation in aqueous environment.
We recently focused on a ligation strategy to conjugate porphyrins to fully deprotected peptides in solution, which relies on the displacement of aromatic fluoride by a thiol. Because aromatic nitro groups can also be efficiently displaced by thiols [6], we reasoned that the meso-nitro 5,15-diaryl porphyrins could provide a suitable substrate for anchoring a fully deprotected cysteine-bearing EGFR-binding peptide, to exploit the higher expression of EGFR in TNBC cells. Here we report the synthesis of the conjugates and their photodynamic activity against two TNBC cell lines. EGFR overexpression correlates with the conjugates uptake and the treatment induces varying degrees of necrosis apoptosis and autophagy. The conjugates also inhibit cellular migration typical of highly metastatic cancers.

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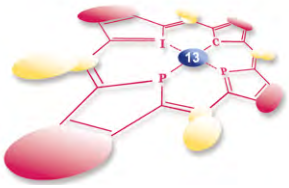

Photo-activatable Prodrugs of Paclitaxel for *In-situ* Photo Vaccination

Prabhanjan S.Giram[a],Ganesh Bist[a], Sewon Kim[a], and Youngjae You[a]*

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PDT is an approved therapeutic modality for the treatment of bladder, bronchial, oesophageal, head and neck cancers [1]. PDT can also be used as a tool of enhancer for antitumor immune response [2]. However, PDT-modulated immunotherapy has some limitations, such as a weak, non-durable immune response [3]. Clinically approved checkpoint blockade inhibitors can be used in combination with PDT to overcome these issues [4]. In this study, we explore (1) Comparative study of efficacy photo-activatable cleavable/non-cleavable paclitaxel pro-drugs (PC-(L-PTX)$_2$) and (Pc-(NCL-PTX)$_2$) with checkpoint inhibitors (a-CTLA-4) for systemic antitumor effects (2) Effectors for immune response, and (3) Rejection of rechallenge for prophylactic effect. A bilateral syngeneic CT26 mouse tumor model was established s.c. with Balb/c mice. PTX prodrug was injected intravenously, and tumours were illuminated using a 690-nm laser for 30 minutes using a cylindrical light diffuser. a-CTLA-4 was then injected intravenously on days 1,4, and 7 at 100 ug/dose. To confirm neutrophils and CD8+ T cells are the effectors of systemic antitumor effects, immune cells are depleted, and fluorescence studies were performed. Through a systemic antitumor effect (i.e. the abscopal effect), this combination therapy delayed distant, untreated metastatic tumor growth. The systemic antitumor efficacy of (PC-(L-PTX)$_2$) combined with checkpoint inhibitors was significantly greater ($p<0.05$) than that of (PC-(NCL-PTX)$_2$).In primary tumor treatment, we observed complete control of treated tumor for (PC-(L-PTX)$_2$) unlike (PC-(NCL-PTX)$_2$). Neutrophils and CD8+T cells are key effectors for controlling the growth of distant, untreated metastatic tumours after immune cell depletion. In the tumor, CD8+ T cells and neutrophils are infiltrated in large numbers. This effect generated immune memory that prevented the metastatic spread of cancer when challenged with freshly inoculated CT26 cells. Photo-activatable prodrugs can be used as an in-situ photo vaccination strategy after local treatment of primary tumours to release tumor-associated antigens that have a systemic antitumor effect, inhibiting secondary tumor growth and the development of immune memory. Combined with Photo-activatable paclitaxel prodrugs, ultra-low doses of paclitaxel, and checkpoint inhibitors, it presents a new paradigm in the metastatic treatment of cancer.

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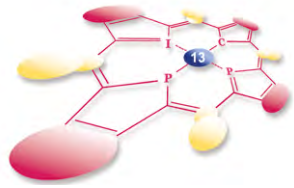

PCET Reactivity in Compound I Analogs: Dramatic and Unexpected Axial Ligand Effects

David P. Goldberg, Jithin Thomas

The Johns Hopkins University, Department of Chemistry, Baltimore, Maryland

The identification of the axial ligand in high-valent iron-oxo heme enzymes and synthetic catalysts is a well-known structural factor that is thought to have an important influence on reactivity. In this presentation, the generation and characterization of three new, thermally metastable, 6-coordinate iron(IV)-oxo porphyrinoid-π-cation-radical complexes with the corrolazine (Cz) ligand will be described. Their proton-coupled electron-transfer (PCET) reactivity was examined and compared with a previously published 5-coordinate analog, $Fe^{IV}(O)(TBP_8Cz^{+\bullet})$ (TBP_8Cz = octakis(p-tert-butylphenyl)corrolazinato^{3-}), (*J. Am. Chem. Soc.*, **2012**, *134*, 7392–7399). The new 6-coordinate complexes, $Fe^{IV}(O)(TBP_8Cz^{+\bullet})(L)$ (L = 1-methylimidazole (1-MeIm), 4-dimethylaminopyridine (DMAP), cyanide (CN^-) can be generated from either oxidation of the ferric precursors or by addition of L to the 5-coordinate Compound-I (Cpd-I) analog at low temperatures. The UV-vis, EPR, and Mössbauer spectra of these different species will be discussed, in addition to cryospray ionization mass spectrometry (CSIMS). The PCET reactivity with 4-OMe-TEMPOH shows that coordination of a 6th axial ligand dramatically *lowers* the PCET reactivity of the Cpd-I analogs (rates up to *7000 times slower*). Extensive DFT calculations were carried out, and together with the experimental data, indicate that the trend in reactivity does not follow the thermodynamic driving force for these reactions. The combined data suggest a concerted mechanism with the asynchronous movement of the electron/proton pair in the transition state.

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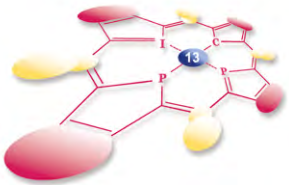

Porphyrins Oxidize Histidine 190 Mimic And Generate Proton Currents – Towards An Artificial Photosynthetic Reaction Center

Edwin Gonzalez[a], Kai Cui[b], Daniel Heredia[a], Rodrigo Dominguez[a], Edgar Reyes[a], Brian Cherry[a], Gary Moore[a], Sharon Hammes-Schiffer[b], Thomas Moore[a] and Anna Moore[a]

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Proton-coupled electron transfer (PCET) is used to couple the flow of electrons and protons together in myriad bioenergetic processes including respiration and photosynthesis. Aiming to explore the thermodynamics and dynamics of PCET, the benzimidazole-phenol (BIP) moiety has been employed to mimic the role of the TyrZ-His190 pair of photosystem II (PSII) [1]. Electrochemical and infrared spectroelectrochemical (IRSEC) studies demonstrated that oxidation of the phenol (TyrZ mimic) drives the phenolic proton to the benzimidazole (His190) mimic and that modifying the benzimidazole by incorporation of polybenzimidazoles creates a Grotthuss-type "proton wire", which is accompanied by a decrease in the redox potential of the phenoxyl radical/phenol couple by 60 mV per benzimidazole unit [2]. Nevertheless, these designs lack a light active unit and light is a crucial element in the photosynthesis process, hence, incorporating a porphyrin as a light-harvesting antenna is a more complex and complete mimic system. Thus, coupling a proton wire to a high-potential porphyrin having an excited-singlet state that can oxidize the phenol and initiate the associated translocation of protons upon irradiation is a relevant photosynthetic mimic of proton management in water oxidation by PSII [3]. Herein, we describe the synthetic path for preparing three beta-fluorinated porphyrins with BIP ligands: **PF_{23}-4OHBIP**, **PF_{23}-BIP-p-OMe-2-py**, and **PF_{23}-BI_2P-p-OMe-2-py**. In **PF_{23}-4OHBIP**, an E1PT process (one proton translocation associated with a one-electron oxidation event) occurred. in **PF_{23}-BIP-p-OMe-2-py** and **PF_{23}-BI_2P-p-OMe-2-py** E2PT and E3PT processes (two and three proton translocations associated with one electron oxidation event), respectively, were observed. Cyclic voltammetry experiments were carried out to determine E_{mid} values and IRSEC was used to confirm the arrival of the proton on the terminal proton acceptor (TPA, methoxypyridine) after the oxidation event.

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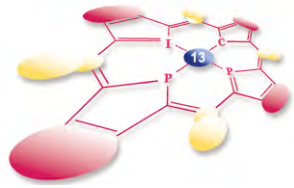

Host-Guest Chemistry within Porphyrin Nanocages

David González-Rodríguez,[a,b] Alberto de Juan,[a] Fernando Garcia-Guijarro,[a] A. Priscila Gia,[a] Beatriz Torres-Calvo[a]

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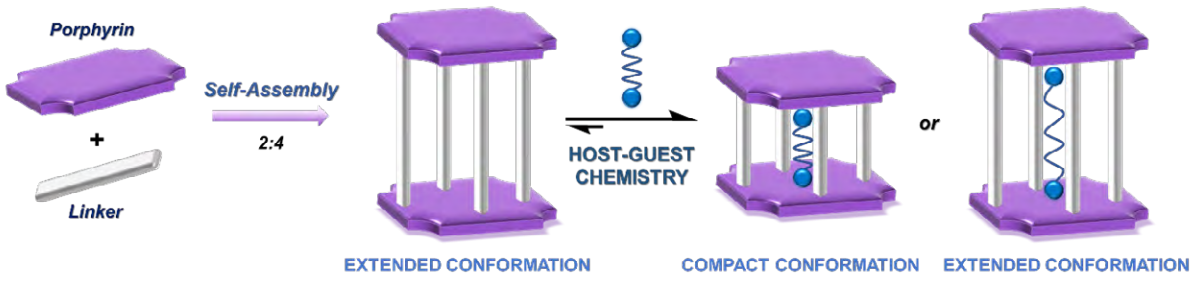
Nature represents a shining model of inspiration on how to deal with energy, waste and raw material source issues. In Nature, optimally organized molecules and enzymes transform solar energy into chemical energy, consuming and regenerating O_2, H_2O, CO_2, H_2…in a perfect-functioning closed cycle.[1] Within this biological cycle, there is an omnipresent family of molecules that work at the core of these (photo)chemical events and transformations: the porphyrinoids.[2] They are responsible for executing many of the essential life processes, such as oxygen transport/storage (*hemoglobin* and *myoglobin*), electron transfer (*cytochrome b5*), CO and NO gas sensing (*guanylyl cyclase*), enzymatic oxidation/oxygenation (*cytochromes P450, peroxidases*), and convert sunlight in photosynthetic systems (*chlorophylls*).
We show here our recent studies on the preparation of a novel kind of bisporphyrin nanocage[3] constructed by imine linkages under thermodynamic control. The cage has two main conformations -extended and compact -, depending on the arrangement of the imine bonds, and can host a wide diversity of ditopic nitrogen ligands that fit into its relatively rigid nanocavity. Remarkably, the cage is also an excellent host for fullerene.



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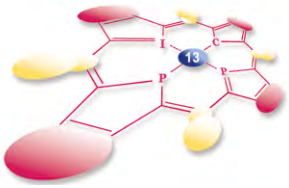

Replicating Functional Features of CO Dehydrogenase: Advancing Catalyst Design for CO_2 Electrocatalysis

Philipp Gotico[a], Asma Khadhraoui[b], Chanjuan Zhang[b], Regis Guillot[b], Marie Sircoglou[b], Winfried Leibl[a], Bernard Boitrel[c], Zakaria Halime[b] and Ally Aukauloo[b]

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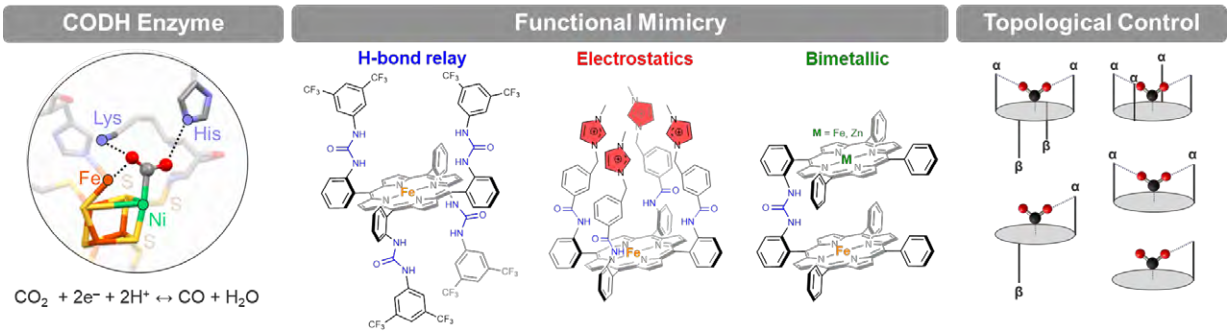
Catalyst design relies heavily on the intricate development of ligand scaffolds to manipulate electronic and structural properties for fine-tuning reactivity patterns [1]. Nature has perfected this in the active sites of enzymes, providing design inspirations for chemists to control the challenging reactivity of carbon dioxide (CO_2) conversion. In this talk, we detail our systematic efforts to enhance the catalytic performance of the iron porphyrin molecular platform by emulating key functional features of the CO dehydrogenase (CODH) enzyme. Renowned for its ability to efficiently and reversibly reduce CO_2 to CO with minimal overpotential, CODH provides invaluable design inspiration. Drawing insights from the enzyme's active state structure, we employ a methodical approach, leveraging electronic effects, hydrogen bonding, electrostatic interactions, bimetallic strategies and their topological positioning to mimic its functionality [3–7]. This provides incremental understanding as to which aspects of the enzyme are worthy to follow.



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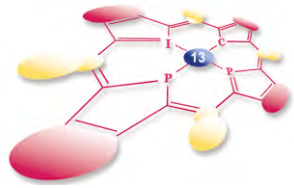

On-Surface Chemistry of Porphyrins with Heavy Main-Group Metals and after Electrospray Deposition

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Metal-organic compounds of heavy main group metals are promising building blocks for novel (opto-)electronic materials, e.g. for application in PHOLED. Despite their potential, dynamic processes occurring at metal/organic interfaces of these compounds remain largely unexplored, posing a significant knowledge gap that could impact device performance. Here, I report on the on-surface chemistry of Pb(II) and Cs(I) tetraphenylporphyrins (PbTPP and Cs_2TPP) on Cu, Ag, and Au surfaces, as studied by XPS, STM, TPD, and DFT calculations. On Cu(111), PbTPP undergoes transmetalation above 380 K, resulting in an exchange of the incorporated Pb ion by a Cu adatom.[1] In contrast, demetalation and formation of a free-base porphyrin was observed on Au(111), along with cyclodehydrogenation side-reactions of the porphyrin ligand starting above 350 K. At 720 K, re-metalation of the porphyrin with substrate Au atoms occurs, resulting in Au(II)-porphyrin. The on-surface reaction of tetraphenylporphyrin (H_2TPP) with Cs in the multilayer and monolayer regime on Ag(111) results in the formation of Cs_2TPP, which was conclusively identified by temperature-programmed desorption mass spectrometry (TPD-MS). Cs_2TPP is thermally stable at least up to 700 K. Due to the large ion radius of Cs^+, Cs_2TPP has a bipyramidal structure with Cs^+ ions on both sides of the molecular plane.

A key challenge in investigating large molecules on surfaces lies in the preparation process, particularly when utilizing thermal evaporation with a Knudsen cell. This method is limited to substances that do not decompose before reaching a sufficient vapor pressure, a condition often unmet by large organic molecules. To address these preparation-related constraints, one viable approach is deposition from solution using electrospray ionization ion beam deposition (ESI-IBD). Although ESI-IBD is gaining increasing use, especially in the preparation of adsorbates of biomolecules, the precise chemical state of the molecules remains elusive. Typically, ions are generated through protonation (H^+ attachment), while neutralization on metal surfaces involves electron transfer, resulting in the production of excess H atoms that may lead to molecular hydrogenation. To elucidate such processes, we selected H_2TPP as a well-established model system. Following deposition via ESI-IBD on Au(111), XPS and STM reveal the presence of room-temperature stable porphyrins with different degrees of excess N-protonation.

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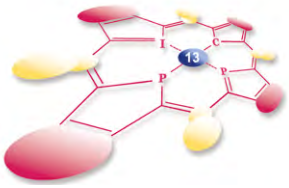

Self-assembled cyclic peptides as receptors for molecular and ion recognition

Juan R. Granja[a], Victoria López-Corbalán[a], Marcos Vilela-Pico[a], Ezequiel Troncoso[a], Manuel Amorín[a]

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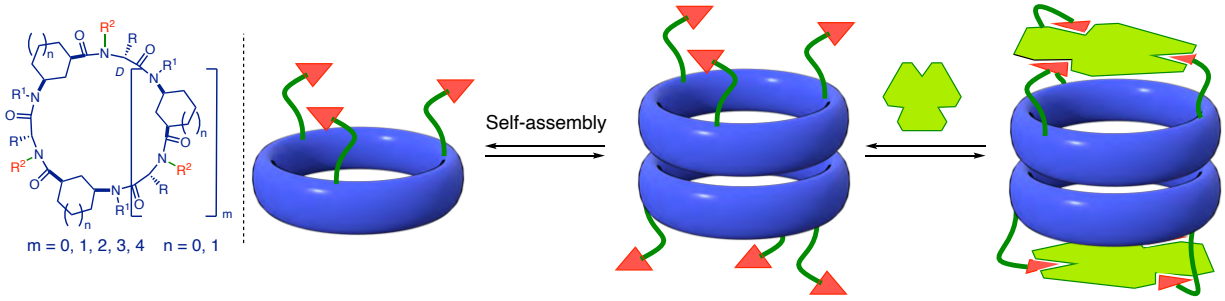
Flat disc-shaped cyclic peptides are a new class of supramolecular tools whose closed β-strand conformation predisposes them to stack, giving rise to hollow cylindrical aggregates whose properties can be fine-tuned [1, 2]. Within this group of macrocycles are the α,γ-derivatives made up of cyclic residues [3]. Our group has shown that these peptides have very valuable supramolecular properties including their large association constants, self-sorting properties, and important ion transport capabilities and that they allow tuning the internal properties of the supramolecular cavity [4].
Specifically, in this lecture we will present our latest finding on supramolecular dimeric structures as chemical receptors and molecular transporters.



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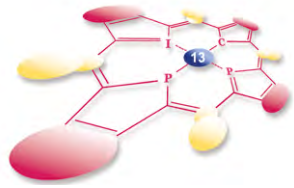
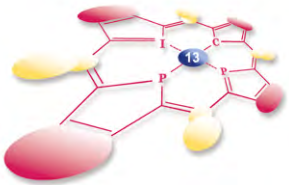


The Importance of Thermodynamics, Tunneling, and Spin Density in Metal Oxo Mediated C-H Bond Cleavage

Michael T. Green[a]

[a]*University of California, Irvine. USA.*

Much of our understanding of metal-oxo mediated C-H bond activation is based on the observation of linear free energy relationships (LFER) between the log of the rate constants for C-H bond cleavage and the strengths of the C-H bonds cleaved. It has become clear, however, that not all metal-oxo species display LFER with respect to C-H bond cleavage, and it has been proposed that other properties of the system (e.g., H-atom tunneling, metal-oxo basicity, or unpaired spin density on the oxo ligand) may play the dominant role in promoting reactivity. We have explored this issue through the lens of cytochrome P450 catalysis. Using a variety of spectroscopies in conjunction with isotopic labelling and rapid mixing and freezing techniques, we have analyzed the importance of thermodynamics (in the form of bond strengths), ferryl basicity, oxyl radical character, and H-atom tunneling in C-H bond cleavage by P450 compound I. Results from these investigations will be presented.



Corroles and Porphyrins based MOFs and MIPS for the Detection of Toxic Gases

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By combining the CO sorption properties of cobalt corroles [1] with the known sorption capacity of MOFs and COFs, we aim to obtain high-performance sensing materials for the detection of CO and other gases (e.g. NH_3 as biomarker). CO detection must be effective at low levels, from ppm to ppb, to provide rapid warning and prevent poisoning. Recently, we have achieved very low levels of CO detection (ppm) using SAW devices functionalized by cobalt corroles deposited as a film on a silica [2] or a gold surface. As we have found that the integration of corroles to the surface of sensing devices is hindered by the π-stacking of the macrocycles, we have considered a porous 3D structure (MOFs and COFs) [3] to create an optimal sensing material with corroles distributed throughout the material, making *a priori* the majority of the cobalt centers accessible. We now wish to present the grafting of corroles (free-base and cobalt complexes) into the pores of PCN-222 MOFs as well as their characterization and CO and CO_2 binding (Figure 1). The synthesis and characterization of new hybrid MOFs with mixed porphyrin and corrole linkers, with the aim of obtaining a stable and sensitive crystallized material, will also be presented. Preliminary results concerning the design of Molecularly Imprinted Polymers (MIPs) as enzyme mimics for the decontamination of pesticides and chemical warfare agents will also be reported [4].

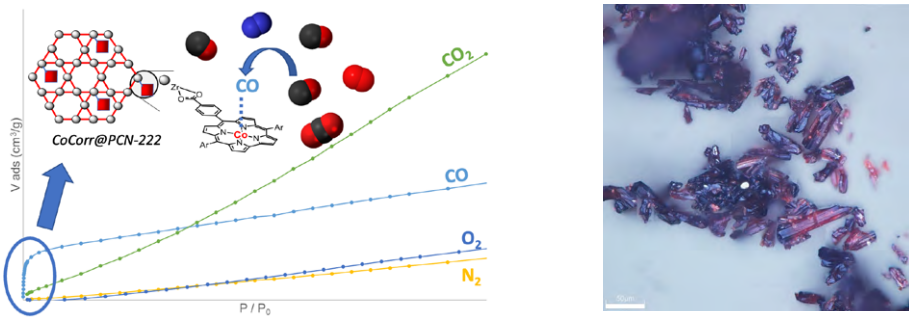

Figure 1. a) CO selective chemisorption by a grafted PCN-222 with cobalt corroles.
b) Optical microscopy view of the grafted PCN-222 MOF with cobalt corroles.

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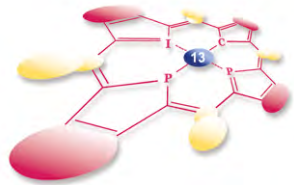

The Silver Anniversary of Catalysis by Triarylcorrole Metal Complexes

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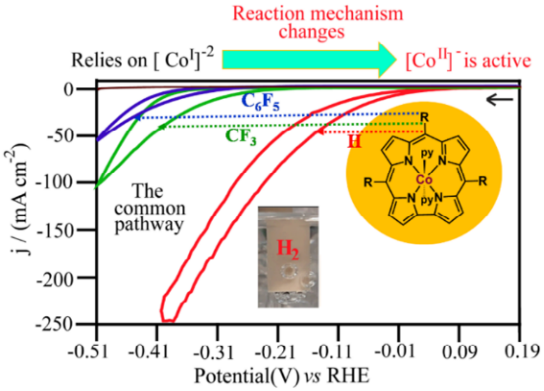
Immediately following the 1999 report on one-pot synthesis of corroles from pyrrole and aromatic aldehydes,[1] the transition metal complexes of the most stable corrole were examined as catalysts for oxygen and carbene transfer to olefins.[2] This initiated the utilization of metallocorroles for catalyzing numerous processes,[3] which include treatment of cancer and metabolic diseases by relying on pro- and anti-oxidant activities, respectively,[4, 5] and for reactions that are of prime importance for fuel cells, batteries, hydrogen economy and other aspects concerning clean energy.[6] The most recent developments are related to the ability to prepare corroles with much smaller *meso*-C substituents,[7] which display several advantages for electrocatalysis by catalyst-modified electrodes.[8, 9]



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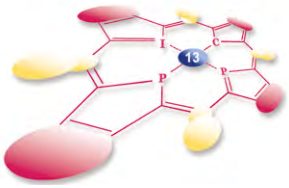

Porphyrin Derived Conversion of Enamines into α-Ketoamides

Nitika Grover

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Molecular oxygen ($^3O_2$) is a paramagnetic biradical molecule that plays a vital role in sustaining life on Earth. Because of its ground state electronic configuration, most chemical reactions involving $^3O_2$ are spin forbidden which reduces its reactivity and thus its applicability in organic synthesis.[1] The more reactive forms of O_2 such as $^1O_2$ ($^1\Delta_g$) an excited state of $^3O_2$, exhibit anti-parallel spin in the same antibond-ing orbital that can be accessed by altering its electronic configuration. Photosensitization is one of the most common techniques for generating $^1O_2$, where a photosensitizer absorbs visible light and undergoes intersystem crossing (ISC), which then transfers its energy to the surrounding $^3O_2$ to generate reactive $^1O_2$. Porphyrin and its analogs represent a unique class of organic photosensitizers that can generate $^1O_2$ with a high quantum yield under white light irradiation.[2] Furthermore, the $^1O_2$ quantum yield of tetrapyrroles can be tuned by peripheral and core functionalization, for example, the introduction of heavy atoms (halogens, metals, etc.) or radicals at meso position(s) exerts a positive effect on $^1O_2$ yield. Given the high reactivity of singlet oxygen, it has appeared as a sustainable reagent in organic synthesis. Despite the considerable progress in enamine chemistry, the reaction of enaminonitrile with singlet oxygen remains elusive and unexplored. Since the cyanide group of enaminonitrile is considered a good leaving group, we envisaged that one-pot [2+2] additions followed by nucleophilic substitution on β-enaminonitriles may generate synthetically useful reaction pathways and value-added products. To this end, we report the reaction of β-enaminonitriles with $^1O_2$ in ACN in the presence of porphyrin and air that led to the formation of α-ketoamides. The conventional methods reported previously to access α-keto amides include oxidative amidation of terminal alkynes, oxidation of α-methylene group of amide functionality, and oxidative coupling of aldehydes and isocyanides.[3] However, most of these methods suffer from moisture sensitivity, the formation of undesired self-coupled products, and foul-smelling reactants like isocyanides. Therefore, a straightforward, eco-friendly, and facile methodology that enables molecular engineering of α-keto amide derivatives is highly desirable. In this work, we report a visible light-mediated conversion of β-enaminonitriles into α-ketoamides catalyzed by porphyrin using air as the oxidant under mild conditions.

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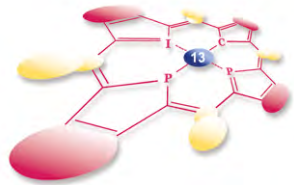

Selective biocatalysis with fungal heme-thiolate peroxygenases

John T. Groves, Wenxuan Li, Dali L. Davis, Kevin J. Speina, Christin B. Monroe, Angelina S. Moncrieffe, Yuan Cao, Chih-Chung Chen

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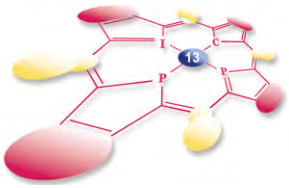
Unspecific peroxygenases (UPO) comprise a novel family of fungal, heme-thiolate proteins with catalytic reactivities reminiscent of cytochrome P450 oxygenases. Earlier work in our lab has shown that UPOs share the radical rebound scenario for aliphatic substrate hydroxylation. Moreover, the reactive UPO compound I, UPO-I, has been spectroscopically captured and kinetically characterized. Thermodynamic considerations have shown that the reduction potential of UPO-I is greater than 1 V and that the O–H bond of the incipient Fe(IV)O–H species, compound II, formed upon hydrogen abstraction has a BDE of at least 100 Kcal/mol.

Unspecific peroxygenases are robust extracellular proteins excreted into the growth medium and, as such, have many attractive features as potential biocatalysts. A shortcoming of UPOs, however, is their general promiscuity regarding substrate oxidation, often producing a shower of various products. Here, we describe the isolation and characterization of a new variant UPO that is produced in a high-yielding culture by a strain of the agaric fungus, *Marasmius rotula* (pinwheel mushroom). This MroUPO variant shows high selectivity for the oxygenation of linear and cyclic hydrocarbon derivatives, producing useful quantities of bifunctional building block molecules in one enzymatic transformation that would otherwise require multiple chemical steps to achieve. In this lecture I will discuss the scope of these biocatalytic transformations and mechanistic studies aimed at elucidating how these reactions occur.



The synthesis of π-expanded corroles

Daniel T. Gryko[a], **Łukasz Kielesiński**[a], **Abhik Ghosh**[b]

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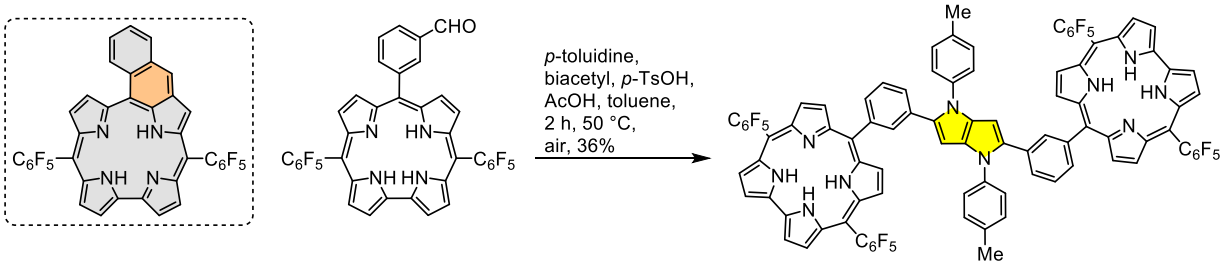
In 1998, it would have been impossible to imagine that only 20 years later the chemistry of corroles would expand to create an independent field of study. The synthesis of *meso*-substituted corroles evolved quickly during the first seven years after Paolesse's and Gross's discovery [1,2,3]. Although the synthetic revolution made it possible to try risky ideas in diverse areas of materials chemistry and in various biology- and medicine-oriented applications, multiple challenges still remain.

One of those challenges is the preparation of corroles possessing CHO groups. Free formyl groups can be reacted with multiple nucleophiles forming more complex and more advanced structures. At the same time CHO is the reacting group pivotal in the corrole synthesis. Attempting to solve this conundrum we recently developed the synthesis of tris(4-formylphenyl)corrole in straightforward fashion. During the realization of this project we discovered that 10-(2-formylphenyl)corrole undergoes intramolecular Friedel-Crafts reaction leading to non-aromatic, π-expanded corrole [4]. This divalent macrocycle possess intriguing photophysical properties and has an ability to form complexes with various metals.

The analogous 10-(3-formylphenyl)corrole was used in the synthesis of 1,4-dihydropyrrolo[3,2-*b*]pyrrole bearing two corrole macrocycles. The multicomponent reaction heavily depends in this case on position of the formyl group.

In parallel project we developed a route to π-expanded corroles possessing dative boron-nitrogen bond. Both synthesis and photophysics of these new macrocycles will be presented.



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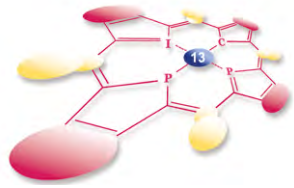

Porphyrins – Effective Photocatalysts for Red Light-Induced Functionalizations of Molecules

Dorota Gryko[a]

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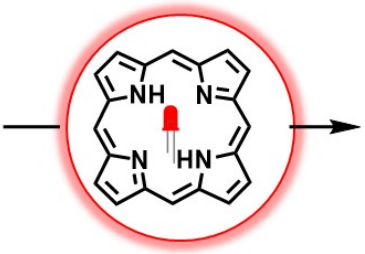
Recently, photoredox catalysis has begun to influence molecular biology and medical sciences for its mild conditions for generating highly reactive species (i.e., radicals), enabling novel and selective functionalisations of biomolecules.[1] In line with this, porphyrins, which can transfer energy (photosensitization) or electrons (photoredox catalysis) when exposure to light, seem to be highly advantageous. Given that their electron absorption shows a characteristic Soret band at 420 nm with a high molar extinction coefficient (105 M^{-1} cm^{-1}),[2] they have been mainly used in blue-light-induced reactions. These molecules, however, absorb red light (four Q-bands at 518, 553, 592 and 648 nm with molar extinction coefficients of 104 M^{-1} cm), which has the benefit of low energy, lower health risks,[3] and more in-depth penetration of various media.[4]



We have established that due to their diverse photophysical properties, porphyrins promote photoinduced electron transfer events under red light irradiation.[5] They act as effective photooxidants (alkylation of carbonyl compounds, thiol-ne reaction and reductive decarboxylation) and photoreductants (in arylation of heteroarenes, selenylation, thiolation and reduction of nitro compounds). These bioinspired photocatalysts exhibit features that outperform other catalysts operating under red light, as they are really non-toxic and can be applied in biological systems. Thus, we believe that free-radical porphyrins are a valuable contribution to the set of red-light photocatalysts, and will be practical in biosynthetic applications.

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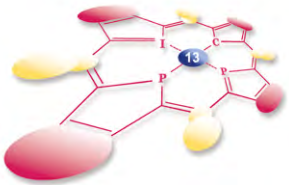

Step-Changing Solar Energy Conversion Schemes *via* Subphthalocyanines

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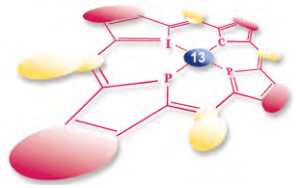
At the heart of unlocking the potential of global clean, renewable energy is the concerted effort of Advanced Charge Management (ACM) and Advanced Photon Management (APM). Recent advances regarding molecular ACM have documented the maturity of energy conversion schemes. Adding now APM to ACM through down- and/or up-conversion and creating synergies is essential to further boost the efficiency of these sun-driven energy conversion schemes. A full-fledged comprehension of APM is essential as an enabler for creating versatile platforms that are broadly applicable not only in the area of solar electricity but also solar fuels. APM is, in the molecular context, based on either down-converting photons utilizing Singlet Fission (SF), on the one hand, or Triplet Fusion (TF) for up-converting them, on the other hand. To harvest photons in the high-energy regime, SF, the molecular analog to multiple exciton generation, stands out. It allows high-energy, singlet-excited states to be down-converted into twice as many low-energy, triplet-excited states, thereby improving solar-cell performance. This is, however, limited to the part of the solar spectrum, where, for example, the SF-materials feature a significant absorption cross-section. Harvesting photons in the remaining regime of the solar spectrum necessitates the use of complementary absorbing chromophores such as subphthalocyanines. Our transdisciplinary research has enabled us in recent years to gather a comprehensive understanding of the role of subphthalocyanines in molecular down- and up-conversion.



Functionalized Porphyrins for applications in PDT and SDT

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Porphyrin and corroles are well-known fluorescent dyes, which are used as theranostic agents in magnetic resonance imaging (MRI) and photodynamic therapy (PDT) of cancers [1]. The substitution of other chromophores viz. carbazole/ triphenylamine/ phenothiazine on the molecular skeleton can be beneficial to fine-tune the spectral properties of these dyes [2]. The attachment of thio-hexose sugars on the *meso*-positions can yield water soluble derivatives; such as thio-glycosylated porphyrins/BODIPYs are highly desirable for optical imaging and can be targeted towards cell receptors rich in lectins for PDT application. Our group at IIT Gandhinagar is involved in the synthesis, photo-catalysis and biological applications of porphyrins [3], BODIPYs [4] and dipyrrinato metal complexes [5].

In this talk, the synthesis, photophysical properties and PDT studies of functionalized porphyrins and corrole will be discussed. Their crystal structures, singlet oxygen generation and *in-vitro* biological studies for anti-cancer applications will also be presented.

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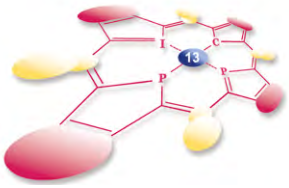

Synthesizing and Evaluating The Photodynamic Efficacy of Phthalocyanine-based Photosensitizers

Ayşe Gül Gürek[a] Gizem Gümüşgöz Çelik[a], Başak Aru[b], Gülderen Yanıkkaya Demirel[b], Emel Önal[c], Özge Tuncel[c], Serdar Özçelik[d], Devrim Atilla[a]

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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 [1].
My laboratory has been developing various types of activatable and dual-targeted photosensitizing agents for selective near-infrared fluorescence imaging and photodynamic therapy of cancers as well as inflammatory diseases. In their native state, photosensitizers are nonfluorescent and nonphototoxic, but they became highly fluorescent and phototoxic at the target sites. Recently, we designed new symmetric and asymmetric phthalocyanine compounds containing different substituted groups such as polyoxoethylene, histone deacetylases (HDACs), or triphenylphosphine (TPP) moiety or their combinations [2-7]. The synthesis strategies of phthalocyanine-based photosensitizers and the results obtained from their *in vitro* studies will be presented.

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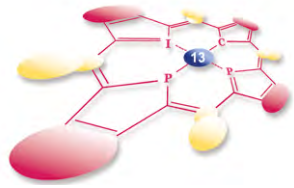

Clinical Importance of PET-ONCO (^{124}I- analog of chlorophyll-a derivative) in Imaging Bladder Cancer with an Option of Photodynamic Therapy

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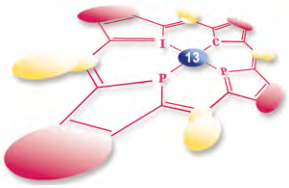
Bladder cancer is the fourth most commonly diagnosed cancer in the US in men and the tenth in women. Approximately two-thirds of newly diagnosed bladder cancers have not invaded the bladder smooth muscle and are considered non-muscle invasive bladder cancers (NMIBC). Despite a 5-year survival rate of 88%, up to 70% of NMIBCs recur after initial treatment. For muscle-invasive bladder cancer (MIBC), the gold standard remains radical cystectomy (RC) and lymph node dissection (LND), with or without neoadjuvant chemotherapy. However, RC remains a major procedure with a high rate of complications. Minimally invasive RC has been incorporated to reduce the morbidity associated with RC Still, 5-year survival rates are only 50-70%, and complication rates exceed 60%. Recently, tri-modality (bladder preservation) therapy has emerged as an alternative to RC, with comparable survival rates in select patients]. However, most guidelines do not recommend it as a standard treatment.

Positron emission tomography (PET) is one of the imaging modalities, which could play a significant role in diagnosing bladder cancer at the initial stages. Unfortunately, most of the clinically accepted PET agents are not suitable for PET due to their accumulation and excretion via urine. However, a novel ^{124}I-analog of chlorophyll-a developed in our laboratory shows its high specificity in a variety of tumors including the bladder. As a non-radioactive analog, it can be used for the treatment of bladder cancer by fluorescence-guided therapy. The current clinically accepted imaging/treatments of bladder cancer and the possible advantages of a highly effective chlorophyll-a analog with limited undesirable toxicity will be discussed.



Cytochrome P450 19A1 dynamics and ligand recognition in membranes

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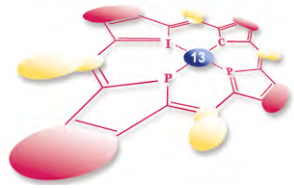
Aromatase (CYP19A1) catalyzes the synthesis of estrogens from androgens and is, therefore, a key target for estrogen-dependent cancers. This talk will describe parallel computational and experimental studies of CYP19A1 dynamics and ligand binding mechanisms. Small angle x-ray and neutron scattering (SAXS/SANS) combined with a hybrid modeling approach was used to orient CYP19A1 in a lipoprotein nanodisc. The orientation of CYP19A1 in an explicit membrane was confirmed by enhanced sampling molecular dynamics simulations and subsequent random acceleration molecular dynamics (RAMD) demonstrated the possibility that androstenedione traverses a membrane-embedded channel to access the active site. Thermodynamic analysis of this pathway revealed a multi-step binding mechanism. Hydrogen-deuterium exchange mass spectrometry of CYP19A1 in nanodiscs supports that androstenedione induces global changes in protein dynamics and the relative changes, for the most part, reflect those predicted by simulations. Together, these studies illustrate the power of combining solution structural and atomistic molecular dynamics simulations to glean novel insight into the functional dynamics of CYPs in native-like environments.



Cell Death Mechanisms in Photodynamic Therapy

Tayyaba Hasan[ab]

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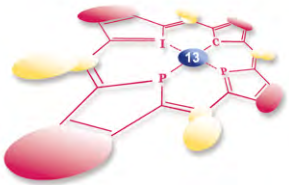
In the early years of photodynamic therapy (PDT) the primary cellular mechanism of cell death was the rupture of the cell membrane leading to death. David Kessel is a pioneer in the field, who probed the detailed mechanisms involved in cell death and the importance of apoptosis and the proteins involved in it. Some of these aspects of PDT along with the impact it has had on the field will be presented in this talk



Catalytic properties of metalloporphycenes in myoglobin matrix

Takashi Hayashi, Koji Oohora

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Heme *b*, iron protoporphyrin IX, can be removed from hemoproteins such as myoglobin and cytochrome P450s, and the corresponding apoproteins are available. It is further known that the addition of metalloporphyrinoids into a solution of the apoproteins provides the reconstituted proteins. Our group has recently focused on replacing the heme cofactor with artificially created metallocofactors in myoglobin and subsequently generating artificial metalloenzymes, although myoglobin is a molecular oxygen storage protein in nature.

Metalloporphycenes are one of the candidates for the artificial metallocofactor of myoglobin. Because the physicochemical properties of metalloporphycenes are quite different from metalloporphyrins, substitution with metalloporphycene cofactors is expected to dramatically change the reactivity of myoglobin. In this presentation, two examples of myoglobins reconstituted with metalloporphycenes having two propionate side chains will be reported as shown in Figure 1 [1-2].

Both myoglobin and cytochrome P450s have the same heme cofactor, but myoglobin does not exhibit the catalytic activity toward alkane hydroxylation that is normally seen in cytochrome P450s. In contrast, our group has recently found that myoglobin reconstituted with manganese porphycene can promote the hydroxylation of inner alkanes under mild conditions. For example, ethylbenzene is catalytically converted to 1-phenylethanol by myoglobin reconstituted with manganese porphycene upon the addition of H_2O_2. In addition, manganese-oxo species as a reaction intermediate was detectable upon the addition of mCPBA by stopped-flow experiments.

Nitrile synthesis from aldoxime is known to be catalyzed by aldoxime dehydratase having heme *b* as a cofactor, whereas myoglobin was not able to promote the same reaction. However, our group has recently found that iron porphycene in myoglobin can catalyze the dehydration of aldoximes and generate the corresponding nitrile products with high turnover numbers under reducing conditions.

Taken together, metalloporphycenes serve as attractive artificial cofactors to convert myoglobin to artificial metalloenzymes.

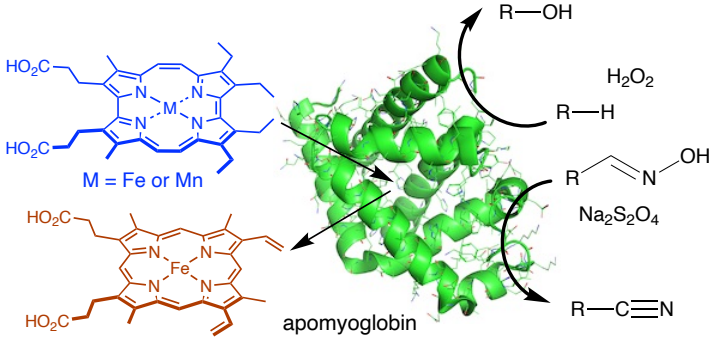

Figure 1. Myoglobin reconstituted with metalloporphycene

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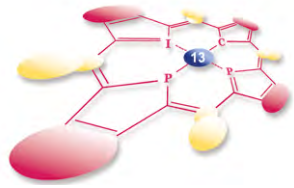

Porphyrins Associated with Stimuli-Responsive Units to Control the Properties of Receptors

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Porphyrins have been incorporated in many multicomponent systems due to their appealing coordination, and electronic and photophysical properties. The synthesis of receptors with metalloporphyrins as active components gave rise to attractive structures for molecular recognition or chemical transformation.[1] The addition of chemical, redox, or photo-responsive units opens the way to controlling the properties of porphyrin hosts such as guest uptake, catalysis, or drug transport.[2] Our group has developed various porphyrin-containing receptors, such as cages and tweezers, which incorporate triazoles or acridiniums as responsive units (Figure 1).[3, 4] We will discuss the synthesis and responsiveness of these structures to different stimuli (chemical, electronic and photonic), as well as their behaviour as multi-state molecular systems and as components of molecular machines.

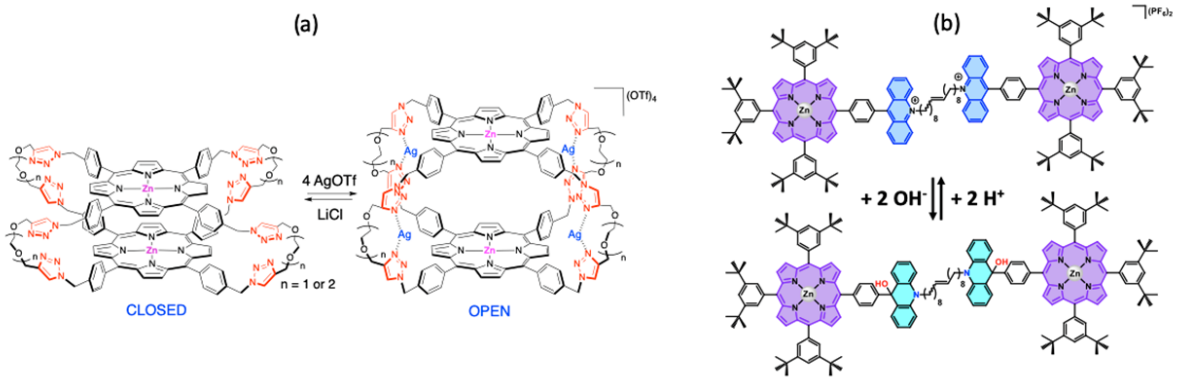

Figure 1. Stimuli-responsive (a) cage and (b) tweezer.

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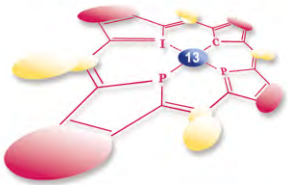

Advances in the field of surface-enhanced vibrational spectroscopies and bioelectrochemistry for the study of the reaction of membrane proteins

Petra Hellwig[a]*, Raaif Siddeeque[a], Ariadna Murillo Bello[a], Ana Filipa Seica Santos[a], Tatjana Gerasimova[a,b], Nicolas Javahiraly[a], Frédéric Melin[a], Thorsten Friedrich[b]

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Although the architectures of several membrane proteins and chemical reactions are known, the interactions on the molecular level, the diversity and efficiency of the reaction mechanisms in for example bacterial systems, are not yet understood. An overview will be given on electrochemical and spectroscopic experiments developed to study coupled electron and proton reactions, identify the contribution of individual amino acids, study the reactivity towards small molecules and, importantly, correlate it with the microenvironment of the cofactors.
First we present the electrocatalytic study of the cytochrome *bd* oxidases from different bacteria. Structural parameters that are crucial for the reactivity towards oxygen are analyzed. The pH dependency of the binding and release of NO, an important signaling factor is presented. The influence of mutants in the proton channel on the NO release is discussed. [1]
In the second part, surface-enhanced infrared absorption spectroscopy (SEIRAS), a powerful tool that allows studying the reactivity of protein monolayers at a very low concentration and independent from the proteins' size is discussed. Different types of nanostructured surfaces have been probed for best enhancement and at the same time, for good stability of the studied proteins. Once optimized [2] we used SEIRAS to study single IR probes introduced into large membrane proteins from the respiratory chain. IR probes such as nitrile- and thiocyanate-derivatized amino acids have been first described for peptides and soluble proteins. They have been found to give specific information on the local environment of the probe, because their IR absorption frequencies strongly depend on the hydrogen bonding with the surrounding protic solvent molecules, backbone, or amino acids.
IR probes were introduced to individual cysteine mutants of the studied protein complex [3] The spectral signature in the presence of different substrates was then monitored. Information on the reorganization of the introduced IR label upon the induced reaction was obtained. An opening of the structure in the membrane arm upon addition of NADH was demonstrated providing evidence for the long-range conformational arrangements taking place in the enzyme during catalysis.

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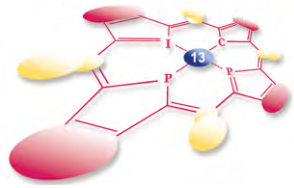

Donor-Appended Flat Corrole Dye Realizing a Long-Lived Charge-Separated State for Efficient Dye-Sensitized Solar Cells

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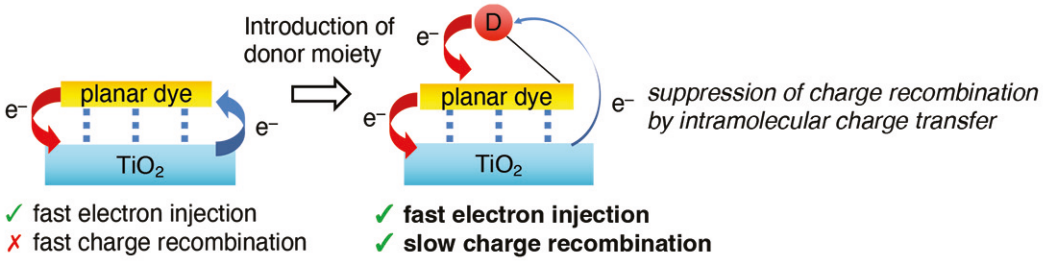
In recent years, dye-sensitized solar cells (DSSCs) have attracted much attention as an alternative to silicon-based solar cells owing to their advantages, such as high power conversion efficiency (η), low-cost production, facile fabrication, and indoor use. Since the cell performance of DSSCs strongly depends on sensitizers, rationally designed organic dyes have been developed and achieved high η-values. Porphyrins and corroles have drawn attention as promising dyes for DSSCs due to their extremely high light-harvesting ability compared to other conventional organic dyes. However, these flat dyes with multiple anchoring groups tend to adopt a horizontal orientation on TiO_2 and suffer from low □-values because of the fast charge recombination caused by the strong electronic coupling between the dye and TiO_2. To suppress the undesirable charge recombination, the introduction of an additional donor moiety would be an effective strategy. Namely, an intramolecular electron transfer from the donor moiety to the oxidized dye can compete with the charge recombination to realize a long-lived charge-separated state ($Dye^{\bullet+}/TiO_2^{\bullet-}$).

Herein, we designed and synthesized a triarylamine (TAA)-appended gold(III) corrole dye **TAA-AuCor** to prove our concept. The DSSC with **TAA-AuCor** using I_3^-/I^- redox shuttle exhibited a higher η value than that with the reference dye **AuCor**[1] without the TAA moiety. The transient absorption measurements revealed that the intramolecular electron transfer from the TAA to the corrole radical cation generated a long-lived charge-separated state **TAA$^{\bullet+}$-Cor**/$TiO_2^{\bullet-}$ efficiently. Consequently, the introduction of the TAA moiety effectively suppressed undesirable charge recombination from an electron in the CB of the TiO_2 to the dye radical cation and enhanced the □ value. Therefore, our unique approach to manipulating charge-separated states is very promising for further improvement of the photovoltaic performance of DSSCs.



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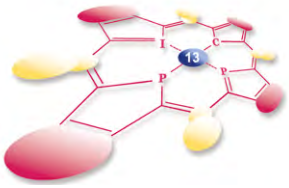

Sensing and singlet oxygen generation using oxocyclohexadienylidene-substituted macrocycles

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Chromophores such as porphyrins or fuchsonarenes[1,2] have physical properties suitable for applications in sensing for the detection of analyte species. Where access to a triplet excited state is allowed, the relevant chromophores can be used to generate reactive singlet oxygen, which can then be diverted for use in such applications as photodynamic therapy (PDT) or bacterial photoinactivation. For instance, *meso*-5,10,15,20-tetrakis-3,5-di-*tert*-butyl-4-oxocyclohexadienylideneporphyrinogen, **OxP**, is a versatile, highly colored chromophore with strong broad absorption in the visible range derived from meso-5,10,15,20-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl) porphyrin by its two-electron oxidation. **OxP** moiety exists in a saddle conformation so that N-Alkylation of the **OxP** core nitrogen atoms can be used to functionalize the chromophore yielding a class of stable molecules with highly substituted peripheries. Substituted **OxP**s can act as singlet oxygen generators[3] under light irradiation and the efficacy of this process is influenced by the multiplicity of N-substitution, and by the chemical identity of those substituents. Bromination of the macrocyclic beta-positions can also be used to control singlet oxygen generation by the relevant derivatives. We report the quantum yields of singlet oxygen generation for a series of differently substituted **OxP** derivatives whose metrics indicate that these compounds possess significant potential in the corresponding applications including photodynamic therapy, bacterial inactivation therapy, and organic transformations. **OxP** chromophores were incorporated in metal-organic-frameworks[4] (MOFs) and covalent organic frameworks (COFs) and their use for selective oxidation of organic substrates was investigated. The synthesis of water-soluble **OxP** derivatives will also be reported.

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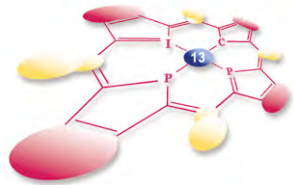

Some insights into the role of solvents in porphyrin self-assembly

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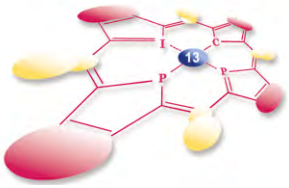
It is relatively easy to compute desorption energies, kinetics, and general desorption thermodynamics for small to medium size self-assembling molecules desorbing into vacuum or vapor, it is still a great challenge to provide the same values for desorption into solution. Mastering this challenge is exceedingly important for understanding the role of solvents in the self-assembly of tectons on various surfaces. This problem becomes even more complex when pseudopolymorphs (self-assembled layers composed of both tecton and solvent) are formed. In this talk, we consider the initial concentration-dependent formation of pseudopolymorphs of cobalt octaethylporphyrin (CoOEP) and common solvents toluene and trichlorobenzyne. Periodic boundary condition DFT is used to compute electronic and vibrational energies. These can be used with absolute reaction rate theory to determine the rate of desorption of the guest solvent into vapor. We then utilize a method recently introduced by Campbell [1] to convert the computed vapor phase desorption energies to those for desorption into solution. Statistical mechanics is used to prove that the pseudopolymorph is a kinetically controlled phase and that the self-assembled CoOEP adlayer (solvent-free) is the thermodynamically stable phase at all practical concentrations. We also consider the computed rate of desorption in the solution and find that we can only set rather large boundaries because of the unknown activation energy in the solution. The method used here should have widespread value in understanding the role of solvents in the self-assembly process.



Fluorescence-guided photoimmunotherapy for peritoneal carcinomatosis

Huang Chiao Huang

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Enhancing conventional therapies through fluorescence-guided intervention proves pivotal in identifying and addressing microscopic tumors before the onset of lethal recurrence. Despite remarkable strides in the realms of photoimmunotherapy and nanotechnology for metastasis treatment, the translation to clinical applications encounters challenges attributed to diverse treatment effects. To address this challenge, our team integrates three cutting-edge technologies: targeted photo-activable multi-agent liposome (TPMAL), fluorescence-guided intervention, and laser endoscopy (ML7710) to augment photoimmunotherapy effectiveness [1]. TPMAL comprises nanoliposomes with labeled fluorophores for tracking and photosensitizer immunoconjugates for photoimmunotherapy. ML7710, integrated with Modulight Cloud, facilitates the capture and analysis of multispectral emissions from TPMAL, enabling fluorescence-guided drug delivery (FGDD) and fluorescence-guided light dosimetry (FGLD) in peritoneal carcinomatosis mouse models. Our FGDD results demonstrate over ten times improvement in drug delivery to metastatic sites with TPMAL. ML7710 successfully captures interpatient variability in TPMAL uptake, prompting FGLD in over half of the animals. The combined approach of TPMAL, ML7710, and fluorescence-guided intervention significantly reduces variations in treatment responses, leading to enhanced tumor control and prolonged animal survival without observable side effects.

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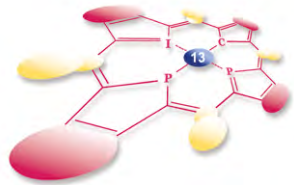

Cobalt-Porphyrin-Phospholipid: Advancing Dual Antigen Co-Delivery *via* Liposomes for Malaria Vaccination

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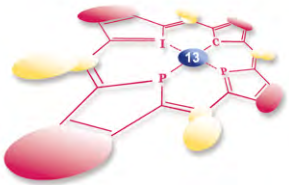
Antigen-displayed liposomal vaccines hold promise for inducing robust immune responses against specific diseases. However, generating antigen particles can be time-consuming and costly. Our study introduces a key innovation: rapidly converting soluble antigens into particulate form by combining them with liposomes containing cobalt-porphyrin-phospholipid (CoPoP). This approach significantly enhances functional antibody responses. Malaria remains a global health challenge, and innovative vaccine strategies are needed. Targeting multiple stages of the Plasmodium falciparum parasite life cycle offers advantages for malaria control but has proven challenging. The Circumsporozoite protein (CSP) is the antigenic target of leading P. falciparum pre-erythrocytic Mosquirix® vaccines, preventing infection in human hosts. Additionally, Pfs230, a sexual-stage P. falciparum surface protein, is currently in clinical trials for malaria transmission-blocking vaccines, inhibiting parasite development within the mosquito vector. In this study, we co-displayed recombinant full-length CSP and a Pfs230 fragment (Pfs230D1+) on immunogenic CoPoP liposomes. Our goal was to induce immunity that simultaneously reduces both infection and transmission.
The bivalent liposomes, with antigens binding via His-tag insertion into the CoPoP bilayer, exhibit serum innovative vaccine strategies that are needed. antibodies recognizing both sporozoites and gametocytes. Notably, the antibody magnitude surpassed that achieved by admixing antigens with other adjuvants. Furthermore, these induced antibodies effectively reduced parasite development in mosquito midguts during a standard membrane-feeding assay (SMFA). To validate the vaccine's efficacy, mice immunized with bivalent liposomes or receiving purified antibodies from immunized rabbits via passive transfer exhibited reduced parasite liver burden upon challenge with transgenic sporozoites expressing P. falciparum CSP.
In summary, our findings advocate for next-generation particle-based immunogens, such as CoPoP liposomes, as promising tools for developing a multi-stage malaria vaccine.



Synthesis and properties of calix[3]pyrrole related macrocycles

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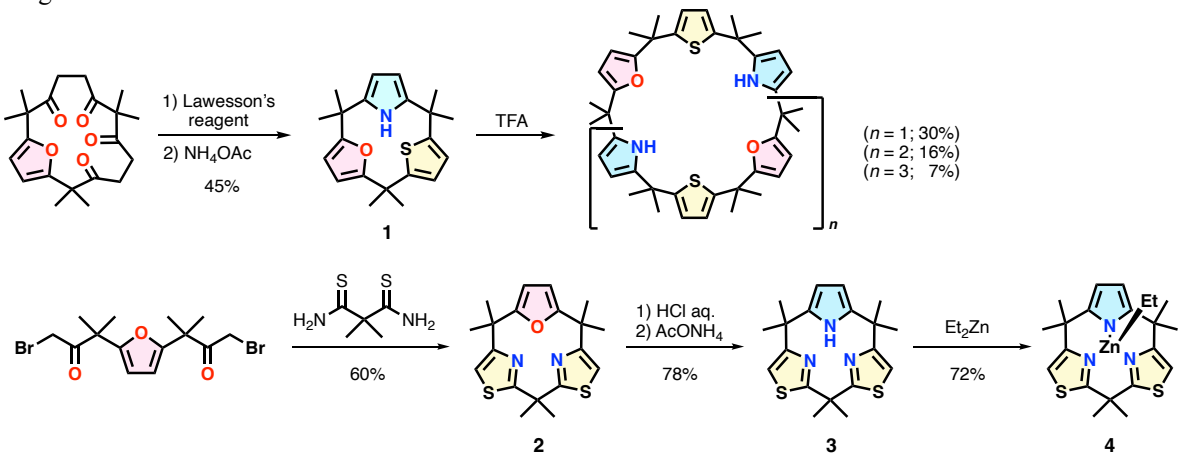
Calix[3]pyrrole is a tripyrrolic porphyrinogen-like macrocycle in which three pyrrole units are linked by three sp^3-hybridized carbon atoms. While tetrapyrrolic macrocycles such as calix[4]pyrroles and porphyrins can be selectively obtained by acid-catalyzed pyrrole monomer condensation reactions, such a conventional strategy has not been available for calix[3]pyrroles. The author's group has developed the cyclic oligoketone-based synthesis of calix[3]pyrrole and its furan derivatives.[1] Here, we have expanded the scope of the synthesis to inherently chiral calix[1]furan[1]pyrrole[1]thiophne (**1**), and direct cyclization of calix[1]furan[2]thiazole (**2**).

Inherently chiral macrocycle **1** was prepared from a furan-embedded tetraketone macrocycle via stepwise formation of thiophene and pyrrole.[2] While enantiomers of **1** were separated by chiral HPLC, they racemized through ring flipping with a half-life of 2.5 h in *n*-hexane. An acid-catalyzed strain-induced ring expansion reaction of **1** led to isolation of calix[3*n*]pyrrole derivatives up to $n = 3$ in 7% yield.

Direct macrocyclization between bis(α-bromoketone) and 2,2-dimethylpropane bis(thioamide) afforded **2** in 60% yield. Due to the absence of inner NH, macrocycle **2** was less-strained and stable under acidic conditions. Thus, acid catalyzed hydrolysis of furan proceeded, and calix[1]pyrrole[2]thiazole (**3**) was obtained after a subsequent Paal–Knorr reaction. Furthre complexation of **3** with Et_2Zn furnished a water-stable organozinc complex **4**. In this presentation, detailed synthetic strategies, reactivities, and other chemical properties of brand-new calix[3]pyrrole analogues will be delivered.



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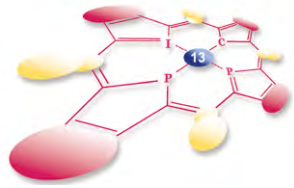

Phthalocyanines as oxidation and reduction catalysts

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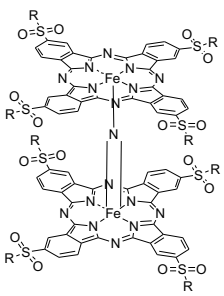
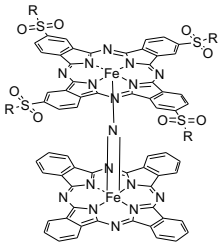
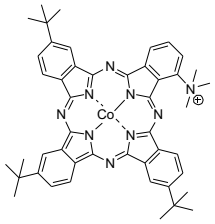
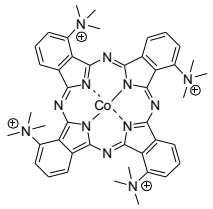
Monomeric and μ-nitrido dimeric iron phthalocyanines are mainly used as catalysts in oxidation and reduction reactions [1,2]. Substituted μ-nitrido diiron phthalocyanines emerged as powerful oxidation catalysts. These complexes have showed significant catalytic properties for oxidation of methane [3], benzene [4], alkyl aromatics [5], and defluorination of poly- and perfluorinated aromatic compounds [6].





Trimethyl-ammonium substituted Co phthalocyanines exhibit excellent catalytic efficiency in the CO_2 reduction reaction [7]. Cu(In,Ga)Se2 (CIGS)/tetraammonium-substituted Co phthalocyanine hybrid material was prepared for photoelectrochemically reduction of CO_2 to CO [8]. Transparent porous ZnO/Tetraammonium-substituted Co phthalocyanine material was used in electrochemical reduction of CO_2 [9].





Monomeric and μ-nitrido dimeric phthalocyanine complexes in catalytic applications will be discussed.

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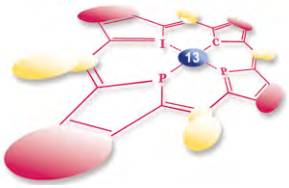

Doubly N-Confused Dioxoheptaphyrin: Near-infrared Photothermal Conversion

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Expanded porphyrins, characterized by more than five pyrrole rings, have emerged as crucial near-infrared (NIR) chromophores. These molecules possess large and flexible π-conjugated scaffolds, offering novel prospects in optical materials across diverse fields, including light-harvesting, sensing, and therapeutic applications.[1] However, certain expanded porphyrins, such as the larger pyrrolic numbered analogs (e.g., heptaphyrins), face challenges due to structural flexibility in solution. This flexibility can lead to environment-dependent conformational changes and optical responses, hindering the efficient delocalization of π-electrons over the scaffold and limiting their desired applications.

To address this issue, we have demonstrated a unique core-modification approach known as N-confusion modification. This approach has yielded a series of N-confused expanded analogs (e.g., **1** and **3**) with rigidified π-conjugated structures upon various metal bindings.[2-3]

In this report, we present the synthesis of a novel doubly N-confused dioxoheptaphyrin (**2**), representing a key addition to the N-confused family. This compound features two *cisoid*-configured confused pyrrole rings, resulting in a distinctive figure-of-eight twisted structure. Upon metal complexation, the resulting complex of the dioxoheptaphyrin exhibits intriguing second NIR optical features. We will provide a detailed exploration of the structure-photophysical property relationship of **2**.

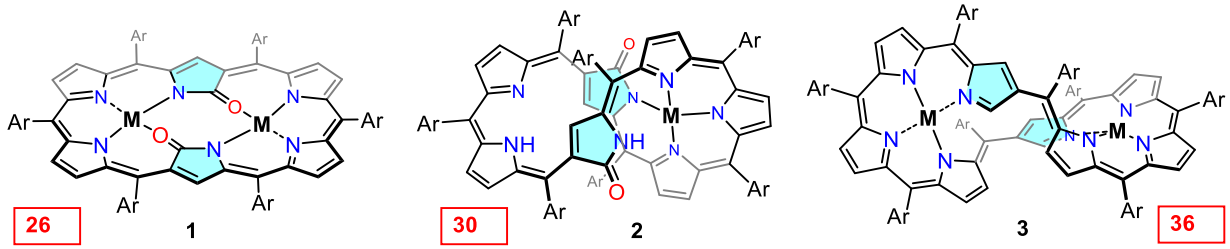

Figure 1. Chemical structures of doubly N-confused dioxohexaphyrins **1** (left), dioxoheptaphyrin **2** (middle), and octaphyrin, **3** (right). Ar = C_6F_5, M = Cu, Zn .

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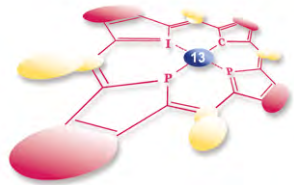

Chiroptical and Magneto-Optical Properties of Porphyrin Aggregates

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Porphyrin aggregates have attracted considerable attention in terms of their flexible nanostructures showing various photophysical characteristics. In particular, their unique chiroptical properties based on their exciton interactions have been intensively investigated due to the development of syntheses and measurement systems. In recent years, the interplay between strong exciton chirality and large aromatic π-electron system-based magnetism may become one of the scientific frontiers. In this talk, our recent progress in chiroptical and magneto-optical properties of porphyrin aggregates will be shown in terms of circular dichroism (CD), magnetic CD (MCD), circularly polarised luminescence (CPL), magnetic CPL (MCPL), second-harmonic scattering (SHS), and magneto-chiral dichroism (MChD) spectroscopies.

1) Magneto-chiral dichroism:[1, 2] MChD, the cross effect of CD and MCD, is an interesting phenomenon in which the absorption coefficient of a chiral molecule is different for an unpolarized light beam when an externally applied magnetic field is parallel and antiparallel to the propagation direction. Because the MChD of two enantiomers is opposite in nature, MChD is one of the plausible candidates for explaining the homochirality of life. By using J-aggregates of diprotonated *meso*-tetra(4-sulfonatophenyl)porphyrins (H_4TPPS_4), we successfully demonstrated the presence of MChD in organic compounds for the first time. Also, the MChD was observed for chiral J-aggregates of zinc chlorins (ZnChls), the model compound of light-harvesting antenna in green photosynthetic bacteria, which suggests the second magnetic field effect in photosynthesis.

2) Mechanical rotation-induced supramolecular chirality:[3] Vortex motions are inherently chiral. We succeeded in showing a novel, highly reproducible, rotary evaporation-induced chiral aggregation of achiral phthalocyanines (Pcs), and proposed the mechanisms for preparing nanoscale chiral supramolecules by the use of macroscopic mechanical rotations. Here, the stable chiral thin films based on H-aggregates of Pcs were prepared on the bottom of the flask by the concentration of the monomeric solution with a rotary evaporator, and the circular dichroism was shown to reproducibly depend on its rotational direction.

3) Vortex-Induced Harmonic Light Scattering:[4] Using J-aggregates of H_4TPPS_4, whose chirality was shown to be induced using the macroscopic vortex motions caused by magnetic stirring, we successfully observed vortex-induced harmonic light scattering under the rotation of a magnetic stirrer.

4) Switching of MCPL/CPL:[5] The emission spectrum of the ZnChl monomer shows a distinguishable, positive MCPL signal in contrast to the negligible CPL signal. On the other hand, in the case of the chiral J-aggregates of ZnChls, although no distinguishable MCPL signal was observed, intense positive/negative CPL signals was observed in the J-band region. These are reasonably explained by the exciton interactions in the J-aggregates. Thus, the switching of MCPL/CPL has been demonstrated.

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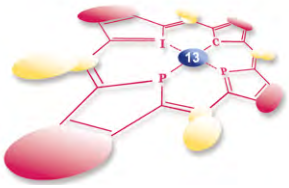

Unique Heme Environments in Iron Regulatory Proteins to Regulate the Binding to Iron Responsive Element

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To maintain iron homeostasis at the cellular level, iron regulatory protein (IRP) plays a central role in regulating the translation of various kinds of proteins including iron uptake, iron storage and iron metabolism. Under low iron conditions in cells, IRP specifically binds a characteristic stem-loop structure, iron-responsive element (IRE), which is located in the 3' or 5' untranslated region (UTR) of mRNA. The IRP binding to IRE at 5'UTR inhibits the access of ribosome to the coding region of the mRNA, suppressing the translation of iron storage proteins such as ferritin (Ft), while mRNAs coding iron uptake proteins such as transferrin receptor (TfR) has several IRE structures at the 3'UTR and the binding to these IREs protects the degradation of the mRNA by endonuclease to promote the translation of the proteins, facilitating the iron uptake into cells. On the other hand, under high iron conditions, IRP dissociates from IRE at 5'UTR to promote the translation of proteins to reduce the available iron contents in cells and dissociation of IRP from IREs at 3'UTR facilitates the degradation of mRNA by endonuclease to suppress the translation of proteins for the iron uptake to cells. In IRP1, one of the homologues of IRPs, while previous studies proposed that the formation of an iron-sulfur cluster in the IRE binding site, the cleft region, abolished the IRE binding ability, we found that the addition of heme to IRP1 also eliminates the IRE binding ability as found for IRP2, another homologue of IRP, suggesting the function for heme as a signal molecule in intracellular iron homeostasis.

However, the heme-binding sites in IRP1 are still controversial. The heme titration experiments clearly showed IRP1 mutants having the mutation at one of the cysteine residues in heme regulatory motifs (HRM) lose one equivalent amount of heme binding, indicating the two cysteine residues in HRM are the ligands for the heme-binding [1, 2]. On the other hand, the X-ray structure of heme-bound IRP1 clearly showed the binding of heme to a cysteine residue not in the HRM regions and the heme-binding and heme-induced inhibition of the IRE binding were also observed for the mutant in which the cysteine residues of both HRMs were mutated. These results suggest that the heme binding sites are altered by amino acid substitutions and the identification of the heme binding sites using wild-type IRP1 is required.

Here, we utilized a heme-specific probe that can generate the adducts to amino acid residues near the heme binding sites to determine the amino acid ligands of heme in wild-type IRP1. The peptide mapping after the digestion of the heme-bound IRP-probe mixture indicated the increase of the mass number of some of the peptide fragments due to the addition of the probe to the side chain of the amino acid residues. Based on the intensity of the mass peak, the primary modification sites are located around the inside of the cleft structure of IRP, where one of the cysteine residues of HRM and cysteine residue for the heme ligand in the X-ray structure are located. Considering that these two cysteine residues are close and that heme cannot bind to both cysteine residues simultaneously, IRP1 is assumed to sterically inhibit the IRE binding by non-specifically heme binding to one of the cysteine residues inside the cleft structure, the IRE binding site. Such low specificity of heme binding has not been observed in proteins with heme as the active center, which is a new mode of heme binding characterizing the heme environments in proteins that use heme as a signal molecule.

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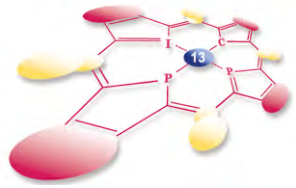

Selective Atropisomerization of a Porphyrin Derivative and Its Supramolecular Applications

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The introduction of substituents to one of the *o*-positions of the four *meso*-aryl groups of 5,10,15,20-tetraarylporphyrins has been effective for the construction of a specific and functional environment in the porphyrin molecule.[1] The substituent introduction induces the formation of a mixture of four kinds of atropisomers (αααα, αααβ, αβαβ, and ααββ), defined by the directions of the *o*-substituents against the porphyrin plane. We have selectively converged a porphyrin derivative (**1**), having mesityl groups at one of the *o*-positions of each *meso*-aryl group, to targeted atropisomers among the four possible atropisomers under appropriate conditions for each atropisomer (Figure 1).[2] For example, protonation and subsequent neutralization of a freebase porphyrin (H_2**1**) affords the convergence of an atropisomeric mixture to the αβαβ atropisomer, H_2**1**-αβαβ. The αααα isomer, H_2**1**-αααα, was also obtained by heating a solution of H_2**1** in $CHCl_3$ in 60% isolated yield, probably owing to a template effect of the solvent molecule. When an atropisomeric mixture of its zinc complex, Zn**1**, was heated at 70 °C in a $ClCH_2CH_2Cl$/MeOH mixed solvent, crystals composed of only Zn**1**-αααα were formed. The hydrophobic space formed by the four mesityl groups in the αααα isomers (H_2**1**-αααα and Zn**1**-αααα) can be used for repeatable molecular capture. Heating the solid of an atropisomeric mixture of Zn**1** to 400 °C afforded the ααββ isomer almost quantitatively. On the other hand, the solid of H_2**1**-αααα can be converted by heating, successively to H_2**1**-αααβ at 286 °C and then to H_2**1**-ααββ at 350 °C.

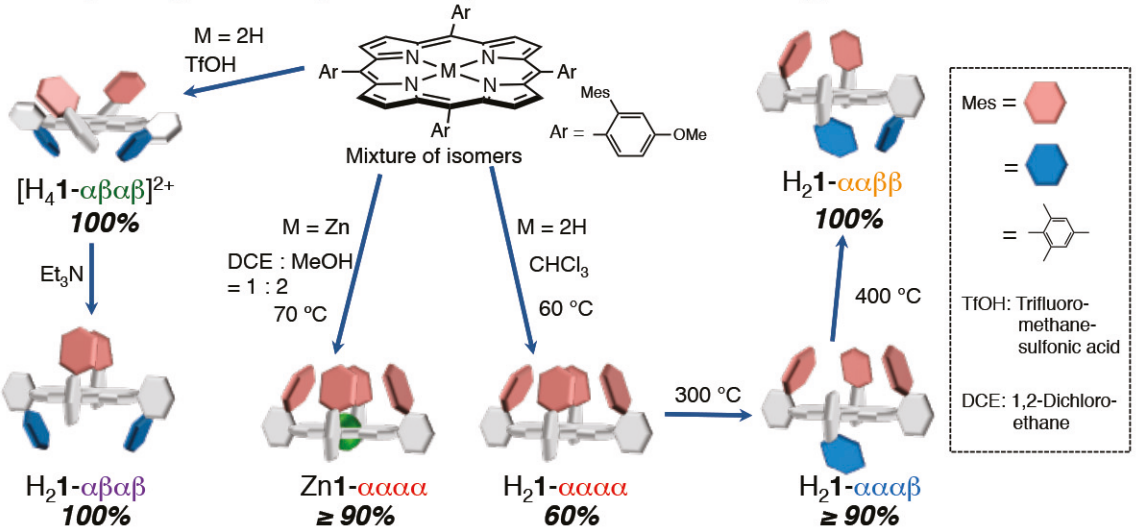

Figure 1. Selective atropisomerization of a porphyrin derivative, **1**.[2]

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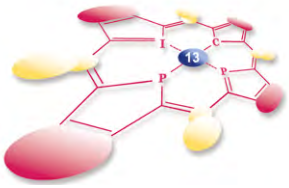

A non-perturbing spin probe to identify catalytic electron transfer pathways via redox-active amino acids: KatG, tryptophans and the isoniazid prodrug paradigm

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In metalloproteins, transition metals are responsible for the redox reactions inherent to their catalytic function, which can be enhanced by concerted metal-radical chemistry [1]. The catalytic cycle of the bifunctional heme-containing peroxidases (so-called KatGs) includes a concerted heme&Trp$^{\bullet}$ reaction for the oxidation of substrates [2, 3]. Site directed-mutagenesis and isotope labeling, combined with multifrequency EPR spectroscopy and X-ray crystallography allowed us to identify Trp330, Trp139, and Trp153 as the radical sites for the Fe^{IV}=O Trp$^{\bullet}$ intermediates in the catalytic cycle of *B. pseudomallei* KatG (BpKatG) [3]. Given the distance between the heme and Trp153, we anticipated that Trp95 and Trp94 should play the role of electron relays, crucially enabling the catalytically-relevant long-range intramolecular electron transfer (iET). Single and double BpKatG mutants on Trp94 and Trp95 allowed us to confirm experimentally their role as electron relays, based on our detailed studies of the catalytic intermediates using multifrequency EPR spectroscopy [3]. In this work, we implemented the use of a nitroxide as a convenient e^- reporter to provide direct evidence of such iET process. We designed the BpKatG triple variant to insert a surface-exposed Cys residue serving to covalently attach a nitroxide (Proxyl) adjacent to Trp94 and Trp95 (the Asp93 to Cys mutation), while removing both natural cysteines (Cys27 to Ser and Cys556 to Ser mutations). Proxyl$^{\bullet}$ is a stable nitroxyl free radical (N-O$^{\bullet}$) with a characteristic 9-GHz EPR spectrum, clearly distinct from those of the protein-based (Trp and Tyr) radicals. We have implemented the, so far unexplored, use of nitroxides that takes advantage of their redox properties, in particular the one-electron oxidation to the oxoamonium cation (Proxyl$^+$), to provide a direct measurement and convenient tool for the identification of iET pathways in metalloproteins [4]. The oxidation of Proxyl$^{\bullet}$ to Proxyl$^+$ as a result of being placed in the catalytic long-range e^- transfer pathway of the distal heme side in BpKatG could be readily monitored by 9-GHz EPR spectroscopy. The estimation of iET rates and direct proof of Trp139 as an oxidation site for the prodrug isoniazid will be discussed, as well as the general use of the approach for catalytic ET in proteins.

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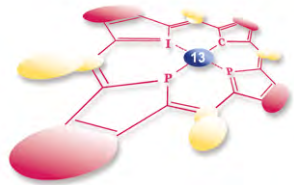

Coordination-based Supramolecular Assemblies Formed by Porphyrin Derivatives

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Porphyrins, as essential pigments in biological systems, are intrinsic to the self-assembly processes crucial for various biological functions, including light harvesting and electron transport. Inspired by the highly symmetric wheel-like supramolecular architecture observed in the crystal structure of light-harvesting antenna complexes in purple photosynthetic bacteria, numerous porphyrin-based nanoarchitectures—ranging from nanofibers and nanosheets to nanoparticles and nanorings—have been crafted for applications across photonics, catalysis, and electronics. Leveraging the unique molecular structures and diverse coordination functions of porphyrins, this study emphasizes their pivotal role in developing coordination-based supramolecular assemblies. The investigation delves into the design and synthesis of novel coordination-based supramolecular assemblies through porphyrin derivatives. Capitalizing on the robust binding affinity between porphyrin derivatives and metal ions, we have successfully engineered stable and intricately organized structures, showcasing their potential applications. The resulting supramolecular assemblies exhibit compelling properties in optics, electronics, and biology, presenting promising avenues in fields such as nanotechnology and sensor development. This study aims to underscore the significance of porphyrins in the realm of coordination-based supramolecular assemblies and explore their diverse applications, thereby contributing valuable insights to the interdisciplinary fields of nanoscience and nanotechnology.

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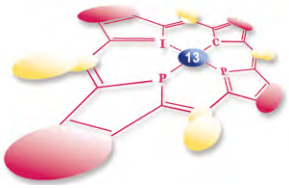
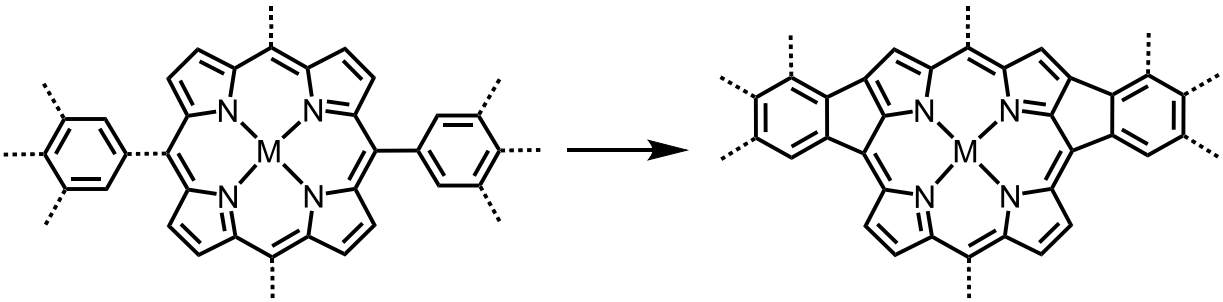


Fusing porphyrins to PAHs

Norbert Jux[a], **Christoph Oleszak**[a]

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

Fusing porphyrins into various polycyclic aromatic hydrocarbons is an excellent strategy to expand the π-system of the porphyrin and add functionality.[1, 2] Thus, new chromophores are obtained which possess, among other interesting qualities, red-shifted UV/vis absorptions.



We present our approach to π-extended fused porphyrins via Scholl oxidation of meso-positioned aryl groups to the core.[3, 4]

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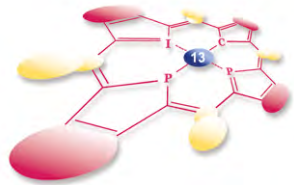

Identification of Cellular Targets of Tetrapyrrolic Pigments derived from Chlorophyll and Heme

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Chlorophyll and heme are among the so-called "pigments of life", colored tetrapyrroles that are essential for life on Earth. Traditionally, their degradation products, the phyllobilins and bilins, have been regarded as mere by-products of detoxification processes. Extensive literature reports have challenged this view by highlighting physiologically relevant bioactivities of bilins, such as their potent antioxidative properties. Promising bioactive properties have also recently been demonstrated for plant-derived phyllobilins [1]. To gain insights into the detailed mechanisms and mode of action of these pigments, the precise identification of direct protein interactions is essential. However, knowledge about relevant cellular target proteins is still limited, and especially in the case of phyllobilins, no human target protein has been identified so far.

In a functional screening in cancer cells, two colored phyllobilins – a yellow phylloxanthobilin and a pink phylloroseobilin – along with the bilins bilirubin and biliverdin demonstrated the ability to inhibit cell migration in cancer cells. The process of cell migration is linked to the dynamics of the actin cytoskeleton. All four compounds were found to inhibit actin polymerization and actin nucleation while facilitating actin depolymerization. Notably, phylloroseobilin emerged as the most potent candidate in various approaches. Affinity chromatography with G-actin beads confirmed the direct binding of phyllobilins and bilins to G-actin and computational studies revealed their potential to interact with a common binding site of the protein [2].

By introducing actin as a human target for both phyllobilins and bilins, we take a significant step toward unraveling the significance behind the degradation of two of the most important pigments on Earth.

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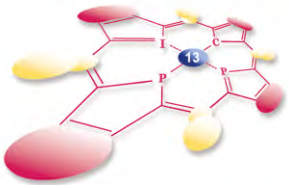

Heme-Copper O_2-Adducts and Thermodynamic Relationships between Superoxide, Peroxide and Hydroperoxide Hemes

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Biologically critical (for ATP synthesis) O_2-reduction to water and concomitant membrane proton translocation is carried out by mitochondrial cytochrome c oxidases; each 2 Fe plus 3 Cu protein subunit utilizes its heme-Cu heterobinuclear active site to bind molecular oxygen and effect reduction-protonation. Our research group has learned to utilize reduced synthetic hemes plus copper(I) chelates, or binucleating heme-copper constructs, to cryogenically study O_2-binding. These efforts lead to the characterization of several types of heme-Fe^{III}-(peroxide)-Cu^{II}(ligand) constructs. Our most recent efforts, utilizing chelates for copper possessing an appended phenol as a potential electron-donor, may be presented. Such studies have also led us to generate and characterize O_2 and reduced derivatives bound to hemes only. Such species are, of course, relevant to analog species critically formed during the catalytic cycles of heme oxygenases and oxidases. With heme-O_2 (ferric heme superoxide) species, reversible chemical reduction reactions afford ferric heme peroxide complexes. These can be reversibly protonated to give ferric heme hydroperoxide species. Thus, heme superoxide/peroxide reduction potentials ($E°'$) and heme hydroperoxide pK_a values have been obtained, these data affording and ferric heme hydroperoxide complex bond dissociation free energies (BDFE's). For the two cases studied, the BDFE's are found to be measurably different and the results to be discussed demonstrate that this is reflected in the hydrogen atom abstraction (HAA) reactivity of the ferric heme superoxide complexes with hydroxylamine substrates. The results observed will be discussed in terms of the variations like the porphyrinate and axial ligand 'base' present.

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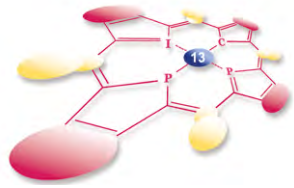

Spectroscopic diagnosis of excited-state aromaticity: Capturing electronic structures and conformations upon aromaticity reversal

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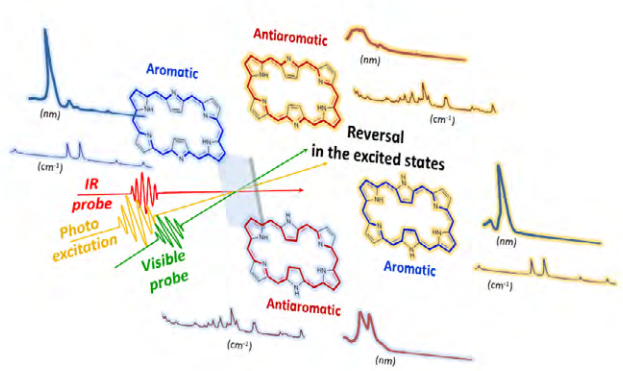
Aromaticity, the special energetic stability derived from cyclic [4n+2]π-conjugation, has been the topic of intense interest in chemistry. Recently, the pioneering work by Colin Baird on aromaticity reversal, postulating that aromatic (antiaromatic) character in the ground state reverses to antiaromatic (aromatic) character in the lowest excited triplet state, has attracted much attention. The completely reversed aromaticity in the excited states provides direct insight into understanding the properties of photoactive materials. However, most studies on excited state aromaticity have been based on the theoretical point of view. The experimental evaluation of excited state aromaticity is still challenging and strenuous because the assessment of aromaticity with conventional magnetic, energetic, and geometric indices is difficult in excited states.
Time-resolved optical spectroscopies can provide a new and alternative avenue to experimentally evaluate excited state aromaticity. By monitoring ultrafast changes in the excited states, they can provide valuable information for excited state aromaticity. In this regard, recent breakthroughs in experimentally assessing aromaticity reversal in the excited states with time-resolved optical spectroscopic measurements are introduced. To scrutinize this intriguing and challenging scientific issue, expanded porphyrins have been utilized as the ideal testing platform because they exhibit perfect aromatic and antiaromatic congener pairs, having the same molecular framework but with different numbers of π-electrons, which facilitates the study of the pure effect of aromaticity. Time-resolved electronic and vibrational absorption spectroscopies capture the change of electronic structure and molecular conformations driven by the change of aromaticity and provide clear evidence for aromaticity reversal in the excited states. These approaches will pave the way for the development of new experimental indices for the evaluation of excited state aromaticity and its applications.



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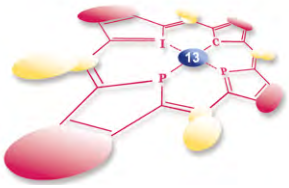

Photogenerated Molecular Spin Qubits and Ground State Spin Polarization

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Radical elaborated spin-bearing Pt Donor-Acceptor and Donor-*Bridge*-Acceptor ligand-to-ligand charge transfer complexes have been used to control spin-dependent ground and excited state processes that include non-radiative lifetimes,[1] magnetooptical activity,[2] and ground state electron spin polarization.[3, 4] These molecules represent a new class of chromophore that can be photoexcited with visible light to produce an initial exchange-coupled, multi-spin, open-shell excited state. Following photoexcitation, the excited state rapidly decays to the ground state by magnetic exchange-mediated enhanced intersystem crossing (internal conversion). This process also generates excited state spin polarization and ground state electron spin polarization of the pendent radicals to enable synthetic control over the sign, magnitude, and nature of the spin polarization. Here we discuss our recent efforts using synthetic design principles to create new molecules that promote long-range electronic coupling and electron correlation,[2, 5] and the development of new platforms for spin control of excited-state processes.[1-4] We also present results that test theoretical hypotheses as they relate to how excited state pairwise superexchange interactions and energy transfer processes control the optical generation and manipulation of molecular spin qubits.[3, 4, 6-8]

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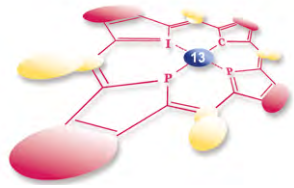

Near Infrared Photoimmunotherapy of Cancer

Hisataka Kobayashi[a]

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Three major cancer therapies; surgery, radiation and chemotherapy, have been mainstays in oncologic therapy since the beginning of modern medicine. Current immunotherapies, such as immune-activating cytokine therapy, checkpoint inhibition, engineered T-cells and suppressor cell depletion, do not directly destroy cancer cells, but rely exclusively on activating the immune system and, therefore, have been effective in limited patients. Simultaneously destroying cancer cells and activating anti-cancer host immunity has never been successfully performed by a single cancer therapy.

Here, we employ a hydrophilic photo-absorbing dye based on a silicon-phthalocyanine dye, IRdye700DX (IR700), which is covalently conjugated to antibodies (mAb) targeting cancer-specific cell-surface molecules.[1,2] When exposed to near-infrared (NIR) light, the conjugates visualize cancer cells with a low dose of non-therapeutic NIR light and induce highly selective cell death *in vivo* with a therapeutic dose of NIR light, a process termed "near infrared photo-immunotherapy" (NIR-PIT). When administered antibody-photo absorber conjugates (APC: mAb conjugated with IR700) bound to target cancer cells, cytotoxicity could be induced within 1 minute resulting in inducing necrotic/immunogenic cell death. No phototoxicity was observed in adjacent receptor-negative cells after incubation with APC in vitro. Greater than 90% of cancer cell death in vivo was demonstrated with bioluminescence imaging and ^{18}F-FDG PET after NIR light exposure. More than 80% of mice showed tumor-free survival with optimized regimens in immunocompetent mouse models, especially when combined with immune-activation therapies including immune checkpoint inhibitors or immune-suppressive cell-targeted NIR-PIT. IR700 fluorescence produced by the APC permitted guidance of light delivery and allowed for monitoring after therapy. The disappearance of IR700 fluorescence indicates sufficient exposure of NIR light for inducing therapeutic NIR-PIT effects.

The mAb-IR700 NIR-PIT was most effective, when conjugates were bound to the cell membrane, but showed no phototoxicity, when unbound because cytotoxicity is induced by photo-induced ligand release reaction that is different from conventional photodynamic therapies based on reactive oxygen species. Now an FDA-designated fast-track global phase 3 trial is ongoing worldwide including US, EU and Asia. The first EGFR-targeting NIR-PIT drug (cet-IR700; AkaluxTM) and a NIR light emitting device (BiobladeTM) for NIR-PIT were approved for clinical use against recurrent head and neck cancers in Japan in September 2020. Since then, NIR-PIT for head and neck cancer has been performed more than 400 times in 200+ patients in over 120 hospitals in Japan. In the summer of 2023, among all reported recurrent head and neck cancer patients, the overall response rate (ORR) and disease control rate (DCR) of NIR-PIT were 63.5% and 84.5%, respectively.[3]

In conclusion, NIR-PIT based on mAb-IR700 allows us to successfully perform selective treatment of cancer with no apparent severe side effects to normal cells or surrounding tissue as well as enhance anti-cancer host immunity, resulting in curing cancers with high complete response rates that were being realized in an oncology clinic in Japan.

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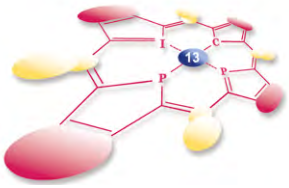

Synthesis and Characterization of Octaphenyltetraaza-porphyrin Si(IV), Ge(IV), Sn(IV), and P(V) Complexes

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Ten years ago we succeeded in producing metallophthalocyanines (MtPcs) having main absorption and fluorescence beyond 1000 nm, by inserting the P(V) ion into the center of H_2Pcs[1]. In this study, we have synthesized and characterized octaphenyltetraazaporphyrins (TAPs) with main group elements such as P(V), Si(IV), Ge(IV) and Sn(IV). These MtTAPs have either electron-withdrawing (EW) or electron-donating (ED) groups at the *para* positions of the phenyl groups. PTAPs were obtained by P(V) ion insertion into the corresponding H_2TAPs, while Si(IV), Ge(IV), and Sn(IV)TAPs were prepared using both metal-template and metal-insertion reactions. Most TAPs showed the Q, CT, and Soret bands in ascending energy. The CT bands were stronger than those of the transition metal TAPs, and their positions shifted from shorter to longer wavelengths with a concomitant increase in intensity with the increase of ED properties of the *p*-substituents (Fig. 1). The change in intensity and position of the CT and Q bands was explained reasonably as a result of configuration interaction (CI) between the excited states[2]. From this analysis, we considered that the order of the Q and CT bands may be altered by introducing very strong ED groups. By using the diphenylamino groups as the ED group, the CT band indeed shifted beyond the Q band (Fig.2), and this was reproduced by MO calculations. The spectroscopic properties of SnTAPs appeared close to those of PTAPs, but those of Si- and GeTAPs showed an intermediate nature between those of PTAPs and transition metal TAPs.

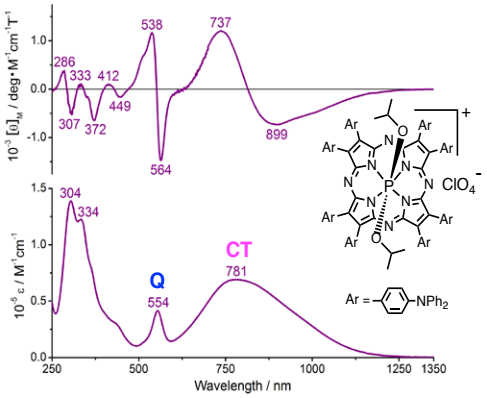

Fig. 1. Electronic absorption spectra of (a~d) P(V)TAP and (e) *tert*-butylated MgTAP in CH_2Cl_2.

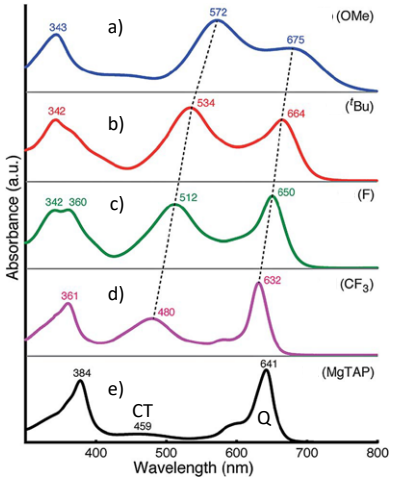

Fig. 2. Electronic absorption (bottom) and MCD (top) spectra of octa(*p*-diphenylaminophenyl)P(V)TAP in CH_2Cl_2.

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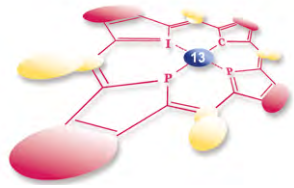

Phthalocyanine Sensing with MoS_2 Field Effect Transistor with Light Injection Toward Chemical Recognition

Tadahiro Komeda[a], Md Iftekharul Alam[b], Tsuyoshi Takaoka[a], Hiroki Waizumi[b], Muhammad Shamim Al Mamun[b]

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There is a great demand for the miniaturized sensor that enables the on-chip integration of the sensor and analysis/process, which can be applied for the operation with an *in vivo* condition. The field-effect-transistor (FET) sensor using the atomically thin channel can be a promising candidate for such an application. Due to the large area-to-volume ratio of the thin channel layer, the atomic layer FET can be more sensitive to the adsorption of the atom/molecule on the channel than the conventional MOS-FET sensor device. However, to realize chemical sensitivity, we must develop a method to make the chemical property of the target molecule manifest in the FET property. For this purpose, exploring how the FET property changes when the molecule on the channel is exposed to light with specific wavelengths might be intriguing. The Ultraviolet–visible (UV-Vis) adsorption spectroscopy for the interface between molecules and atomically thin MoS_2 surface revealed many intriguing electronic features such as HOMO-LUMO excitation energy, the molecule-induced interface feature, and the dissipation dynamics of the excited electrons. However, it is not revealed yet whether such features of the adsorbates and the interface can be revealed in the electrical properties of FET. Spectroscopic measurement of the FET property by injecting monochromatized light onto the channel is mandatory to judge such a capability of the FET. If such a behavior is confirmed for the FET device with a MoS2 channel, it is possible to give a chemical sensitivity to the MoS2-FET sensor.

Experimentally, exfoliated MoS2 flakes transferred to SiO_2 substrate were used as a channel of a FET device in which the lithography technique forms source and drain electrodes. For the injection of light, we used the light emitted from the tungsten-halogen lamp, which was monochromatized and guided by optical fiber. The rotating chopper controlled the light injection time.

As a result, we found an increase in the drain current (I_d) by injecting the light, whose difference between light-on and off state is defined as $(\Delta I_d)_{ph}$. We examined $(\Delta I_d)_{ph}$ vs light wavelength (λ) by injecting a continuous light spectrum. The $(\Delta I_d)_{ph}$-λ plot for the pristine channel shows a clear onset and a split-maxima corresponding to the excitation from the valence band minimum (VBM) to conduction band minimum (CBM), whose spectrum is similar to the previously reported photo absorption spectroscopy of the single layer MoS_2 sample. Chemical sensitivity was demonstrated using the CuPc molecule. After the deposition on the channel, we found a newly appeared peak in the $(\Delta I_d)_{ph}$ vs. λ spectrum corresponding to the excitation from the HOMO state to the molecule-induced state (MIS) formed near the CBM of MoS_2. We believe this technique can be employed for molecular sensing with the chemical recognition capability.

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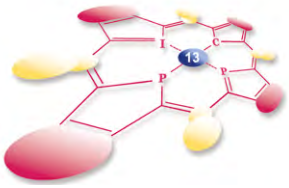

From porphyrins towards FeN_4 centers embedded in carbon – Impact on the electrocatalysis

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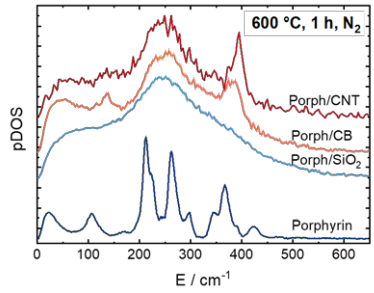
Metal N_4 macrocycles enable a broad playground for tuning the chemical properties and thus the applicability in electrocatalysis, e.g. by variation of substituents, axial ligands or selection of the metal center. Already 50 years ago it was discovered that a pyrolysis of such macrocycles improves the electrocatalytic activity and the stability.[1] By now, it is clear that the heat-treated analogues metal-nitrogen-carbon (MNC) catalysts still contain MN_4 moieties that are of relevance for the electrochemical activation of small molecules.[2,3] The share in MN_4 sites, however, significantly depends on the pyrolysis conditions and the precursor system of choice. During pyrolysis, typically also side phases such as metallic iron, iron carbide or iron nitride are formed.[4,5] Moreover, the integration into a conducting carbon framework also changes the electronic signatures.[6]
From a scientific perspective the ultimate goal would be obtaining a pure FeNC catalyst without any side phases. This would enable us to systematically explore the role of functional groups or side phases on the electronic state and electrocatalysis of the FeNC. A central question is to what extent the fundamentals obtained for the macrocyclic systems can also be transferred to the pyrolyzed system or if other principles need to be applied.



Comparison of the phonon density of states related to iron of the pure porphyrin and the materials obtained after pyrolysis at 600 °C for 1 h in inert gas atmosphere. As indicated, prior to pyrolysis the porphyrin was immobilized on different supports. The results indicate that the extent of structural transformation changes with the selection of the support.

Motivated by this goal, I will present our recent results on the effect of substituents on the interaction of iron porphyrins with carbon support followed by nuclear resonance techniques and study the related impact on cyclic voltammetry and electrocatalysis. Moreover, I will discuss to what extent the selection of the support affects the pyrolysis behaviour and obtained composition. It will be shown that indeed the support affects the retention of FeN_4 moieties and as such has a strong influence on the electrocatalytic properties. **Acknowledgment**: This work was funded by the German Research Foundation via PAK981 (KR3980/8-1) and via CRC 1487 (Funding ID: 443703006). NRVS and NFS measurements were made at the P01 beamline at DESY, Petra 3, Hamburg, Germany.

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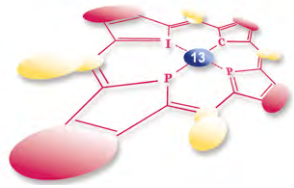

Structure and properties of novel macrocyclic structures: A first-principles perspective

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Our understanding of the structure and properties of novel macrocyclic structures can be enhanced strongly through the juxtaposition of experimental data and first principles computational data. Here, I will present recent examples of such insights. Specifically, I will discuss structure, bonding, and electronic properties in novel corroles and subphthalocyanines.

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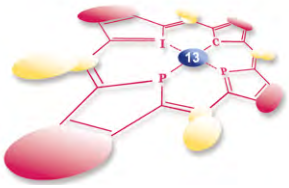

Vitamin B_{12} - the Magic of Cobalt and Rhodium

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The natural vitamin B_{12} derivatives are fascinatingly complex, ring-contracted corrins binding cobalt ions.[1] The preeminent use of cobalt in the B_{12}-cofactors [1-3] has stimulated the quest for understanding the specific biological selection of cobalt, as well as a fundamental interest in finding ways of replacing cobalt with other transition metals.[4-8] A particularly close and chemically attractive alternative for cobalt is represented by the direct homolog rhodium. This lecture discusses rational synthetic roads from the metal-free corrinoid hydrogenobyric acid [9] to rhodium analogues of the biologically most intriguing natural cobalt-corrinoids and presents insights into the structures of a range of such rhodium corrins [6, 10, 11] and reports on their use as close structural mimics of their natural B_{12} derivatives.[7] Rhodium analogues of the B_{12}-cofactors are potentially very effective antivitamins B_{12},[7, 12, 13] thus, representing promising candidates for interesting chemical and structural biological, as well as medical applications.

Acknowledgment: Financial support by the Austrian Science Fund (FWF, P33059) is gratefully acknowledged.

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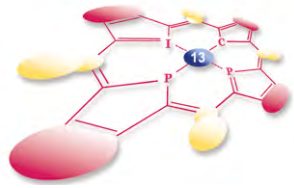

Chlorophyll-a Derived Photosensitizers for Improved Photodynamic Therapy

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Photodynamic therapy (PDT) being a safe and noninvasive modality has shown great potential for cancer treatment [1]. The efficiency of a photosensitizer is one of the major reasons for the successful implementation of PDT, therefore, continued efforts have been directed toward the development of water-soluble and NIR-absorbing photosensitizers. In recent years, pyrrole-based photosensitizers such as porphyrins, chlorins and bacteriochlorins have created enormous interest due to their ability to localize in a variety of tumors [2]. The chemical conjugation of the photosensitizer with tumor-targeting moieties causes an increase in the accumulation of drugs in tumor tissue [2]. In particular, chlorophyll-a derived photosensitizers such as pyropheophorbide-a and its analogues with unique long-wavelength absorption, high efficiency in generating reactive oxygen species and low dark toxicity have been widely used as phototoxic agents in photodynamic therapy [2]. In recent years, ligation of photosensitizers with known tumor-targeting molecules such as cholesterol, carbohydrates, folic acid, biotin, antibodies and peptide ligands have been reported with improved tumor uptake and PDT efficacy. The addition of alcohols across the vinyl group of pyropheophorbide-a methyl ester led to access to a potent photosensitizer hexyl ether derivative which is in advanced-stage clinical trials for oncologic PDT treatment [3]. Further improvement in PDT necessitates the development of new PSs with enhanced selectivity for tumor cells and reduced side effects. In our continued efforts [4-5] we successfully prepared pyropheophorbide-tryptamine conjugates and bezyloxyethyl pyropheophorbides with improved photodynamic activity and selectivity. Synthesis, photophysical properties and photodynamic activity of newly prepared pyropheophorbides will be presented during the conference.

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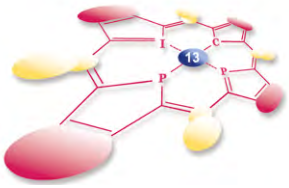

Enhancing PDT Efficacy in Non-muscle Invasive Bladder Cancer

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Background: Photodynamic therapy (PDT) using protoporphyrin IX (PpIX) has been tested for the treatment of non-muscle invasive bladder cancer (NMIBC) with limited success [1]. To improve the efficacy of PpIX-based PDT, we have developed singlet oxygen-cleavable prodrugs [2]. The prodrug treatment with PpIX-PDT kills cancer cells by both PpIX-PDT effect and preferentially released drugs in cancer cells. Inhibition of PpIX efflux was reported to be an effective strategy to improve PpIX-PDT in certain cancer cells.
Aim: The main goal of this experiment is to investigate whether adding an efflux inhibitor to the combination of PpIX and prodrugs can improve the PpIX levels in bladder cancer cells and the release of active drugs, thus improving the overall efficacy of the treatment.

Materials and Methods: We treated bladder cancer cell lines with lapatinib and evaluated intracellular PpIX fluorescence using a spectrofluorometer. We also determined the cytotoxic effect of lapatinib in combination with our prodrugs and PpIX-PDT. Additionally, we evaluated the prodrug uptake using fluorescence imaging and a quantitative fluorescence method.

Results: Lapatinib significantly increased intracellular PpIX fluorescence in bladder cancer cells, indicating enhanced PpIX accumulation. Combining lapatinib with our prodrugs resulted in a significant decrease in cell viability compared to prodrugs or PpIX-PDT alone. It was observed that the effect of lapatinib mainly depended on the expression level of the efflux pump in bladder cancer cells. Interestingly, lapatinib increased PTX prodrug uptake 3-fold compared to prodrug alone.

Conclusion: Adding an efflux inhibitor (e.g., lapatinib) could be a promising strategy for the combination treatment of NMIBC. Since various efflux inhibitors are clinically available and can be simply added to a bladder instillation solution, this new strategy could be highly translatable to the clinic.

Keywords: Bladder cancer, Photodynamic therapy, Hexyl amino levulinate, Prodrugs, Lapatinib, Efflux inhibitor

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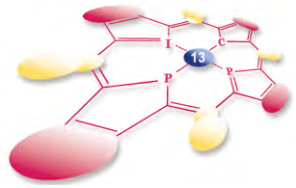

Carbenaporphyrin complexes: the stronger electron donor character and its consequences

Doris Kunz[a], **Theo Maulbetsch**[a], **Viola Munzert**[a], **Malín Moya Llasat**[a]

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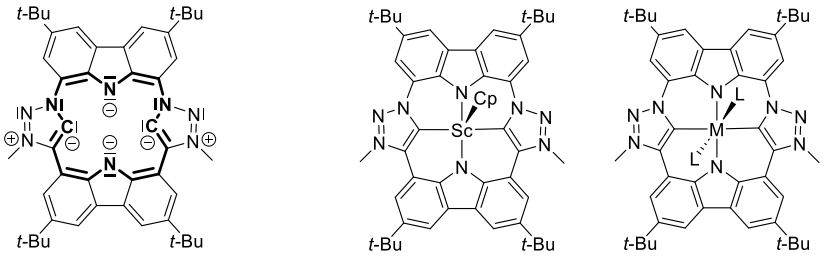
The electronic properties of porphyrins are usually altered by respective substituents at the macrocyclic framework.[1] Besides, the donor atoms can also be modified, either by replacing the pyrrol moieties with suitable heterocycles[2] or, in rare cases, by turning them under the formation of N-confused porphyrins.[2] The latter can be regarded as containing carbene donor atoms.[3]

We have replaced two of the pyrrol moieties with triazolinylidenes, so-called mesoionic carbenes, to enhance the electron donor properties further. The resulting porphyrinoid ligand CTP would formally be an antiaromatic 20 electron π-system, but we have shown that instead, the individual aromatic character of the heterocycles is kept. The geometric parameters of its scandium complexes are surprisingly similar to the respective porphyrin complexes.[4]

To investigate the electronic properties of the CTP ligand further, we have now investigated iron(II)- and iron(III)- as well as silver-CTP complexes.

The stronger electron-donating property of the CTP ligand is revealed by the enhanced reactivity of its complexes towards oxidation as well as the influence on the spin state of Fe(III) complexes.

In addition to the porphyrinoid coordination behaviour of the CTP ligand, we observe in the silver-CTP complexes also the typical coordination mode of carbene-containing macrocycles.



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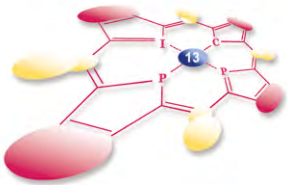

Challenges for the photodynamic inactivation of bacterial biofilms

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Photodynamic inactivation (PDI), also known as antimicrobial photodynamic therapy, is a relevant option for the use of antibiotics in infectious disease treatment. There is an urgent need to develop efficient and safe alternative methods due to the increasing problem of antimicrobial resistance. PDI has proven high efficacy over bacteria, fungi, and viruses, based on the broad action of the reactive oxygen species on lipids, proteins and nucleic acids. Unfortunately, the PDI response highly decreases when the microorganisms are organized in biofilm, a single or multi-species cell community that produces the extracellular polymeric substances (EPS) providing composition support and protection against harsh environments. In the majority of infectious diseases, the microorganisms are in the biofilm form, especially when considering only the chronic infections, in 80% the pathogen is organized in a biofilm [1]. PDI, as the antibiotics, shows a much lower inactivation rate in biofilms, when compared to the response against planktonic cells, mostly due to the lower photosensitizer interaction with the bacterial cells. The biofilm extracellular matrix (ECM) plays an important role in trapping the photosensitizer molecules, impairing their diffusion and availability for cell interaction within the biofilm. In this talk, we will discuss different approaches to improve the PDT inactivation response in bacterial biofilms based on the more efficient delivery of the porphyrin (Gang Zheng's porphysomes) [2] or with the association of mechanical treatment (ultrasonics) and chemical (surfactant, inorganic salts) or biological agents (enzymes) [3, 4].

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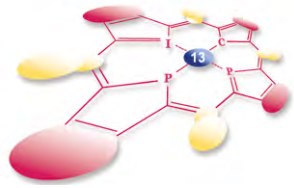

Naphthalocyanine-Based Nanophotosensitizer: Approach to Antimicrobial Photodynamic Therapy for Pneumonia

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Hospital-acquired pneumonia poses a significant threat with reported mortality rates of 20-50%, primarily attributed to antibiotic-resistant pathogens.[1] Antimicrobial Photodynamic Therapy (aPDT) emerges as a promising alternative, demonstrating low resistance potential. However, its application to pneumonia faces challenges, necessitating deep lung activation and overcoming pulmonary surfactant barriers.

This study introduces a new aPDT therapeutic platform to address these challenges. Our objective is to synthesize a naphthalocyanine photosensitizer with optimal near-infrared (NIR) light absorption for deep lung activation. This photosensitizer will then serve as the foundation for developing nanoparticles designed to surmount the pulmonary surfactant barrier, enabling targeted delivery to bacteria. Our collaborative research group has recently developed a NIR light irradiation device for non-invasive deep lung aPDT.[2] Therefore, we designed and synthesized a photosensitizer with an excellent extinction coefficient in the near-infrared region (ε_{807nm} = 295,700), resulting in an absorption capacity nearly 10 times higher than that of conventional photosensitizers. This naphthalocyanine molecule is utilized to create a nanosensitizer platform through nanoemulsification and functionalization.

The anticipated outcome is a transformative aPDT therapy effective against various bacterial strains, including antibiotic-resistant ones. This approach aims to significantly reduce the high mortality rate associated with nosocomial pneumonia, offering a promising avenue for improved treatment outcomes.

Figure 1. UV-vis absorption spectra at different concentrations and extinction coefficients of the naphthalocyanine derivatives synthesized in this study.

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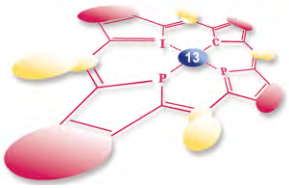

Shape Matters: On-surface Chemistry of Subphthalocyanines

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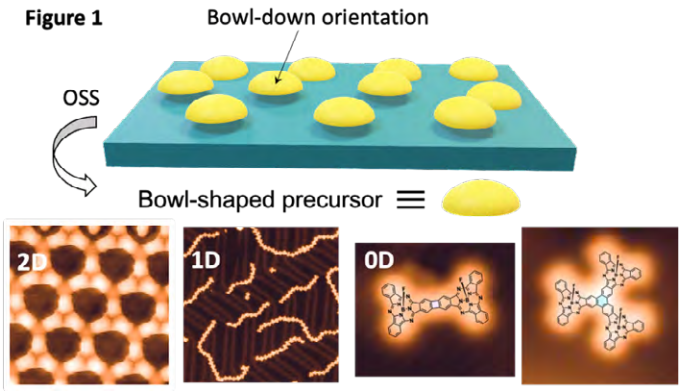
In past decades, on-surface synthesis (OSS) has emerged as a powerful tool to prepare 2D materials from simple building blocks bearing reactive groups (e.g., halogen atoms).[1] If these building blocks present a bowl-shaped – rather than flat – structure, the peripheral (reactive) groups would be oriented toward the surface when a bowl-down configuration is adopted (Figure 1). This orientation is expected to influence the electronic and structural properties of such substituents. Based on this premise, an open question arises: could the bowl shape affect the on-surface behavior of organic molecules, potentially activating bonds that typically exhibit poor reactivity?

We have recently found that SubPcs, well-known contracted porphyrinoids, exhibit the aforementioned bowl-down configuration on Au (111), rendering them ideal molecular models to study the concept of "shape-assisted" on-surface chemistry. In the first part of this talk, the on-surface reactivity of SubPcs peripherally functionalized with groups that, in principle, are expected to be inert toward Ullmann-type C-C coupling (e.g., fluorine atoms), is described. Firstly, it is shown how fluorinated SubPcs can undergo C-F activation at room temperature, leading to the formation of organometallic/supramolecular arrays (Figure 1). Then, the further activation of this polymer to produce remarkably large, organometallic frameworks is disclosed. The stability of these particular 2D materials, as well as their molecular and electronic structure, is detailed.

In the second part of the talk, it is demonstrated that SubPcs serve as excellent starting materials for the "toposelective" preparation of 0D and 1D curved π-systems (Figure 1). Remarkably, the size, shape, or even chemical nature (covalent or metalorganic) of the resulting product depends on the halogen used in the on-surface Ullmann coupling.



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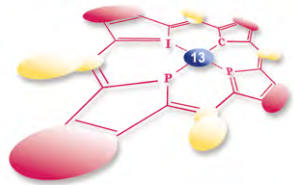

Thirty Years of Carbaporphyrin Chemistry: Recent Advances

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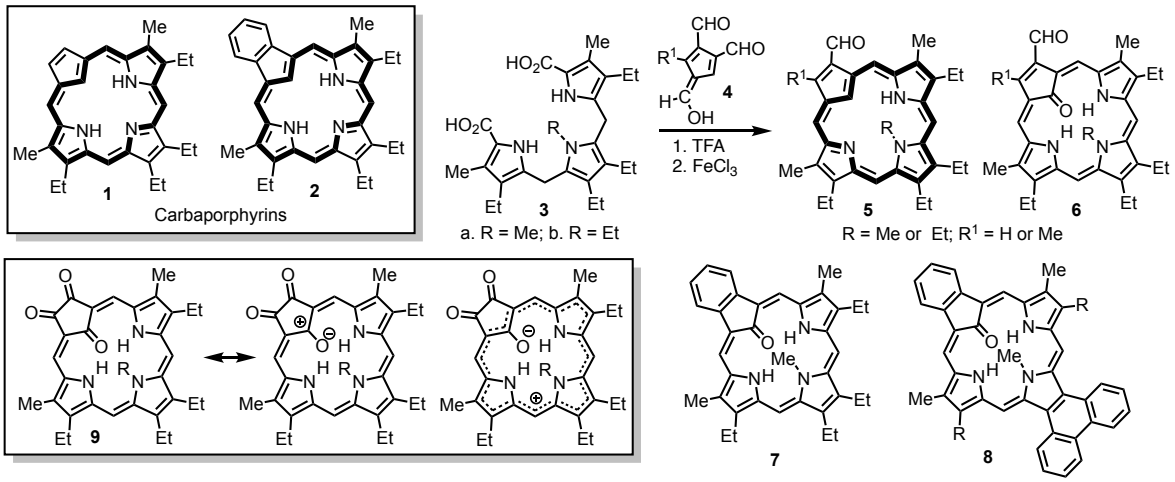
Carbaporphyrins such as **1** and **2**,[1] porphyrin analogues in which a carbon atom replaces nitrogen within the macrocyclic core, have attracted a considerable amount of attention of the last thirty years.[2] Our initial publication in this area on the synthesis of oxybenziporphyrin, the first example of an aromatic porphyrin analogue with a carbocyclic ring in place of the pyrrole unit, appeared in 1995.[3] Subsequently, we investigated the synthesis, reactivity and aromatic character of numerous carbaporphyrin-type systems, including azuliporphyrins,[4a] tropiporphyrins[4b] and carbachlorins.[4c] These systems proved to be versatile organometallic ligands[5a] and provided insights into the nature of aromaticity within porphyrinoid frameworks.[5b] Advances continue in this area, including studies on N-alkyl carbaporphyrins. Condensation of tripyrranes **3** with trialdehydes **4** gave N-alkylcarbaporphyrins **5** together with weakly diatropic oxycarbaporphyrins **6**; related 21-oxyhetero-carbaporphyrins have also been described.[6] A series of related porphyrinoids have been discovered, including oxycarbaporphyrins **7** and **8**, as well as the fully aromatic carbaporphyrin triketone **9**.



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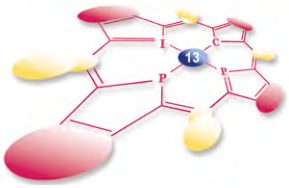

Organic Materials for Energy Conversion: Molecular Approaches Based on Subphthalocyanines and Beyond

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Organic optoelectronics plays a critical role in addressing the global challenge of sustainability. In organic devices, material performances are determined by intrinsic molecular properties and emergent functions arising from supramolecular organization. A fundamental understanding of the structure-assembly-properties interplay is therefore essential to enable advances in the field. At the core of the outlined research is the exploitation of novel molecular architectures and unconventional assembly motifs to unlock new opportunities in energy conversion technologies. On the one hand, tailored molecular design enables targeted functionalities in covalent systems based on curved porphyrinoids.[1] Examples of ground-state charge transfer *vs* exciplex formation in subphthalocyanine-tetracyanobutadiene derivatives and sensitization of singlet fission in pentacene dimers using light-harvesting subphthalocyanine antennas will be presented.[2, 3] On the other hand, non-covalent interactions are exploited to regulate emergent properties in supramolecular assemblies. In this context, mobile long-lived triplets from singlet fission in pentacene-decorated supramolecular polymers and tunable aggregation-induced emission in optical nanocavities will be discussed.[4, 5]

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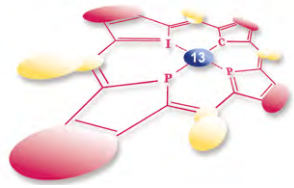

B12-Mediated, Light-Triggered Drug Release from Cell-Conveyed Phototherapeutics

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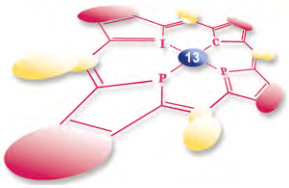
Light-responsive therapeutics offer the promise of targeted therapy, whose benefits include (a) prolonged action at the target site, (b) reduced dosage due to enhanced therapeutic efficiency, (c) reduced systemic concentration as a consequence of direct action on target, (d) reduced adverse effects as a result of selective enhancement, (e) and localized delivery of multiple agents resulting in targeted combination therapy. Although photo-activatable pro-drugs have received considerable attention, these species are dependent upon short wavelengths (<450 nm) for activation. However, maximal tissue penetrance by light occurs within the "optical window of tissue" (650 – 900 nm), well beyond the wavelength range of most photo-cleavable functional groups. We've developed a vitamin B12-based technology that (a) uses light within the optical window to control drug delivery, (b) provides the means to assign distinct wavelengths to the photo-delivery of different drugs, (c) employs circulating lipid bilayer-containing carriers (e.g., RBCs, liposomes) as the drug transporters, and (d) applies to therapeutic agents that range in size from small molecules to proteins. The application of this technology to thromboembolic disorders will be discussed.



Introduction of the keto groups during heme d_1 biosynthesis

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The isobacteriochlorin heme d_1 serves as an essential cofactor in the cytochrome cd_1 nitrite reductase NirS in denitrifying bacteria such as *Pseudomonas aeruginosa* or *Dinoroseobacter shibae* [1]. The heme d_1 macrocycle contains several unusual substituents and functional groups such as the keto groups on pyrrole rings A and B and the acrylate side chain on pyrrole ring D [2]. While most steps of heme d_1 biosynthesis were elucidated within the last decade, the introduction of the keto groups remained unresolved. So far, it has been shown that the Radical SAM enzyme NirJ catalyses the removal of the two propionate side chains on pyrrole rings A and B of the intermediate 12,18-didecarboxy-siroheme [3]. However, neither the leaving group nor the actual reaction product of the NirJ reaction were identified. The introduction of the keto groups was not catalysed by NirJ and it was speculated that an additional enzyme is required for this step.
Here, we report that NirJ cleaves off the propionate side chains producing acrylate as the by-product. Moreover, we provide evidence for the replacement of the propionate side chains with hydrogen resulting in the formation of unsubstituted methylene groups during NirJ catalysis. Using recombinant, purified NirF we could show that this enzyme uses the NirJ reaction product as substrate and introduces the keto groups yielding dihydro-heme d_1 as reaction product. For this reaction, NirF requires the presence of NirC, a small *c*-type cytochrome, as an external electron acceptor.

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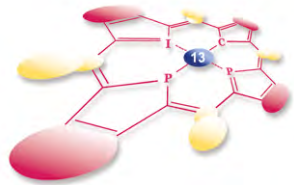

Parallel Chirality Inductions in Möbius Zn(II) Hexaphyrin Transformation Networks

Stéphane Le Gac[a], **Thomas Nédellec**,[a] **Bernard Boitrel**[a]

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Networked chemical transformations[1] are key features of biological systems, in which complex multi-component interactions enable the emergence of sophisticated functions. Being interested in chirality induction phenomena with dynamic Möbius π-systems,[2-3] we have designed a pair of Möbius [28]hexaphyrin ligands in order to investigate mixtures rather than isolated molecules.[4] Thus, an hexaphyrin bearing a chiral amino arm was first optimized and found to bind a ZnOAc moiety, triggering an impressive quasi-quantitative chirality induction over the Möbius π-system. Secondly, this amino-type hexaphyrin was mixed with a second hexaphyrin bearing a chiral carboxylate arm, affording at first ill-defined coordination assemblies in the presence of zinc. In contrast, a social self-sorting behavior occurred upon addition of two exogenous achiral effectors (AcO^- and $BuNH_2$), leading to a well-defined 1:1 mixture of two Möbius complexes featuring a sole Möbius twist configuration (parallel chirality inductions). We next successfully achieved a compartmentalized switching, *i.e.* a single-component transformation from such a complex mixture. The $BuNH_2$ effector was selectively protected with Boc_2O, owing to a lower reactivity of the arm's NH_2 function intramolecularly bound to zinc, and subsequent addition of $BuNH_2$ restored the initial mixture retaining parallel chirality inductions (five cycles). By changing the nature and twist configuration of only one of the two complexes, at initial state or by switching, this approach enables a 'two-channel' tuning of the chiroptical properties of the ensemble. Such multiple dynamic chirality inductions, controlled by selective metal-ligand recognition and chemical reactivity, set down the basis for Möbius-type stereoselective transformation networks with new functions.

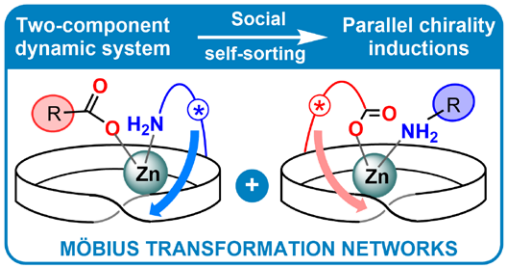

Figure 1. Multiple chirality inductions in mixtures of Möbius rings.

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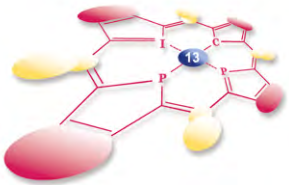

Planar, π-Extended Anti-aromatic Hexapyrin(1,0,1,0,1,0); Synthesis and Properties

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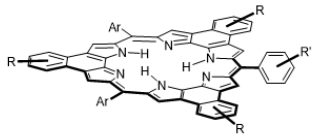
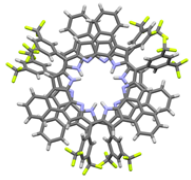
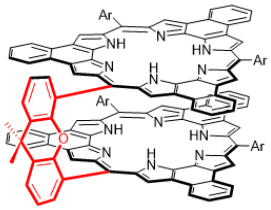
A novel, planar, pi-extended hexaphyrin(1.0.1.0.1.0) and their derivatives, so-called, naphthorosarins have been synthesized and characterized. The study indicates that the naphthorosarins are structurally planar possessing 4nπ (n=6), 24π) conjugated system with stable anti-aromatic character. Annulation of the β,β′-position of non-planar, weakly antiaromatic hexaphyrin(1.0.1.0.1.0) by two-carbon bridge becomes rigid, planar with enhanced anti-aromaticity. The noble synthetic methods of peripherally substituted naphthorosarins are also developed utilizing Susuki and intramolecular oxidative coupling reaction, resulting establishment of the synthetic protocol of new naphthobipyrroles, which are the key building blocks of naphthorosarins. Naphthorosarins exhibit unusual redox chemistry and the spectroscopic studies indicate that the conformationally rigid, planar antiaromatic naphthorosarins display unique redox reactivity in association with the degree of protonation. Naphthorosarins become a stable one-electron reduced species (stable 25π radical cation) upon the addition of HCl, TFA or HBr. The crystal structural analysis indicates that the 25pi-system adopts a severely bent structure with the coordination of two counter anions. This radical cation shows unusual stability both in solution and in solid state with no sign of decomposition. When naphthorosarin is treated with HI, on the other hand, two-electron reduced, 26π-aromatic naphthorosarin is formed. The formation of these 26π-aromatic analogs is ascribed to the proton proton-coupled electron transfer (PCET) mechanism. The mechanistic study indicates that the acid (HI) is quantitatively oxidized to iodine during the reaction. . The time-dependent absorption spectral change indicated that the peripheral substituents affect the redox potentials and their corresponding anti-aromaticity. The rate of one electron reduction is faster when fluoride is introduced on the periphery. Naphthorosarins are aggregated in aqueous THF forming tight dimeric pairs showing charge-transfer behavour. On the other hand, the covalently linked dimer shows slightly diminished anti-aromaticity. The time-dependent absorption spectral change indicated that the peripheral substituents affect the redox potentials and their corresponding anti-aromaticity. The rate of one electron reduction is faster when fluoride is introduced on the periphery.



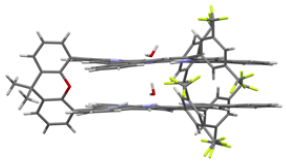
naphthorosarin



Aggregated dimer



Covalently linked dimer



Covalently linked dimer

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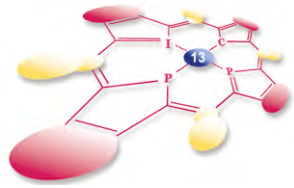

Click Procedure with Porphyrin-, Phthalocyanine- and Subphthalocyanine Star Mesogens – New Donor-Acceptor Columnar Liquid Crytals

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Porphyrins, Phthalocyanines, and Subphthalocyanines are known as robust chromophores, which were transformed to the liquid crystal state of matter by attaching suitable numbers of flexible chains to their periphery. These mesogens could be tailored to show phase transitions (clearing transitions) to the isotropic phase below 200 °C. [1] Our group was interested in increasing the size of these mesogens with conjugated, shape-persistent arms (Figure). Such arms are antenna systems collecting light and at the same time generate free intrinsic space for the uptake of fullerene guests as electron acceptors. We recently discovered that the mixture of empty (**1a**) and fullerene-filled derivatives (**1b**) results in a click mechanism and consequently the formation of highly ordered donor-acceptor columns, which are of high interest as photovoltaic materials.[2, 3] However the size of the so-called star mesogens increased the clearing temperature so much that the correct alignment for this application could not be achieved. Therefore, we search in the families of smaller cores like the porphyrins (**2**) and the polar subphthalo-cyanines (**3**) to lower the clearing temperatures and subsequently to realise the click procedure and the alignment.
The present contribution highlights the synthesis of phthalocyanine **1**, porphyrin **2** and subphthalocyanine **3** star mesogens and the corresponding derivatives, in which fullerenes are attached *via* spacers to the core. Their structure-property relationship is studied for the star mesogens and their mixtures.

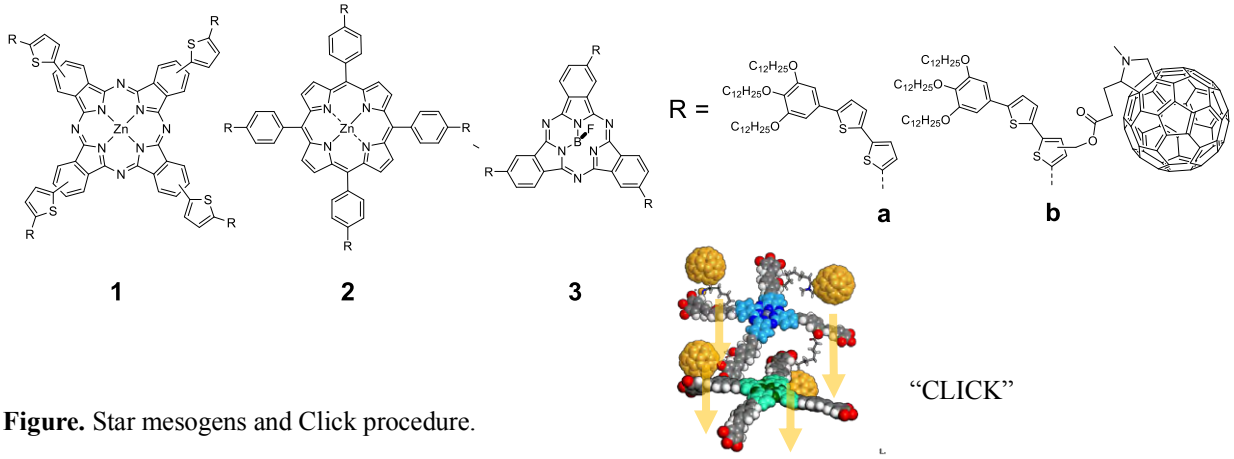

Figure. Star mesogens and Click procedure.

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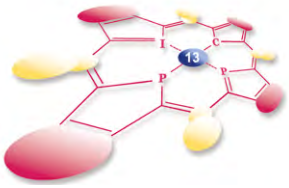

Ag(III)···Ag(III) Argentophilic Interactions in Silver Corroles

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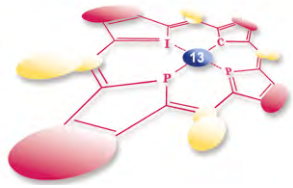
Closed-shell metallophilic interactions are exemplified by d^{10} ions, but this phenomenon also extends to d^8 species. While aurophilic interactions between Au(III) centers are prevalent, analogous interactions between Ag(III) ions are uncommon. Here, we utilize a combination of structural analysis and computational methods to identify argentophilic interactions in silver corroles. These complexes are examined using a variety of analytical techniques, including electrochemistry, X-ray photoelectron spectroscopy, and ^{109}Ag NMR spectroscopy. These corroles are authentic Ag(III) species with an innocent ligand, in contrast to non-innocent copper analogs. The solid-state structure of the *meso*-triaryl silver corrole exhibits an atypical domed conformation, which enables close contact (3.75 Å) between silver centers. To evaluate if this represents an authentic metallophilic interaction or a crystallographic artifact, we synthesized the analogous cofacial or "pacman" corrole. The conformation of the monomer is recapitulated in the silver pacman complex. Significant compression of the xanthene backbone is observed, resulting in a short 3.67 Å distance between metal centers. In the purification of the corresponding Au(III) pacman complex, a novel isomer of [34]octaphyrin(1.1.1.0.1.1.1.0) is also isolated, where the tetrapyrrole units cross over a *meso* position. This contrasts previously reported octaphyrins, where the tetrapyrrole units cross over the bipyrrole linkage. It is likely that the xanthene backbone templates the formation of this unique molecule. The Ag(III) pacman was analyzed using theoretical calculations, including Bader and NBO analyses, which support the presence of a metallophilic interaction between silver ions. Together, the structural and computational results indicate that the pacman corrole is a rare example of a Ag(III)···Ag(III) argentophilic interaction.



Catalytic Nanomaterials Based on a Porphyrin-Containing Artificial Mini-Enzyme

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The ascent of nanotechnology has stimulated the widespread applications of nanomaterials in catalysis, sensing, and biomedicine. Due to their nanoscale dimensions, they display quantum confinement effects, which result in peculiar optical, electronic, and magnetic properties [1]. Among them, metal-based nanoparticles have attracted considerable interest and have been customized with a wide array of biomolecules, endowing them with specific functions. These enzyme-loaded materials represent a promising class of catalysts, filling the gap between homogeneous and heterogeneous systems [2]. In this context, we have developed functional nanomaterials by exploiting a porphyrin-based artificial peroxidase named FeMC6*a [3,4]. Its reduced size (~3.5 kDa) compared to natural horseradish peroxidase (HRP, ~44 kDa), coupled to the exceedingly high catalytic properties, makes it an excellent candidate for conjugation to nanosurfaces [5,6]. In particular, our most recent studies have been focused on the immobilization of FeMC6*a onto differently shaped gold-based nanomaterials, investigating the effect of shape anisotropy on the catalytic properties of the nanoconjugate (Figure 1).

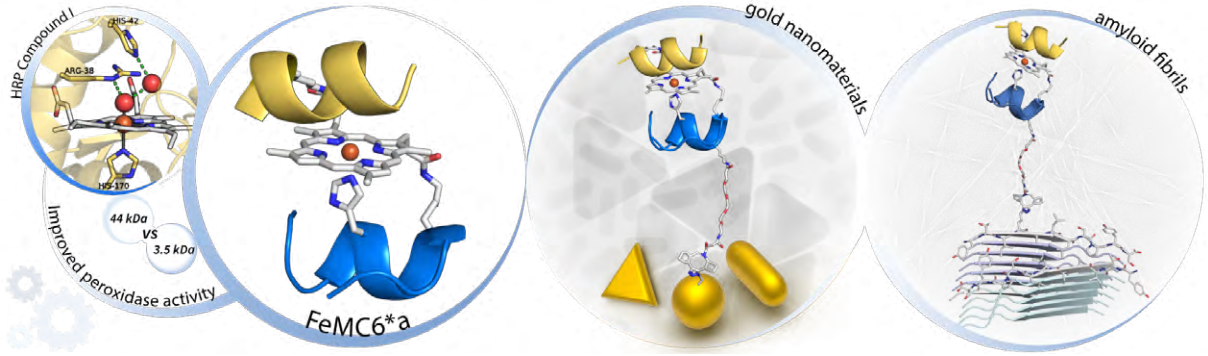

Figure 1: Conjugation of the miniaturized peroxidase FeMC6*a to different nanomaterials.

Moreover, in the effort to produce novel, sustainable, and cost-effective functional nanomaterials, we are also developing entirely peptide-based nanostructures. In particular, we have selected and functionalized amyloid sequences, achieving nanofibrils conjugated with FeMC6*a. The validity of this approach has been demonstrated by structural and functional studies, offering a wealth of opportunities for catalytic and sensing applications.

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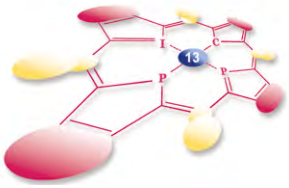

Using modified lignin nanoparticles as a versatile and environmentally friendly formulation for photosensitizer for photodynamic antimicrobial chemotherapy as photodegradation of antibiotics.

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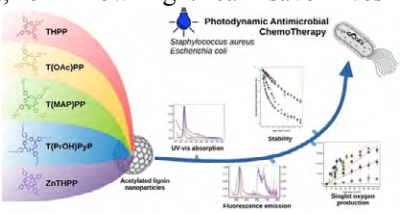
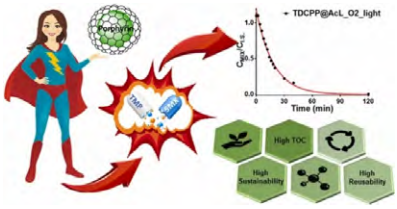
Antimicrobial resistance (AMR) is threatening to overshadow last century's medical advances. Previously eradicated infectious diseases are now resurgent as multi-drug resistant strains. Researchers are now willing to investigate novel antimicrobial treatments that may be able to deal with AMR, such as photodynamic antimicrobial chemotherapy (PACT). PACT relies on the generation of toxic reactive oxygen species (ROS) in the presence of light and a photosensitizer (PS) molecule. PACT has a non-target specific mechanism of action, based on the generation of ROS, decreasing the risk of bacteria developing resistance. In addition, antibiotics overuse and their potentially detrimental effects in the environment are also believed to accelerate resistance spread. Interestingly, PACT and antibiotic photodegradation can rely on the same photoinduced oxidation process. However, for both applications, PS usually are large molecules, prone to aggregation, diminishing their efficiency. The development of materials, and especially obtained from natural sources, as delivery systems for PS is of uppermost importance. In this framework, the results obtained with the POLYTHEA project, or "How light can save lives" (www.polythea.eu) intend to address the global problem of AMR, following both an upstream approach, preventing antibiotic misuse/overuse by developing new therapeutic solutions, and a downstream strategy, through the design of alternative antibiotics degradation process. Porphyrin-loaded nanoparticles were tested against two bacteria models: a Gram-negative (*Escherichia coli*) and a Gram-positive (Staphylococcus aureus) [1]. Furthermore, they were as well used in the aqueous photocatalyzed degradation of trimethoprim (TMP) and sulfamethoxazole (SMX) [2].





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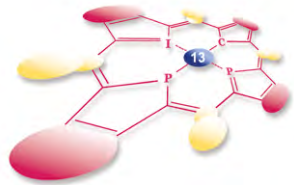

Modulating Porphyrin Spectroscopic Properties through Integration with 2D Materials or Ferromagnets

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Growing demand for new *functional materials* could contribute to: *i*) solving the problem of energy generation and storage *ii*) resolving key environment-related issues *iii*) developing faster and low-energy consuming optoelectronic devices and sensors and *iv*) widening the scope of biomedical diagnostics resulting in the development of various multi-component hybrid materials. The discovery of graphene and other 2D materials as well as the development in recent years, of so-called molecular (organic) spintronics has opened new possibilities to construct porphyrin-based materials. Integration of 2D-layered materials or ferromagnets with porphyrins is a promising approach, allowing targeted fabrication of hybrid functional materials.

Our primary focus was given to the fundamental understanding of the *structure–property relationship* in newly constructed hybrid materials composed of 2D materials (graphene oxide, reduced graphene oxide, MXene) or thin ferromagnetic films and porphyrins.[1-4] The interaction of porphyrin with diverse supports/substrates has been studied in various aspects, starting from the detailed spectroscopic characterization by steady-state and time-resolved absorption and emission techniques. By studying different combinations of 2D materials and porphyrins (free porphyrins vs metalloporphyrins) and by varying types of connection (covalent vs non-covalent) we could better understand the link between the structure of hybrid materials and their properties (photoinduced electron transfer, singlet oxygen generation) which are important in terms of possible application in solar energy conversion or photodynamic therapy.

Our primary objective in working with ferromagnets was to fabricate inorganic/organic hybrids by self-assembly of chiral porphyrins onto the thin Co/Ni films with the ultimate goal of probing the spin-polarized (spin-selective) photoinduced electron transfer and its influence on the faith of the photoexcited chromophores and dynamic magnetic properties of the underlying ferromagnet.

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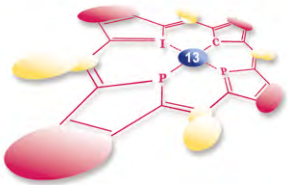

Using Axial and Side-Pocket Ligation Sites to Impact the NIR Optical Properties of Metallophthalocyanines

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A large majority of PcM complexes exhibit Q-band absorbances between 625-750 nm and are generally blue to green in colour.[1] Our group has been targeting non-traditional PcM complexes, especially those containing early-transition metals and those that have oxidized or reduced Pc-rings incorporated therein.[2] By alteration of the metal centre and ring-oxidation state, as well as the more traditional modifications of ring-substituents, control over the position of the Q-band can be achieved.[1]

We have recently illustrated two other very accessible synthetic methods by which the absorption and emission properties can be readily tuned, which will be highlighted in this presentation. In one example, a series of PcMn(III) complexes with different ring-substituents and axial ligands are red in colour and show Q-band absorbances out to 948 nm,[3a] while using unsubstituted Pc-rings enables substantial visible colour shifts;[3b] our recent advances using a range of axial ligands and related metal centres will be discussed. In another example, the addition of simple acids to PcZn(II) species with weak donor "side-pockets" shows protonation (and accompanying axial ligand addition), strongly impacting both the absorption and emission of the material (see Figure). This preferential formation of axially substituted $[Pc'ZnX]^-$ "ate" complexes and their sequestration of both protons and lithium cations, opens a new series of materials with unique structural and electronic properties and their ability to both absorb and emit in the NIR region makes them desirable for numerous applications.[3c]

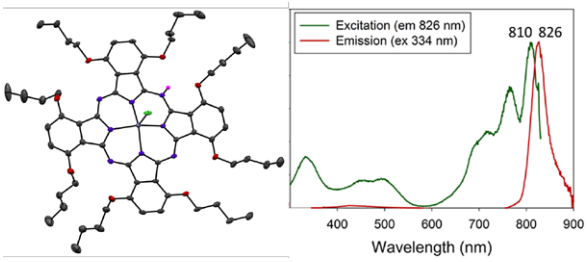

Figure (Left): Solid-state structure of $(OBu)_8PcZn$ side-pocket protonated with HCl. (Right): UV-vis-NIR excitation and emission spectra of $(OBu)_8PcZn$•HCl in $CHCl_3$.

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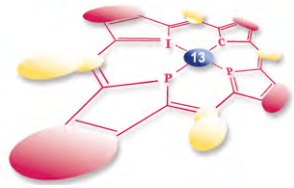

Recent advances of nitrosyl heme analogues

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Nitric oxide (NO) is a critical messenger with important roles in both normal cellular physiology and pathology.[1-3] The interaction of NO with heme proteins is vital to a number of biological processes including smooth muscle relaxation, vasodilation, blood clotting, nerve-signal transduction, and immune regulation.[4, 5] Iron porphyrins and corroles have been thoroughly studied as nitrosyl model complexes since the first structural characterization of [Fe(TPP)(NO)] (TPP = tetraphenylporphyrin dianion) which was reported by Scheidt et al. in 1975.[6] A hypothetical dinitrosyl heme intermediate has been propsoed in the reactions of heme proteins with NO. While evidence of the key dinitrosyl intermediate is lacking in heme proteins, reports on synthetic analogues have been available since the 1970s. For example, dinitrosyl Ru^{II} and Fe^{II} porphyrinates with two NO stretch frequencies (1786 and 1838; 1870 and 1690 cm^{-1}, respectively) have been reported by Tsutsui[7] and Wayland, respectively, and in the latter case, the two bands were assigned as a linear Fe^{II}–NO^{+} unit and a bent Fe^{II}–NO^{-} fragment.[8] Recently, we have reported the first isolation of a dinitrosyl metalloporphyrin complex, the six-coordinate, low-spin $\{Mn(NO)_2\}^7$ species $[Mn(TPP)(NO)_2]$.[9] The complex shows distinct features, such as an elongated axial bond (1.877(9) vs. 1.641(5) Å), a higher NO stretching bond position (1760 vs. 1735 cm^{-1}) and an isotropic resonance at $g = 2.0$, in sharp contrast to those of five-coordinate mononitrosyl analogues. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) and EPR studies provided deep insight into the reaction processes, demonstrating different responses of porphyrinates to NO.

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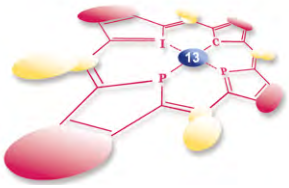

Porphyrin and Phthalocyanine Framework Materials for Cancer Therapy

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In photodynamic therapy (PDT), photosensitizers absorb photons and transfer energy to nearby oxygen and other molecules to generate reactive oxygen species (ROS). The efficacy of PDT depends on the aqueous solubility and ROS generation efficiency of photosensitizers. The most well-known photosensitizers based on porphyrins and phthalocyanines tend to have poor aqueous solubility and severely aggregate under physiological conditions. We have developed a series of framework materials (metal-organic frameworks and covalent organic frameworks) based on porphyrins and phthalocyanines and examined their applications as novel nanophotosensitizers in the PDT of cancer.[1-5] We have also explored the applications of these framework materials in sonodynamic therapy and radiotherapy.[6-8] I will also discuss our efforts in the clinical translation of these novel framework materials in the treatment of cancer patients.

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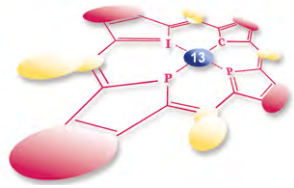

Synthesis of native bacteriochlorophylls and analogues

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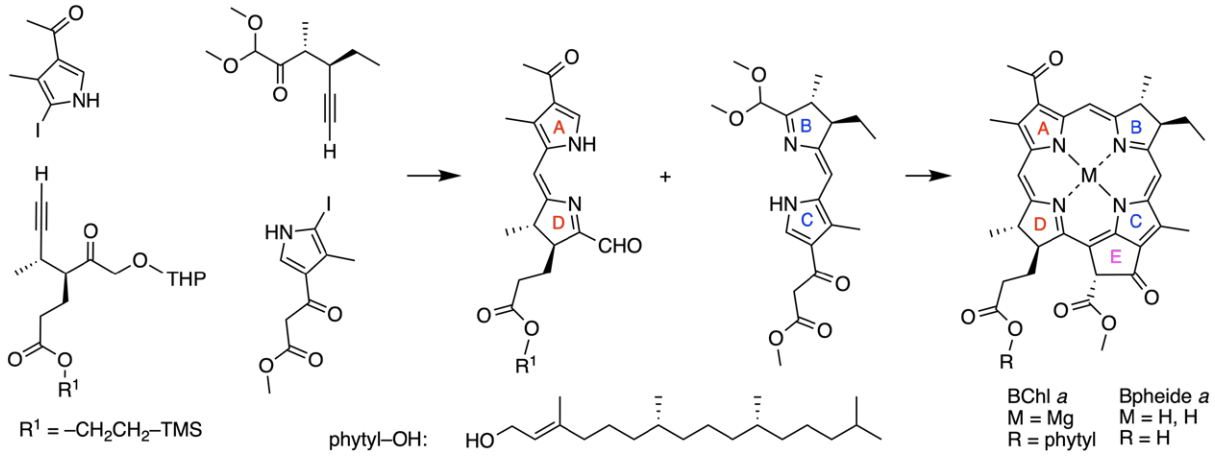
The advent of synthetic routes to the native photosynthetic pigments (e.g., chlorophyll *a*, bacteriochlorophyll *a*) is expected to open a portal for addressing diverse questions in the plant sciences. An approach to bacteriochlorophylls relies on joining AD and BC halves via (i) Knoevenagel condensation followed by (ii) Nazarov cyclization, S_EAr, and MeOH elimination, which together form ring E and the aromatic macrocycle. The *trans*-dialkyl substituents of each pyrroline ring (B, D) are introduced via chiral hexynones, which are prepared in a stereoselective manner. To date, we have prepared the individual A–D constituents (≥10 mmol each) as well as synthetic bacteriopheophorbide *a* (Bpheide *a*) The results validate the ability to carry stereochemically defined substituents over the entire course of the synthesis [1–5]. Extension to analogues of bacteriopheophorbide *a* is under investigation. This research is supported by the NSF (CHE-2054497).



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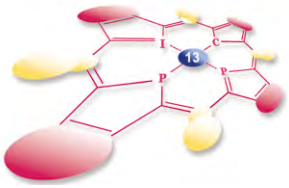

Interplay of Redox Properties, Host-Guest Chemistry, and Reactivity in Metalloporphyrin Nanocages

Mark C. Lipke[a], Kaitlyn G. Dutton[a], P. Thomas Blackburn[a], Rupak Saha[a] and Taro J. Jones[a]

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Porphyrin-based nanoporous materials, ranging from discrete nanocages to extended frameworks, are of considerable interest for catalytic applications, such as the reduction of CO_2 to value-added products. While many examples of catalytic activity have been established in porphyrin-based porous structures, far fewer studies have examined fundamental redox properties and reactivity of metal sites embedded in the porphyrin units of these nanomaterials, leaving a dearth of knowledge that would be needed to develop a mechanistic understanding of their catalytic behavior. To address this limitation, redox properties, host-guest chemistry, and reactivity were examined for several nanocages equipped with porphyrin walls that support a wide range of metals, [1] including Mn, Fe, Co, Ni, Cu, and Zn. Inner- and outer-sphere redox reactions were used to access Co^{III}, Co^{II}, and Co^{I} states of the cages, [2] and the manganese derivatives exhibit at least five redox states. Notably, the redox processes of the Mn cages span from reductions of the porphyrins all the way to proton-coupled oxidations that generate Mn^{IV}=O species. Host-guest chemistry of the cages will also be discussed, especially the binding of sulfonate guests.[3, 4] Equipping these guests with benzoic acid functionality allowed the study of acid-base chemistry inside the Co and Zn versions of the cages, including measurement of how the pK_a of the guest is altered by redox processes at the Co centers. The possible relevance of these results to understanding nanoconfined (electro)catalytic processes will be discussed.

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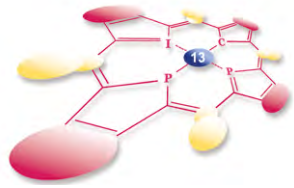

Porphycenes as Useful Models for Studying Intramolecular Hydrogen Transfer

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Independently from numerous potential applications typical of photoluminescent materials, porphycene became a compound readily used in basic research. Almost forty years after its first synthesis, porphycene remains an excellent model for studying the mechanism of intramolecular double hydrogen transfer.[1] The geometry of two hydrogen bonds present in this molecule, well-defined and insensitive to the environment, can be easily modified by an appropriate pattern of substitution. Observation of the behavior of *meso*-substituted porphycenes leads to very interesting conclusions, especially when the substitution pattern lifts the degeneration of pairs of tautomers, which affects the absorption and emission spectra.[2] Easy preparation of *meso*-fluorosubstituted porphycenes[3] combined with their diverse photophysical properties prompted us to prepare a series of novel, asymmetrically substituted porphycenes, for which we have determined their tautomeric, spectral, and photophysical properties. As demonstrated by the comparison of isomers of differently functionalized porphycenes, these characteristics strongly depend on the position of substitution.

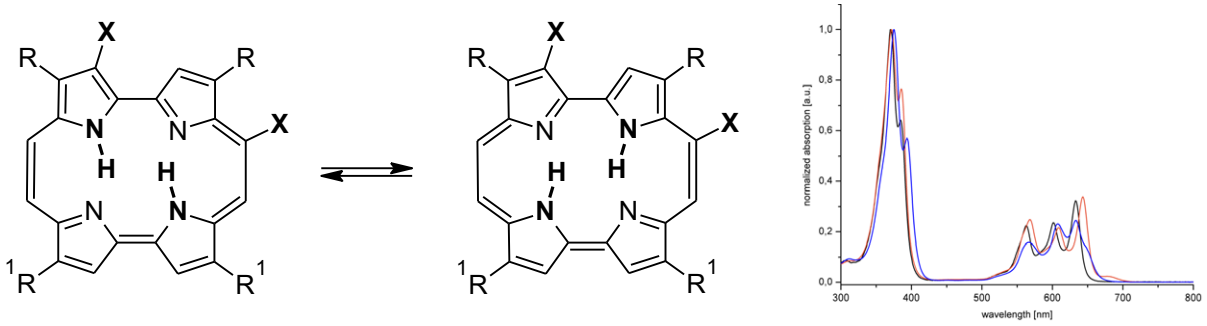

Figure: Two possible tautomers of non-symmetrical porphycenes and the manifestation of their presence on UV-Vis spectra of 9-chloro-2,7,12,17-tetra-*tert*-butylporphycene (blue) in comparison with 2,7,12,17-tetra-*tert*-butylporphycene (black) and 3-chloro-2,7,12,17-tetra-*tert*-butylporphycene (red).

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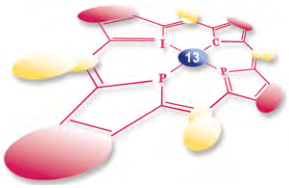

Protein-derived cofactor: It takes two to tango

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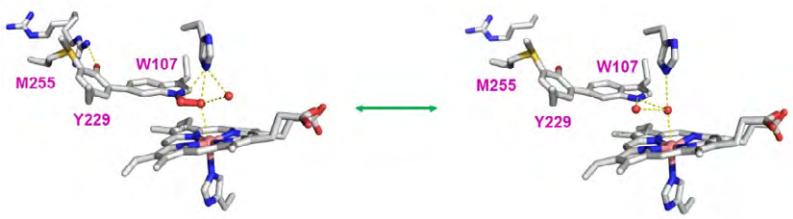
Within metalloenzymes, protein-derived cofactors formed by unidirectional covalent side-chain crosslinks orchestrate unique functionalities impacting diverse biological processes. The interplay between the heme and a protein-derived cofactor takes center stage in *Mycobacterium tuberculosis* (Mtb) catalase-peroxidase KatG, where a methionine$^+$-tyrosine-tryptophan (M^+YW) cofactor crosslink empowers the enzyme's catalase prowess. The catalase activity in KatG is a defense mechanism to counteract hydrogen peroxide generated by the infected host immune system. Thus, its catalase functionality, equipped with the unique M^+YW cofactor, aids the pathogen in evading peroxide-induced host defenses. Our research takes KatG's performance to a new level by revealing a previously unreported partner in this dance: the indole-*N*-linked hydroperoxyl adduct, M^+YW-OOH, in the as-isolated native protein both in solution and crystalline state. This groundbreaking discovery marks the first line of strong evidence for a stable *N*-linked hydroperoxyl adduct in solution in cell-synthesized Mtb protein, highlighting a remarkable twist in M^+YW's functionality. It is worth noting that an *N*-linked hydroperoxyl species is intrinsically unstable, and M^+YW-OOH in KatG has not been convincingly identified before as a stable species in solution. Within KatG's distal heme pocket, intricate non-covalent interactions stabilize M^+YW-OOH, a feat typically elusive in other systems. Importantly, we found that M^+YW-OOH is no mere bystander. It embodies a dormant yet primed catalase state, poised to leap into action upon peroxide oxidation or temperature shifts. We revealed the intricate tango between M^+YW and M^+YW-OOH in isolated proteins (see figure below),



and our finding uncovered their interconversion conditions. This novel observation unveils M^+YW-OOH as an alternative, naturally occurring state of Mtb KatG, offering an unexpected layer of catalase activity regulation. Unveiling this dynamic partnership between M^+YW and its *N*-linked hydroperoxyl adduct M^+YW-OOH re-programs KatG's heme-mediated oxidation, prioritizing peroxidase activity for energy outside the body. This "catalase on-demand valve" strategy, driven by a naturally occurring adduct, allows Mtb to play against the host's peroxide defense by preserving rapid catalase resurgence upon host entry. Our discovery of this heme-mediated, reversible catalase modulator illuminates this elegant survival strategy and opens exciting avenues for anti-tuberculosis therapies. By targeting the dynamic interplay between M^+YW and its hydroperoxyl partner, we may unlock novel ways to thwart Mtb's early colonization, potentially leading to new drugs that cripple its ability to establish infection.

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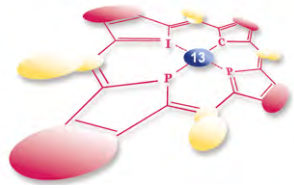

Resonance Raman Studies of Heme Pocket Residues in Globin-Coupled Sensors: Impact of Mutations on Structure and Diguanylate Cyclase Activity

Yilin Liu[a], Emily E. Weinert[b], Nushrat J, Hoque[b], Shannon Rivera[b], Dayna C. Patterson[b]

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Globin-coupled sensor (GCS) proteins are heme-containing proteins proposed to serve as *in vivo* oxygen sensors that are widely distributed in prokaryotes. Some GCSs may contain diguanylate cyclase domains, which catalyze the production of c-di-GMP, a bacterial second messenger that regulates biofilm formation.[1-3] In this talk, we discuss the structural basis for functional effects observed upon introducing key active site mutations of the globin-coupled sensors from *Pectobacterium carotovorum* subsp. *carotovorum* (*Pcc*GCS), which is considered to be necessary for modulating O_2 binding and signaling events. The studies on ligand affinity and enzyme activity for the PccGCS S82A and Y57F mutation showed an increase in O_2 dissociation rates, with corresponding Raman studies verifying the appearance of the non-hydrogen bonded Fe-O-O fragment, suggesting the roles of these residues in stabilizing bound O_2.[4] The heme edge residues W86 and V122 residues, which do not directly interact with the bound ligand in crystal structures of sensor globins but are within Van der Waals contact with the heme, resulted in dissociation kinetics similar to *Pcc*GCS WT. Satisfyingly, both W86H and V122Y mutants produced Fe-O-O fragment conformations that were distinct from the wild-type, indicating their impact in modulating the heme conformation. Moreover, the Fe-CO and C-O stretching frequencies in the globin-coupled sensor domain of PccGCS were probed using resonance Raman spectroscopy. The observed frequency changes in these heme pocket mutants highlighted the important roles of these key residues in the H-bonding network involved in ligand binding. In general, these mutations alter the heme electrostatic environment, vinyl group conformations, and spin state population, and these protein conformation changes resulted in altered signaling transduction and enzyme kinetics. This knowledge is key for developing methods to control GCS signaling *in vivo* and may result in new strategies to alter bacterial phenotypes involved in pathogenesis, such as biofilm formation.

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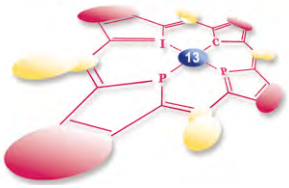

Enhancing the Tumor Specificity and Modulating the Oxygen Content for Advanced Photodynamic Therapy

Pui-Chi Lo[a]*, Lin He[a], Feijie Xu[a], Leo K. B. Tam[b], Junlong Xiong[b], Evelyn Y. Xue[b], and Dennis K. P. Ng[b]

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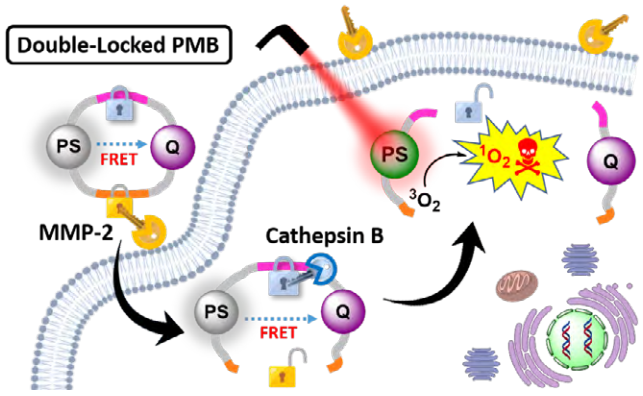
Photodynamic therapy (PDT) utilizes reactive oxygen species (ROS) for elimination of malignant cells and tissues. These highly reactive cytotoxic species can be generated through the excitation of photosensitizers by light, followed by interactions with the endogenous oxygen. This modality is now a clinically approved procedure for the treatment of a variety of localized and superficial cancers [1]. However, there are still some hurdles to be addressed to promote its clinical translation. The effectiveness of PDT is largely contingent on two factors, namely the tumor specificity of the photosensitizers and the oxygen concentration in the tumor microenvironment. If these two conditions are not optimized, the therapeutic outcome of PDT could be compromised. In this presentation, we will highlight our recent endeavours to address these limitations of PDT, including the construction of double-locked photodynamic molecular beacons [2], utilization of a bioorthogonal strategy to actualize targeted delivery and site-specific activation of photosensitizers [3], and development of oxygen-replenishing and oxygen-economized photosensitizing systems [4].

(a)



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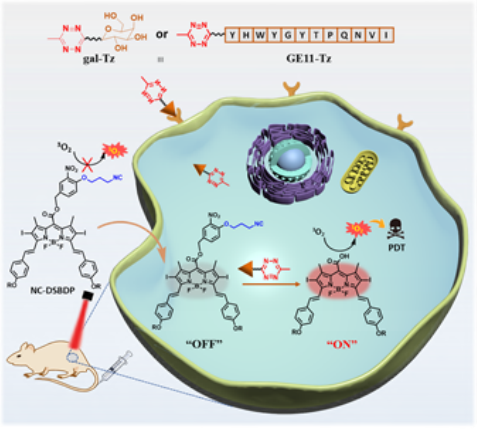

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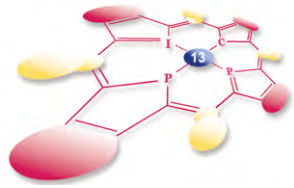

Altering the Reactivity of Mimochrome Mini-Enzymes

Linda Leone[a], Maria De Fenza[a], Marco Chino[a], Alessandra Esposito, Serena Damian[a], Edelberto O. Niola[a], Ornella Maglio[a,b], Flavia Nastri[a], Angela Lombardi[a]

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Recent advances in the field of protein design and engineering have significantly expanded the chemist's toolbox, providing a collection of artificial metallo-enzymes, tailored for specific applications [1].
In this context, we have developed a class of small (~3 kDa) heme-enzymes, named Mimochromes (MCs). The prototype was patterned after the F-helix of the hemoglobin β-chain, through a miniaturization design strategy (Figure 1). MCs consist of a simple scaffold, made up of two short helical peptides, covalently linked to the deuteroporphyrin, in a helix-heme-helix structure. Either one or both peptide chains contain a His residue acting as an axial ligand to the metal ion inserted into the porphyrin ring [1]. Inspired by the peroxidase active site, MC6*a has been identified as the lead compound, for its excellent catalytic performance and promiscuity. It can host and modulate the reactivity of different metal ions, in the frame of oxidation and energy-related catalysis. In particular, FeMC6*a behaves as a highly efficient artificial peroxidase, overcoming the catalytic efficiency of its natural counterparts in the oxidation of different substrates [2, 3]. Swapping iron with manganese or cobalt enables MC6*a to promote oxygen transfer reactions [4] and proton reduction from neutral water [5, 6]. Finally, the zinc derivative has been shown to function as a photosynthesizer in an artificial electron transfer chain [7].

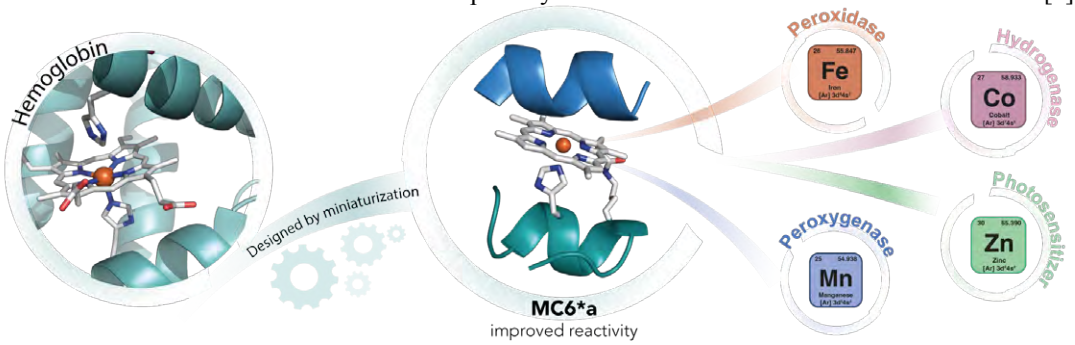

Figure 1: Design by miniaturization of MC6*a and metal-dependent reactivity.

The stable scaffold of MC6*a tolerates amino acid substitution well and allows exploring the effect of the axial ligand on the metal cofactor properties, when switching from a His to a thiolate ligand, as in Cytochome P450.
Altogether, our studies demonstrate that simple, properly designed scaffolds are able to tune and control the reactivity of the metallo-porphyrin cofactor, providing active and robust bioinspired catalysts.

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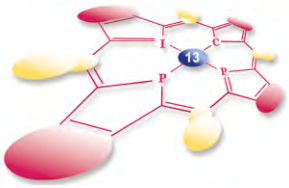

Lactoperoxidase Catalytically Oxidizes Hydrogen Sulfide *via* the Intermediate Formation of Sulfheme Derivatives

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The chemistry of hydrogen sulfide (H_2S) has as targets physiologically important hemeproteins, such as myoglobin (Mb), hemoglobin (Hb), lactoperoxidase (LPO), horse radish peroxidase (HRP), and other hemeproteins system. However, despite extensive efforts, today, there is a need to further comprehend the species involved in the reaction between hemeproteins and molecular dioxygen (O_2) or hydrogen peroxide (H_2O_2) in the presence of H_2S. Our results show, contrary to Mb, Hb, or HbI from the clam *Lucina pectinata,* that under strictly anaerobic conditions, the addition of H_2S to native LPO and HRP does not form the heme-H_2S complex. However, data indicate that LPO in aerobic conditions (O_2 or H_2O_2) and H_2S leads to the sulfheme LPO (sulfLPO) derivatives with characteristic bands at 638 nm and 727 nm, assigned to the ferrous and ferric states, respectively. Interestingly, in the presence of H_2S, throughout the reactions of LPO with H_2O_2, a continuous turnover of the formation of ferrous and ferric sulfLPO followed by a recovery of native LPO was observed, indicating LPO-catalyzed oxidation of hydrogen sulfide by the peroxide. This catalytic oxidation of H_2S is inconsistent with sulfheme decomposition to regenerate hydrogen sulfide. In other words, H_2S trafficking via sulfLPO was not observed. Pilot product analysis suggests that the turnover process generates oxidized sulfur species, most likely sulfate (SO_4^{2-}) and inorganic polysulfides (HS_x^- x = 2-9), as products. Under the experimental time scales, this sulfheme turnover is not observed for Hb, Mb, or HRP. The data implies that LPO, with its heme peripheral substituents and the His-Arg couple in its pocket, allows sulfheme derivatives can be formed and rapidly converted back to the active native form of the enzyme. Also, sulfheme formation was observed to be slower in the reaction between oxyLPO and H_2S than in the LPO-catalyzed hydrogen sulfide oxidation by H_2O_2. We speculate that this might be due to the intermediate formation of compound III in the reaction of oxyLPO with hydrogen sulfide while generating the compound 0 state, which is a proposed central intermediate in the formation of sulfheme derivatives [3].

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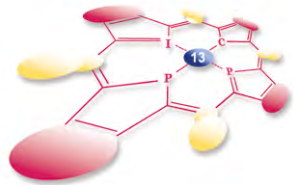
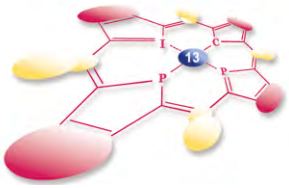


Translational efforts with Cobalt-porphyrin-phospholipid as a vaccine excipient

Jonathan F Lovell[a]

State University of New York at Buffalo

The metal chelated pyropheophorbide-a conjugate cobalt porphyrin phospholipid (CoPoP) can integrate into liposomes, burying the metal within the hydrophobic bilayer. This enables recombinant proteins that are modified with polyhistidine tags to coordinate with the cobalt, leading to biostable surface display of proteins on liposome surfaces. This approach enhances the immunogeniticy of recombinant protein antigens, leading to rapid prototyping of nanoparticle vaccines candidates. In addition, lipid-phase vaccine adjuvants can be incorporated for co-delivery of antigen and adjuvant. In collaboration with infectious disease researchers and industry partners, CoPoP technology has been used to test vaccine candidates for numerous indications including HIV, malaria, SARS-CoV-2, influenza virus and others including cancer. Recently, a SARS-CoV-2 RBD protein vaccine was advanced through phase 3 trials, meeting the primary endpoint. These recent data will be discussed.



Biosynthetic modeling of heme-copper oxidases

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Heme-copper oxidases (HCO) are terminal oxidases that catalyze the reduction of O_2 to H_2O and convert the energy to a proton gradient that drives the synthesis of ATP. Even though the 3D crystal structures of HCOs have been available for some time and much progress has been made in studying the enzyme, there are remaining questions. To answer some of these questions, we have made biosynthetic models of HCO using myoglobin that mimic HCO both structurally and functionally, including a catalytic rate of O_2 reduction similar to that of native HCO. Using the model, we have shown that replacing Tyr next to the His ligand with Trp can also promote the oxygen reduction reaction (ORR), albeit with lower activity [1]. An X-ray crystal structure of the Trp variant shows a hydrogen-bonding network involving two water molecules that are organized by Trp, similar to that in the Tyr variant, which is absent in the crystal structure with the native Phe residue. Additional electron paramagnetic resonance measurements are consistent with the formation of a Trp radical species upon reacting with H_2O_2. We attribute the lower activity of the Trp variant to Trp's higher reduction potential relative to Tyr. Together, these findings demonstrate, for the first time, that Trp can indeed promote the ORR and provide a structural basis for the observation of varying activities. The results support a redox role for the conserved Trp in *bd* oxidase while suggesting that HCOs use Tyr instead of Trp to achieve higher reactivity.

While the His-Tyr crosslink in the HCO active site is known to play an important role in HCO activity, how such a crosslink is formed and how much the crosslink contributes to the activity remain unknown, because HCO is always isolated from the crosslink. Since our biosynthetic models can be isolated without the His-Tyr, it provides an ideal system to investigate the mechanism of the crosslink and understand its contributions to the HCO activity. We have obtained evidence of crosslink and showed that the crosslinked HCO models have higher activity than those without the crosslink.

Together, these two examples demonstrate the power of using biosynthetic models to better understand native enzymes by answering questions that are difficult to do by studying native enzymes alone.

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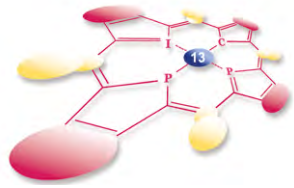

Bio-inspired Design of Porous Porphyrinic Framework for Heterogeneous Catalysis

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Over the past two decades, the rapid growth of metal-organic framework (MOF) that features tunable, designable, and functionalizable nanospace has provided plenty of opportunities for heterogeneous catalysis. Inspired by nature, various design approaches will be discussed for the systematic development of porphyrin-based MOF as a new and sustainable platform for heterogeneous catalysis particularly selective catalysis.

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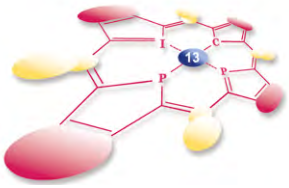

Water soluble phthalocyanines in combination with short drug-to-light interval: an effective tumour eradication

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Photodynamic therapy (PDT) in its "classical form" utilizes irradiation after the photosensitizer (PS) reaches its maximum concentration in tumour tissue. On the other hand, in vascular targeted PDT (VTP), PS is activated while still in the lumen of the vessels or taken up by the endothelial cells. Thanks to the relatively short lifetime of singlet oxygen, the direct damage is limited to endothelium and vessel wall and leads to the formation of thrombi and/or vascular collapse [1]. Currently, VTP is employed in clinical practice for the treatment of age-related macular degeneration (verteporfin; although anti-VEGF treatment is gaining more attention as well as combinational therapy) [2] and localized prostate cancer (padeliporfin) [3]. While phthalocyanines possess suitable properties for PDT (e.g., strong absorption in "phototherapeutic window" and effective production of singlet oxygen), the only phthalocyanine-based PS in clinical use is sulfonated aluminium phthalocyanine, and only in Russia. The main disadvantage of phthalocyanine derivatives is their tendency to aggregate in a water-based environment, which is associated with mutilated photodynamic activity – this can be effectively avoided by modification with suitable axial or peripheral moieties. We have developed several water-soluble (aza)phthalocyanines suitable for PDT and subsequently selected promising charged candidate compounds for VTP–cationic/anionic and hydrophilic/amphiphilic PSs. *In vitro* results on 2D and 3D (multicellular tumour spheroid) models confirmed high photodynamic activity against malignant and endothelial cell lines even with short drug-to-light intervals (DLI). It is worth mentioning that experiments on HUVECs shown that treatment with short DLI (0 h) induces oxidative stress (HMOX) and inflammation (PTGS2) together with the activation of ENG (antiangiogenic effect) and KLF6 (tumour suppressor) gene. *In vivo* experiments on a mouse tumour-bearing model (*s.c.* colorectal carcinoma) showed promising results with complete tumour eradication (100 J/cm^2; dose down to 30 nmol/kg) with DLI = 0 h. Application of high doses of PSs (1 μmol/kg; without irradiation) did not induce any adverse effects (no changes in weight, behaviour, and plasmatic biochemical parameters of organ damage; histological examination did not show any changes in organ morphology), including the absence of skin phototoxicity (mice were kept in ambient light the whole time).

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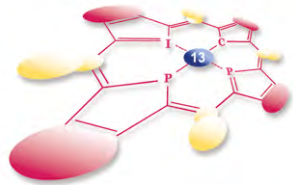

The photodynamic antimicrobial and anticancer activity properties of structurally analogous porphyrin, corrole, chlorin and N-confused porphyrin complexes

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Over the last five years, considerable progress has been made with a rational structural modification approach [1,2] guided by an application of Michl's perimeter model to prepare porphyrin analogues with significantly red-shifted and intensified Q bands that are suitable for use as photosensitizer dyes in photodynamic therapy and/or photodynamic antimicrobial chemotherapy [2-13]. When corrole, chlorin and N-confused porphyrins are formed by introducing a pyrrole-pyrrole bond, a reduced peripheral pyrrole bond and a confused pyrrole nitrogen atom, respectively, there is a significant red shift of the lowest energy Q band into the therapeutic window (620−850 nm) relative to the parent metal porphyrin. The introduction of thienyl *meso*-substituents further enhances the red shift of the Q band [2,3,7] and facilitates the preparation of gold nanoparticle conjugates [5].

Novel triarylcorrole [3-5], tetraarylchlorin [6-10], and N-confused [10-13] tetraarylporphyrins have been prepared along with their Sn(IV), Ga(III) and/or P(V) complexes. *Trans*-axial ligation hinders aggregation effects, while the heavy central ion promotes intersystem crossing, resulting in relatively high singlet oxygen quantum yields [3-6,8-11,13]. When series of structurally analogous complexes have been prepared with the same *meso*-aryl groups [4,8,10,13], significantly lower IC_{50} values have been obtained for the corrole, chlorin and N-confused analogues during *in vitro* photocytotoxicity studies against MCF-7 breast cancer cells relative to the parent porphyrins. Interestingly, high log reduction values have been observed with tetraarylchlorin and N-confused tetraarylporphyrin complexes against both Gram-(+) *S. aureus* and Gram-(−) *E. coli* strains despite the absence of positively charged moieties on the ligand. Further progress made with similar studies that are currently in progress will be described.

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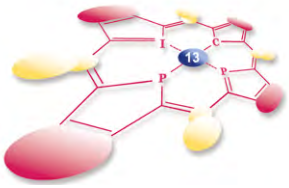

Charged Porphyrins That Form Electronically Functional Ion Pairs and Assemblies via $^{i}\pi$–$^{i}\pi$ Interactions

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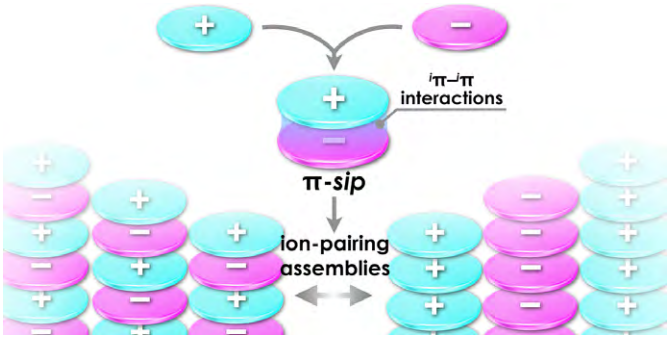

π-Electronic ions with appropriate geometries and peripheral substituents provide assemblies through the interactions between charged building subunits, resulting in fascinating electronic properties. Structures and properties of the assemblies can be controlled by the combined positively and negatively charged species in the assemblies.[1–3] In fact, π-electronic ion pairs comprising porphyrin-based π-electronic anions have exhibited characteristic assembling modes via $^{i}\pi$–$^{i}\pi$ interactions and resulting electronic properties such as solid-state absorption, which was correlated with the arrangement of constituent charged π-systems, and photoinduced electron transfer.[4] Among various combinations of the porphyrin anions with porphyrin–Au^{III} complexes as π-electronic cations,[5] the "activated" ion pair of *meso*-EWG (electron-withdrawing group)-substituted cation and *meso*-EDG (electron-donating group)-substituted anion exhibited the electron transfer in the ground state, resulting in the production of the heterodiradical in a close stacking structure as revealed by the ESR.[6] Further modifications of charged porphyrins and analogs have been examined for the electronic properties that are derived from ion pairing.

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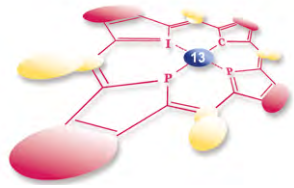

More than Oranges and Lemons: Recent Advances in Enantioselective Electronic Noses

Gabriele Magna[a], **Manuela Stefanelli**[a], **Marko Šakarašvili**[b], **Victor Borovkov**[b], **Riina Aav**[b], **Donato Monti**[c], **Corrado Di Natale**[a], **Roberto Paolesse**[a]

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The mechanisms underlying biological olfaction inspired the development of artificial counterparts able to recognize from single molecules to complex mixtures characterizing odors relying on only partially selective receptors [1]. In this context, a great benefit of the e-nose approach may involve the chiral fields where enantiomer recognition requires specific receptors and, thus, great synthetic efforts. Here, we introduce the recent progress in e-nose based on porphyrins to the recognition of volatile compound enantiomers. For example, we recently produced chiral films using the two enantiomers of hemicucurbit[8]urils – (R,R)- and (S,S)- cycHC[8] – and different metalloporphyrins [2]. CD measurements confirmed the transfer of chiral information from cycHC[8] to porphyrins. Thus, a gravimetric electronic nose was set up using Quartz Microbalances (QMBs) based sensors that included chiral and achiral sensing elements and tested to different chiral analytes at different concentrations. Even if single sensors displayed a partial selectivity to some of these enantiomers, an improved separation could be achieved by multivariate techniques (such as Principal Component Analysis, PCA) and by an ad hoc normalization purposely developed. The obtained results confirm the possibility of extending the olfaction paradigm to broad enantioselective arrays, allowing the recognition of odor chirality and, at the same time, significantly reducing the synthetic effort usually required in this field.

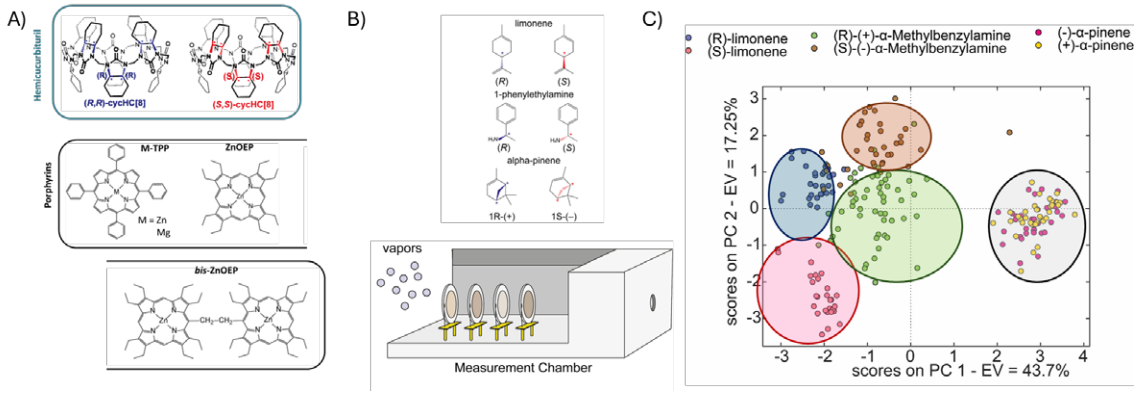

Figure 1. A) Compounds utilized for receptors, B) chiral vapor tested, and C) PCA results.

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Two-Dimensional Oxidative Polymerization of Zn Porphyrin to Porphene: Mechanistic Issues

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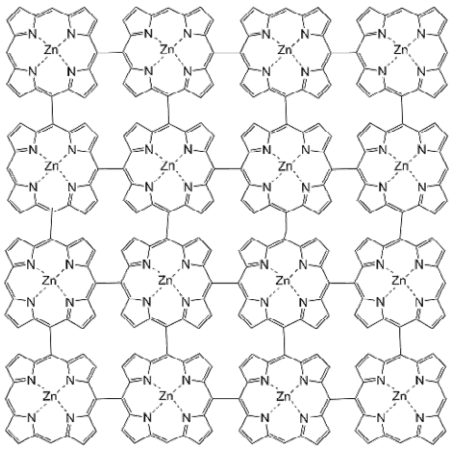
The recent finding[1] that Zn porphyrin can be oxidatively polymerized into large and fairly defect-free polycrystalline 2D sheets of Zn-porphene at the air/water interface of a Langmuir-Blodgett trough, with the meso CH bonds disappearing the fastest, raises mechanistic questions. The formation of a well-ordered 2D sheet suggests either a rigid pre-ordered arrangement of the monomers or more likely, reversible thermodynamic control. Reversibility would indeed be expected for an anticipated C-C coupling mechanism (initial formation of a radical cation followed by reversible aromatic substitution on an uncharged neighbor, loss of a proton, oxidation of the resulting radical to a cation, and another deprotonation). Yet, calculations[1] suggest quite strongly that porphene is not the most stable isomer among those possible and that kinetic control intervenes. We have addressed the apparent contradiction in a kinetic study using in situ (Brewster's angle microscopy, transmission UV-vis-NIR and reflectance FTIR) and ex-situ (Raman, multi-internal reflection IR and transmission UV-vis-NIR and FTIR on transferred films) measurements. A key to an answer is the recognition of the intermediacy of the meso-meso coupled polymer **1**, calculated to be by far the most stable among its isomers.



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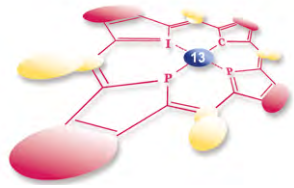

Synthesis and Applications of New Phosphorus Corroles

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The synthetic accessibility of triarylcorroles led to the introduction of numerous elemental ions chelated by them, of which phosphorus receives increasing attention. The reason is that phosphorus corroles are very stable, have outstanding photophysical properties, and their axial ligands are easily modified.[1] These features have been demonstrated to be useful for quite adverse applications, ranging from photodynamic therapy and inactivation to advanced photocatalytic processes. We now report how the photophysical variables and redox potentials of phosphorous corroles may be tuned, by focusing on the series of complexes depicted in Figure 1. They differ by the identity of the phosphorus axial ligands, hydroxide *vs.* fluoride, and by the chelating corrole: three C_6F_5 *vs.* three CF_3 groups on the respective *meso*-C atoms of **1-PL$_2$** and **3-PL$_2$**, the eight Br atoms on the β-pyrrole positions in **2-P(OH)$_2$**, and the bimetallic dimer (through β-pyrrole C-C bonds) **4-PL$_2$**. These compounds are currently explored as metal-free photocatalysts for organic synthesis.

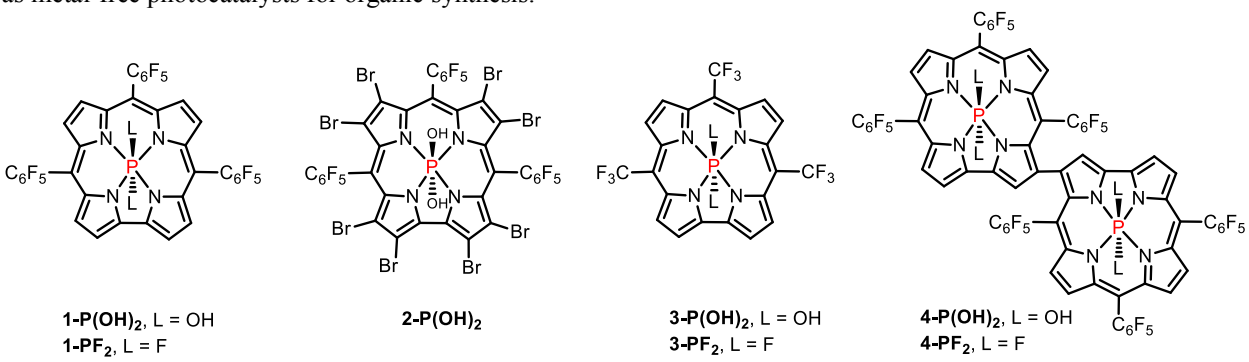

Figure 1. Chemical structures of the investigated phosphorous corroles.

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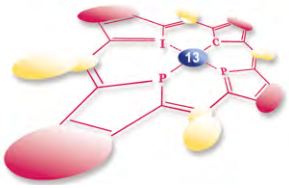

Experimental evidence for oxidizing intermediates in the enzymatic cycle of noncanonical heme oxygenases

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The primary function of heme-degrading enzymes in pathogens is the utilization of extracellular heme as a vital source of iron, an essential nutrient for their survival. Noncanonical heme oxygenases, MhuD from *Mycobacterium tuberculosis* and two others from *Staphylococcus aureus*, namely IsdG and IsdI, are responsible for the transformation of heme into mycobilin and staphylobilin, respectively.[1] These products differ significantly from biliverdin produced by canonical human heme oxygenase (HO), implying different mechanisms of heme degradation reaction. The mechanism of heme degradation is complex and controversial, with ferric hydro/peroxo or ferryl heme species being proposed as reactive intermediates.[1,2] Here, we report the spectroscopic characterization of the first, relatively stable ferric superoxy intermediate, which can provide information about its subsequent evolution throughout the enzymatic cycle. Furthermore, a combination of resonance Raman (rR) spectroscopy and cryoreduction methodology allowed a unique insight into the nature of reactive species in the enzymatic cycle of the MhuD protein. Irradiation of oxy MhuD samples generated an intermediate state whose Fe-O-O associated modes are not enhanced with the 406.7, 413.1, or 441.6 nm lines. Interestingly, the interpretation of the absolute rR spectra indicates that the cryoreduction occurs at the Fe atom rather than the dioxygen moiety, forming a ferrous superoxo intermediate instead of the expected ferric peroxo species. This species has been proposed to exist in equilibrium with ferric superoxo porphyrin anion radical (FSPAR) intermediate, which DFT modeling showed earlier to be associated with a ruffled heme.[3] Annealing to higher temperatures, while still not resulting in the observation of oxygen isotope sensitive modes, revealed new weak spectral features consistent with partial accumulation of hydroxyheme product.

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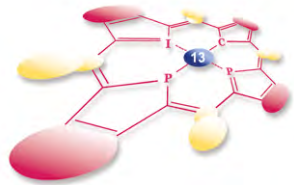

Novel generation of Porphysomes with improved photodynamic properties against bacteria and cancer cells

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Due to their amphiphilic character and their similarity to phospholipids, Phospholipid-Porphyrin (PL-Por) conjugates can self-assemble into liposomal structures named "Porphysomes" which exhibit unique photophysical properties. [1] Indeed, porphysomes show an intensive fluorescence quenching because of the high packing of the porphyrin moieties enabling them to be used as photothermal agents in photothermal therapy (PTT), in photoacoustic imaging but also for photo-triggerable release applications.[2] However, these nanosystems suffer from weak photodynamic activity (PDT) unless they are dissociated passively in the human body.[3]
To overcome these limitations, we have designed the second generation of PL-Por conjugates which consist of coupling different phospholipid backbones to the porphyrin derivatives (Pyropheophorbide-a or Pheophorbide-a) via ROS-responsive linker.[4]
Our results demonstrated that all of the newly synthesized conjugates can efficiently assemble into porphysomes which dissociate to release the free porphyrin moieties upon illumination. Moreover, their PTT/PDT activities were tested on Gram + and Gram–planktonic and biofilm bacteria. Compared to conventional porphysomes, the new assemblies showed a 2 order of magnitude and a 2-fold improvement in their antibacterial against Gram + and Gram – bacteria respectively. Interestingly, a similar tendency has been obtained *in vitro* on the PC3 prostate cancer cell line, thus showing the potential of our strategy in improving the PDT efficiency to combat cancer or bacterial infections.

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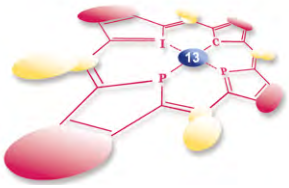

Silicon phthalocyanines in Surface-Anchored Metal-Organic Frameworks Materials

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The integration of chromophoric compounds into surface-anchored metal-organic frameworks (SURMOFs) based optoelectronic applications has gained attention, offering materials suitable for various devices like photovoltaics, LEDs, and transistor-related applications.[1] Silicon phthalocyanines (SiPcs) represent a unique class of compounds with two axial valences, allowing flexible chemical modifications with minimal impact on the optical and electronic properties of the compound.[2] SiPcs, adorned with axial coupling groups, are promising candidates for combining with metallic atoms to form SURMOF-based chromophoric assemblies. We have recently highlighted SiPcs efficacy as ditopic linkers in assembling MOF thin films, resulting in a porous material that can be used as an optical resonator.[3]
This communication presents novel SiPc compounds, axially functionalized with carboxylic acid appends and peripherally substituted with bulky groups (Figure 1). Moreover, their potential to generate, in combination with Zn atoms, of optically active SiPc-based SURMOF thin films is explored, exhibiting a systematically tuned J-type electronic coupling.[4, 5]

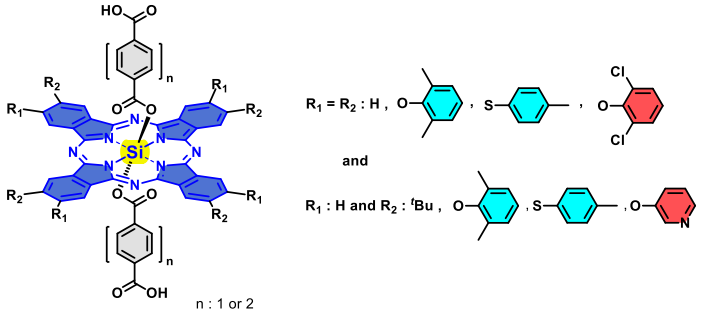

Figure 1. Chemical structure of ditopic SiPc linkers.

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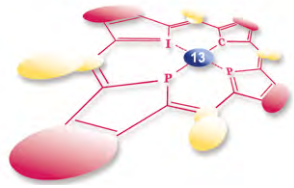

Graphene-phthalocyanine composite thin films as electrochemical sensors for neurotransmitters and screening of interferents

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The relevance of neurotransmitter detection arises from the role they play in neurodegenerative disorders that result in Alzheimer's, Huntington's and Parkinson's diseases due to their elevated or sub-optimal concentrations. Monitoring concentrations of neurotransmitters during a psychotic event is crucial. Electrochemical detection of catecholamine neurotransmitters has been widely studied and lots of potential still exists for point-of-site testing (bedside analysis). Electrochemical sensors, however, have limitations that are due to strong interfering species that exist in the same sample matrix as the analyte of interest. In addition, the stability of the fabricated electrochemical sensor is important for reusability and reproducibility. In this work, we report on the fabrication of metallophthalocyanines bearing carboxylic acid substituents onto a stable grafted electrode surface to induce pH sensitivity and screening of ascorbic acid. The flexible structural modification of phthalocyanines allowed for the incorporation of pH-sensitive functional groups and different metal ions for electrocatalysis. The formed thin films exhibited excellent stability and electroanalytical and electrocatalytic properties. The use of pH-sensitive electrocatalysts is a step away from using insulating and negatively charged polymers for screening interferents. The evaluation of modified electrodes was conducted in the negative and positively charged redox systems, such as $[Fe(CN)_6]^{3-/4-}$ and $[Ru(NH_3)_6]^{2+/3+}$. Excellent electrocatalytic properties were obtained and the electrodes could detect the neurotransmitters selectively and screen off ascorbic acid, and uric acid using the solution pH. The work has been published in the following journals.

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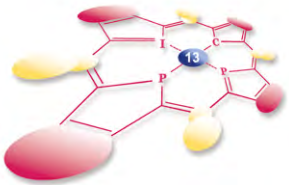

Synthesis, Properties, and Application of Azaporphyrinoids Bearing *meso*-N-Substituents

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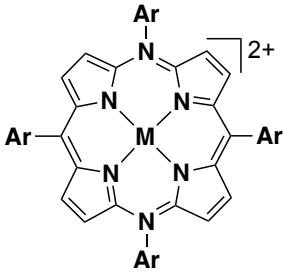
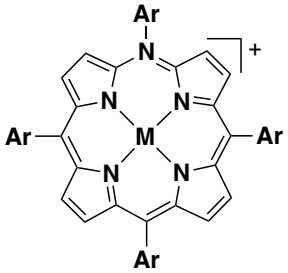
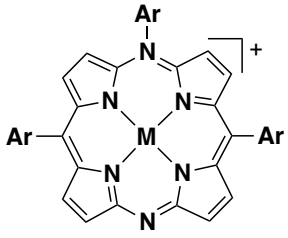
Porphyrins in the reduced oxidation state (19π and 20π porphyrins) have received significant attention because of their unique magnetic and optical properties. However, these species are intrinsically reactive under ambient conditions and readily undergo oxidation back to the parent 18π porphyrins to acquire aromatic stabilization energies. To date, various approaches have been reported to increase the stability of 19π and 20π porphyrins.[1] Our approach is *meso*-modification of 5,10,15,20-tetraarylporphyrins with nitrogen atoms; we have reported 5,10,15,20-tetraaryl-5,15-diazaporphyrinoids (Ar_4DAP) **1M**,[2] 5,10,15,20-tetraaryl-5-monoazaporphyrinoids (Ar_4MAP) **2M**,[3] and 5,10,20-triaryl-5,15-diazaporphyrinoids (Ar_3DAP) **3M**,[4] which are cationic species in the 18π-electron state. Most importantly, the reduced species of these azaporphyrinoids are neutral or cationic, and therefore considerably stable compared with the isoelectronic porphyrin counterparts. The redox reactions of **1M**, **2M**, and **3M** proceed reversibly, and **1M** has been used to evaluate the aromatic characters by simply switching the oxidation states. In this presentation, the synthesis, structures, and magnetic and optical properties of **1M**, **2M**, and **3M** and some results on the catalytic behavior of the cobalt complexes of **1M** are reported.



Ar_4DAP **1M** (18π)



Ar_4MAP **2M** (18π)



Ar_3DAP **3M** (18π)

M = Ni, Cu, Zn, Co, SiF_2

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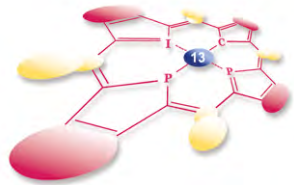

Computationally guided Rational design of the heme active site in a bacterial Cytochrome P450

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Cytochrome P450 is a large superfamily of heme-containing mono-oxygenase enzymes involved in the activation of C-H bond to form mono-oxygenated products. The overall catalytic reaction involves the following steps: (i) binding of the substrate at the active site of the enzyme located near the heme so that the target site of the substrate lies close to the iron centre of the heme for rapid transfer of active oxygen; (ii) first electron transfer to the heme producing five coordinated ferrous heme; (iii) binding of molecular oxygen to the iron centre of the heme and subsequent second electron and proton transfer accompanied by electronic rearrangement leading to the formation of the putative compound I intermediate containing oxo-Ferryl heme radical; and (iv) transfer of oxygen atom to the target site of the substrate forming the product, and release of water along with the product from the active site of the enzyme at the final step. Detailed molecular structure analyses of all these steps in a cytochrome P450 enzyme, and subsequent optimization of each of these steps could help to guide suitable modifications of the enzyme packet by appropriate mutations of specific amino acids in the vicinity of the heme centre for the reaction of a given unnatural substrate. This approach can provide a rational design of the active site of the enzyme necessary for the enhanced enzymatic activity of the cytochrome P450 for any unnatural substrate of interest. Our group has designed a large number of modifications in and around the active site of a thermostable cytochrome P450 to achieve tunability in substrate recognition with enhancement in the catalytic activity of the enzyme. The present talk will discuss the current status of the development of efficient biocatalysts by rationally designed cytochrome P450 and outline our efforts in this area.

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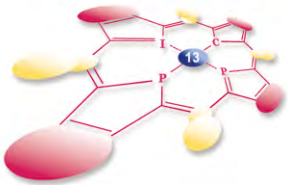

Single-molecule approach to probe kinetics and thermodynamics of oxygenation of Co(II) porphyrin at the solution/solid interface

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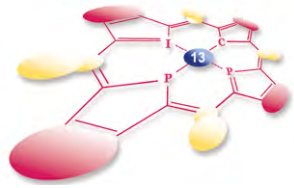
Obtaining thermodynamic and kinetic quantities and a better understanding of the fundamental chemistry of reactions of dioxygen with metal−organic complexes at the solution/solid interface is particularly relevant in chemical events of biological oxidation and heterogeneous catalysis. Here, we present a single molecule level study of an unusual oxygen binding system, *cobalt (II) octaethylporphyrin (CoOEP)*, which *does not bind to O_2 in solution, but will bind oxygen when adsorbed on a graphite or MoS_2 substrate*. The pressure and temperature dependence of the reversible binding of O_2 with CoOEP was studied using scanning tunneling microscopy (STM) and the thermodynamic parameters for the process were derived. Kinetic analysis was accomplished using a stochastic approach and involved monitoring fluctuations from reaction equilibrium using sequential imaging. This is the first use of stochastic dwell time analysis with STM to study a chemical reaction, and the results suggest that it has great potential for application to a wide range of surface reactions. Expanding the thermodynamic and stochastic studies to further systems is key to unlocking energetics and kinetic information for surface-confined reactions at the molecular level, especially at the solution/solid interface.



Cyclodextrin/Photosensitiser Supramolecular Constructs: A Short Journey From Nanoassemblies to Hydrogels with Photoantimicrobial Response

Nina Burdujaa,b, Mariachiara Trapani,a Giuseppe Nocitoa, Antonia Nostrob and Antonino Mazzaglia[a]

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The search of microbial control strategies is a current challenge to fight emerging infection in the treatment of surgical and traumatic wounds, by overcoming multidrug resistance (MDR). One of the approaches points to the design of "smart" nanoassemblies entrapping photosensitisers (PS) for antimicrobial photodynamic therapy (aPDT). Due to partial photostability of free PS, the design of novel delivery systems are highly required to decrease PS photodegradation, thus improving the therapeutic efficacy. Within our ongoing research on nanophotosensitisers (NanoPS) [1, 2], here we will discuss novel nanohydrogels incorporating cyclodextrin/PS constructs to control wound infections. In particular nanocomplexes of cationic porphyrin (N-methyl- 4-pyridyl)-21H,23H-porphyrin (TMPyP)) assembled with the trade sulfobutylether-β-cyclodextrin (CAPTISOL®) were entrapped in fast-resorbable hydrogel named DAC®. The polymer is composed of hyaluronic acid grafted with poly-lactic acid (HA-PLA) and has already proved to prevent biofilm formation *in vitro* and *in vivo*, and to prevent the onset of periprosthetic joint infection (PJI) in a large number of patients. Rheology and erosion release studies were carried out on DAC® based photo-antimicrobial. Upon dilution, nanohydrogels which represent the erosion products for the local application on infected wound were characterized by UV/Vis absorption, steady-state and time-resolved fluorescence emission and DLS technique. Nanohydrogels exhibited photo-bactericidal activity against Gram-positive and Gram-negative bacteria, such as methicillin-resistant *Staphylococcus aureus* (MRSA) ATCC 43300, vancomycin-resistant *Enterococcus faecium* (VREfm) DSM 17050 and VIM-2 producing *Pseudomonas aeruginosa* DSM102273. Altogether *in vitro* photo-antimicrobial studies elucidated the aPDT efficacy of our photosensitizing nanohydrogels incorporating cyclodextrin/PS constructs.

Acknowledgment: NOVAGENIT (Mezzolombardo, Trento) for providing the DAC and PON BONE++ (ARS01_00693) for foundings

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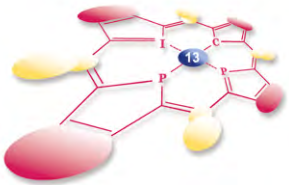

The Design of Polypeptide-Based Nanoconjugates as Advanced Theranostics

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INTRODUCTION: Synthetic polypeptide-based nanomedicines represent highly versatile, advanced therapeutic platforms, with multiple examples currently under clinical evaluation and polypeptidic drugs (Vivagel® and Copaxone™) achieving market approval [1]. As a drug delivery component, imaging represents a crucial means of improving nanomedicine-based therapy by optimising patient stratification/treatment and accelerating the development/translation of personalised nanomedicines [2]. Theranostics combines therapeutic and diagnostic components into a single agent, providing real-time monitoring that can address remaining challenges in the field [2, 3]. Introducing a porphyrin group can afford disease monitoring as part of theranostic approaches. Porphyrins and Phthalocyanines are robust organic compounds bearing interesting photophysical properties, such as their attractive absorption and emission [3], and have been used for various applications that include diagnostic (e.g., fluorescence or magnetic resonance imaging [4]) and therapeutic (through photodynamic effects [5]) uses. Using two-photon fluorescence lifetime imaging, Yeh et al. demonstrate that subcellular localisation can be determined based on differences in porphyrin fluorescence lifetime properties in the cell membrane and the cytosol [6].

RESULTS AND DISCUSSION: In this study, we exploited well-defined biodegradable polypeptide-based architectures prepared using N-carboxy anhydride ring-opening polymerised (NCA-ROP) [3, 7] to obtain four-armed polyglutamic acid (PGA) constructs that self-assemble to yield stabilised supramolecular nanostructures with therapeutically-relevant properties [7]. Employing porphyrins and Phthalocyanines as a core supports intrinsic imaging properties due to their photovoltaic properties [6]. Deprotection steps ensured the complete removal of protecting groups without racemisation. This approach has obtained structures with different characteristics depending on the number of PGA units, going from cylindrical to spherical. They can be combined with imaging and photodynamic therapy using this characteristic because they also have different circulation times in the body and cell accumulation. Biological evaluation of these novel architectures has highlighted their robust imaging and photodynamic therapy potential.

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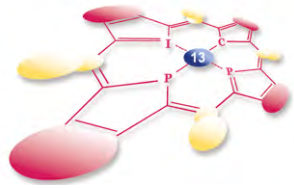

Tumor-homing nanobioparticles (NBPs) delivering theranostic corroles to resistant and metastatic cancers

Lali Medina-Kauwe[a], Simoun Mikhael[a], Nelyda Gonzalez[a], Ryan Cho[a], Christina Gloady[a], Teddy Berger[a], Nhan Nguyen[a], Jae Youn Hwang[b], Ravinder Abrol[c], Harry B. Gray[d], Zeev Gross[e]

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[c]*California State University Northridge, USA.* [d]*California Institute of Technology, USA.* [e]*Technion Israel Institute, Israel*

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Resistance to targeted therapies is an important clinical problem in cancer treatment. Many targeted molecules currently used in the clinic are designed to block signals from particular cell surface receptors that support growth and survival. However, the majority of tumors treated with targeted signal blockers become resistant within one year even if such inhibitors are used in combination treatment. This problem is compounded for brain metastases, as most targeted therapies are unable to cross the blood-brain barrier (BBB). Soluble corrole molecules that are physiologically compatible can circumvent the need to modulate growth signaling by directly disrupting vital intracellular processes for tumor survival as long as a robust delivery system can penetrate across cell membrane barriers to deposit the corroles inside the cell cytoplasm. Here we have bioengineered a biodegradable, protein-based nano-carrier designed to target and penetrate resistant and metastatic tumors for corrole delivery by leveraging the endosomolytic activity of the adenovirus serotype 5 (Ad5) penton base capsid protein combined with a naturally occurring ligand whose affinity for the human epidermal growth factor receptor 3 (ERBB3/HER3) enables missile-like targeting to highly aggressive tumors.[1] The nano-carrier is comprised of a single recombinant fusion protein, HerPBK10 (or HPK), containing three main domains: a HER3 targeting ligand (derived from the neuregulin protein), an endosomolytic function (derived from the Ad5 penton base), and a cargo loading function (decalysine sequence) with each domain separated by flexible amino acid linker sequences. The penton base domain drives the self-assembly of HPK into homopentamers that form a highly stable barrel structure containing a solvent-accessible central pore lined with charged residues that may be key to triggering membrane lysis in acidifying endosomes after receptor-mediated endocytosis. The decalysine tails rapidly interact with anionic cargo such as sulfonated corroles to nucleate convergence of the pentamer barrels into polyhedral structures encapsulating the cargo. The resulting nano-sized bioparticles, or NBPs, position the targeting ligands over the surface of the polyhedron creating a multivalency that evades anti-viral antibodies and mediates homing to tumors displaying high densities of HER3 on the cell surface, which associates with resistance and metastasis. NBPs carrying different types of soluble corrole molecules have assumed multifunctional or theranostic activities, including the detection and therapy of tumors. Corrole NBPs delivered systemically in preclinical models demonstrate missile-like targeting and penetration of tumors at relatively low pharmacological doses in comparison to current non-targeted chemotherapeutic treatments used in the clinic, reducing the growth of metastatic breast tumors and triple-negative breast tumors established in the brain. The latter finding has revealed a potential new route of nano-therapeutic passage across the blood-brain barrier and presents corrole NBPs as nano-sized bio-hybrid materials with potential clinically translatable properties.

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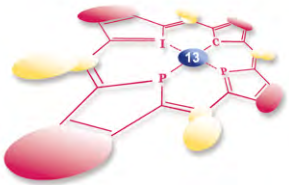

Carboxylate BODIPY functional zinc-based metal-organic frameworks: Towards solid state luminescence

Clément Michelin[a], **Marion Leroux**[a], **Alexis Tran**[a], **Damien Boyer**[a], **Federico Cisnetti**[a]

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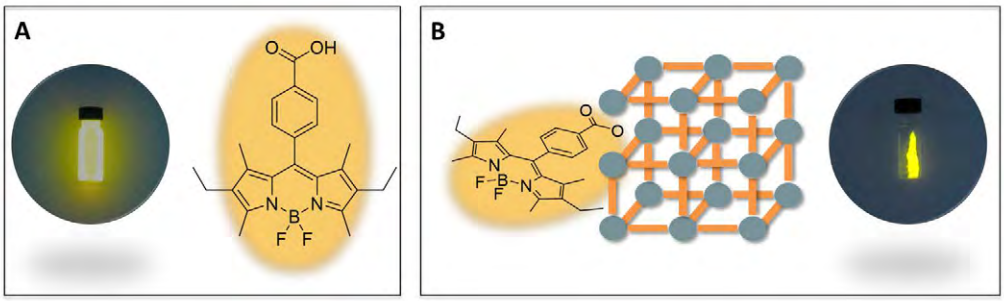
BODIPYs are widely used organic fluorophores thanks to their excellent fluorescence properties. They have very good quantum yields, extinction coefficients, thermo- and photo-stability properties, and tuneable fluorescence emission from the visible to the near-infrared. As a result, these molecules are used in a wide range of fields, from bioimaging to photoactive materials or even as sensors.[1],[2] However, they do have certain limitations. Indeed, their low Stokes shift (around 30 nm) is an intrinsic one. In addition, due to intermolecular interactions such as π-π stacking most BODIPYs suffer from the Aggregation-Caused Quenching (ACQ) phenomenon, which prevents their fluorescence emission in the solid state. To overcome the latter problem, the idea of dispersing Bodipys in a crystalline structure has emerged. Several studies have already demonstrated the possibility of integrating these compounds into polymeric structures or Metal-Organic Frameworks (MOFs).[3]

MOFs are considered versatile self-assembled porous crystalline solids. The zinc-based MOF with a terephthalate ligand, called MOF-5, is the most described in the literature due to its simple access and low precursor cost. Among other conditions, this MOF is accessible at room temperature within a few hours using bases to accelerate the crystallization mechanism. These mild conditions are compatible with organic molecules such as BODIPYs.

Here we report an easy, room-temperature method for incorporating carboxylated BODIPYs into MOF-5 by replacing a certain amount of the ligand with the luminescent molecule.[4] We demonstrated the successful integration of BODIPYs into the MOF structure and this made it possible to observe solid state fluorescence.



Bodipy structure and solution fluorescence (Fig A), Bodipy/MOF structure and solid state fluorescence (Fig B)

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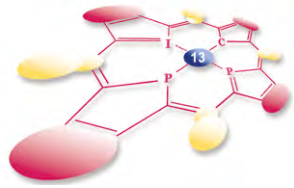

Metalloporphenes: Two-Dimensionally Fused Metalloporphyrins

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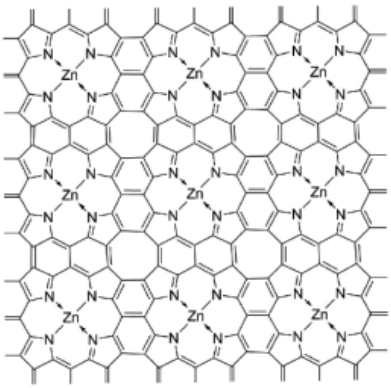
Two-dimensional conjugated polymers are of considerable interest for electronics, spintronics, and photonics on the nanoscale, but most are difficult to tune and functionalize. Single layers of porphenes (e.g., Zn porphene **1**), composed of fused porphyrin rings, have been obtained by oxidative polymerization of a layer of parent zinc porphyrin on aqueous subphase containing K2IrCl6 in a Langmuir-Blodgett trough and subsequent reversible insertion of various metal ions into the porphene square grid of binding sites.[1] They were characterized in situ by a variety of methods such as grazing incidence X-ray diffraction. They can also be transferred to other substrates as monolayers or multilayers for spectroscopy, imaging, measurements of electrical conductivity, etc. The wide choice of metals and their axial ligands offers exquisite tunability. For instance, calculations suggest that electrical conductivity will range from metallic to semiconducting with small or large bandgaps, depending on the choice of metal.[2] This promises access to meaningful patterning of circuits using nanolithography or nanoprinting. Stacking the monolayers in the registry could then permit the fabrication of monolithic chips analogous to those made today of silicon, but flexible.



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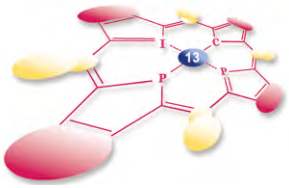

Conjugation of Tetrapyrazinoporphyrazine, BODIPY, Indocyanine and Acridine to Oligonucleotides on Solid Phase

Miletin M., Beranova M., Demuth J., Kaushik R., Kostelansky F., Grossova P.

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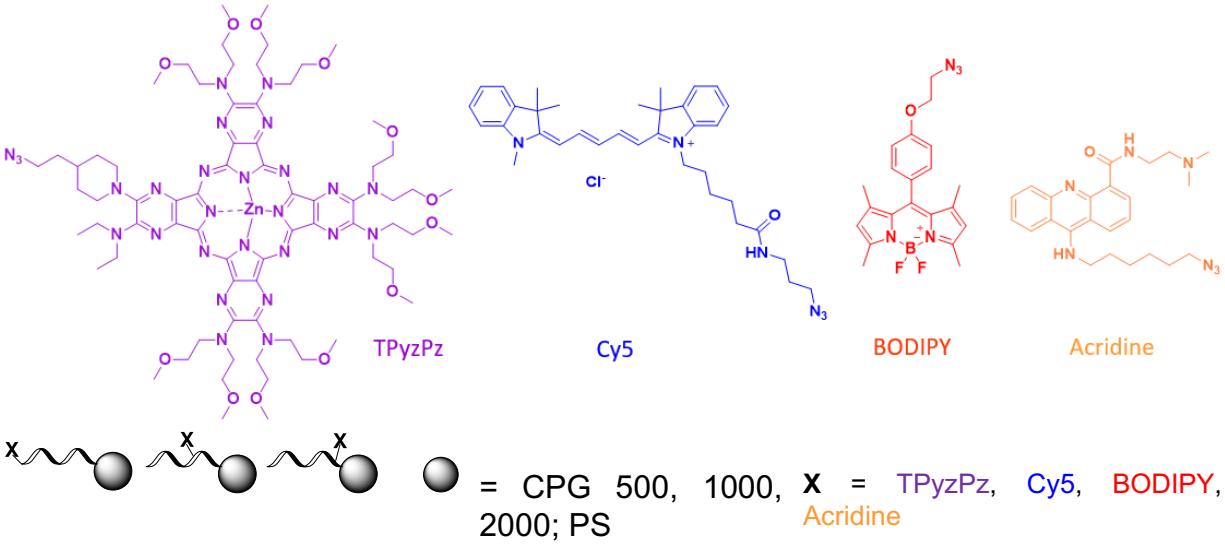
Chemically modified oligonucleotides, including their conjugates with functional molecules (fluorescent, fluorescence quenching, photodynamic, intercalating, etc.) are essential tools in science, diagnosis (e.g. Taq-Man and other types of molecular probes), and even therapy (aptamer-drug conjugates).[1] Phthalocyanines (especially their aza-analogues tetrapyrazinoporphyrazines, TPyzPz)[2] bearing electron-donor peripheral substituents are highly efficient quenchers of fluorescence, while properly substituted BODIPY dyes, as well as indocyanines (e.g. Cy5), belong among established fluorophores, and acridines are known as DNA intercalating molecules.[3] Strain Promoted Azide Alkyne Cycloaddition (SPAAC)[4] performed on solid phase bound oligonucleotide is a comfortable method of conjugation of the functional molecules with oligonucleotides. However, optimal conditions for such conjugation reactions have not yet been studied in detail. In our study, we have explored the influence of concentration, size, and character of four conjugated molecules, as well as type of the solid phase used for oligonucleotide synthesis (controlled pore glass, CPG and polystyrene, PS), and the position of the modification in the oligonucleotide chain relative to the solid phase.



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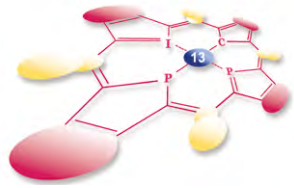

Bulk Photovoltaic Effect in Polar Assemblies of Subphthalocyanines

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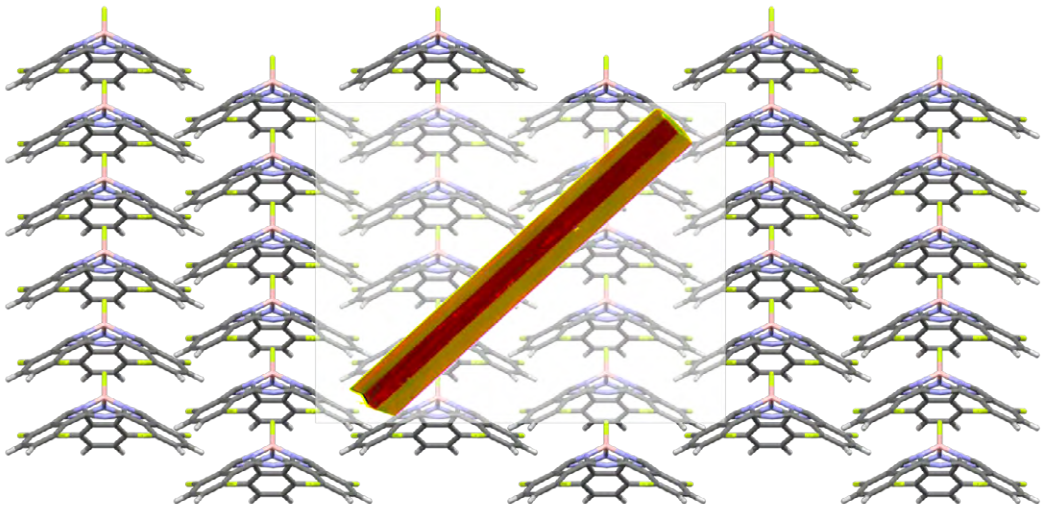
Polar materials attract wide research interest due to their unique properties, such as ferroelectricity and the bulk photovoltaic effect (BPVE)[1-3], which are not accessible with nonpolar materials. Currently, it is widely accepted that photocurrent in BPVE originates from the quantum-mechanical shift of the center of mass of an electron in the real space upon the optical transition, which is termed "shift current". However, these detailed studies have been almost exclusively limited to inorganic materials. In this study, we have carefully characterized the BPVE in polar assemblies with subphthalocyanines (SubPcs). As a result, we confirmed that the BPVE of the polar crystal with SubPcs is originated in the shift current mechanism. Furthermore, we could correlate photocurrent generation and exciton formation.



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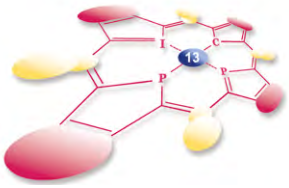

Vibrational Analyses of Nitric Oxide Scavenging Reactions Using a Photolabile NO Donor at Cryogenic Temperatures

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The high reactivity of nitric oxide (NO) toward other radical species and transition metals leads to broad toxicity crucial to NO's role in the mammalian immune response to infections. In macrophages, NO can reach the micromolar concentration range and combine with superoxide produced by NADPH oxidase in a diffusion-controlled fashion to generate peroxynitrite: $NO + O_2^{\bullet-} \rightarrow ONOO^-$. The peroxynitrite ion is highly reactive and versatile with a near neutral pKa of 6.8 and cis and trans isomers of comparable energies. While peroxynitrite decays via isomerization to nitrate in aqueous solution, it also reacts with a wide range of biomolecules including metalloenzymes to produce additional reactive nitrogen species. Pathogenic microorganisms depend on flavohemoglobins and other heme-containing proteins such as truncated hemoglobins to convert NO to inert nitrate: heme-$Fe^{II}(O_2)$ + NO → heme-Fe^{III} + NO_3^-. The first step of this catalysis is expected to be a second-order radical combination of NO with the heme iron(III)-superoxo complex to form an iron(III)-peroxynitrite intermediate. Monitoring this reaction in myoglobin with time-resolved resonance Raman (RR) spectroscopy, we showed that a millisecond intermediate previously assigned in the literature as an Fe(III)-peroxynitrite complex [1] was an Fe(III)-nitrato complex before nitrate release [2]. This work implied that the isomerization rate of peroxynitrite at the enzyme active site is much faster and facile than initially thought. Accordingly, theoretical modeling of the NO dioxygenase reaction in mycobacterial truncated hemoglobin predicts very low transition state energy barriers throughout the reaction with lifetimes for putative Fe(III)-peroxynitrite and ferryl Fe(IV)=O in the picosecond timescale [3]. Given recent work with photolabile caged NO compounds and NO reductases by Tosha, Shiro and coworkers [4], we decided to reinvestigate the NO dioxygenation reaction of oxymyoglobin through uncaging of NO at cryogenic temperatures. This oral presentation will focus on these latest unpublished results and will discuss the pros and cons of this approach for vibrational characterizations and identifications of trapped intermediates in metalloenzymes.

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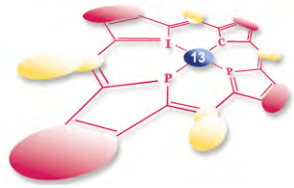

Mechanistic and Structural Aspects on the Supramolecular Assembling Process of $TPPS_4$ J-Aggregates

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Under acidic conditions and at high ionic strength or in the presence of templating species, 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin ($TPPS_4$) and similar species self-organize into J-aggregates.[1,2] In these species, the porphyrins align in a general edge-to-edge geometry, responsible for their peculiar optical properties. The self-assembling process is hierarchical, and the kinetics are strongly dependent on the mixing protocols.[3,4] In the case of sigmoidal profiles, the kinetic data have been treated using a model proposed in literature by R.F. Pasternack.[5] Accordingly, an autocatalytic growth with the formation of an m-mer of porphyrin units is the rate-determining step (RDS) leading to the eventual J-aggregates whose size spans from nano- up to the micro-scale. The kinetics of growth in these aggregates has a deep impact on their final structures, the spectroscopic features and the expression of chirality. The role of different experimental parameters, together with inorganic counter-anions,[6] and various cationic and anionic species (organic anions, metal ions, porphyrins, and metal complexes) [7-9] will be reviewed.

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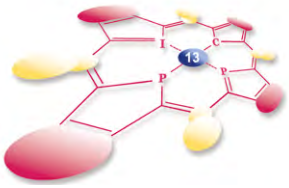

Selective Synthesis of Bonellin and Other Naturally Occurring Hydroporphyrins

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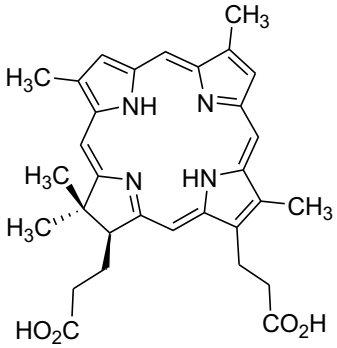
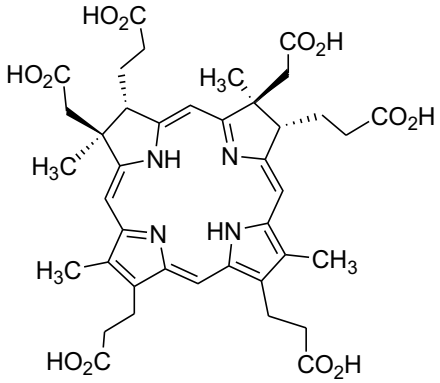
Until the mid-1970s hemes, chlorophylls, bacteriochlorophylls and vitamin B_{12} were the few representatives of the class of naturally occurring cyclic tetrapyrroles. From then on two developments were responsible for the discovery of novel hydroporphyrinoid structures from natural sources. The first line was coined by the search for biosynthesis intermediates between urogen III and vitamin B_{12}. The second development is characterized by the deliberate search for new porphyrinoids in marine organisms and microorganisms. Typical compounds from these investigations are bonellin and sirohydrochlorins. Dialkylated parts in the saturated five-membered rings of the novel compounds are common structural characteristics. In particular, these geminal dialkylations represent the main challenge for the synthesis of the structures.



Bonellin



12.18-Didecarboxy-sirohydrochlorin

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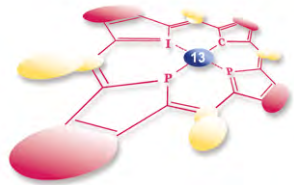

Exciton-Band Engineering of Glassy Porphyrin Assemblies for Near-Infrared Luminescence: Synthesis, Supramolecular Organization, and Femtosecond Photodynamics

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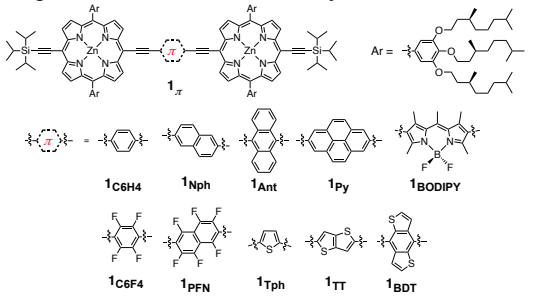
Near-infrared (NIR)-luminescent materials have provoked considerable interest in materials science, aiming at extensive potential applications including non-invasive *in vivo* imaging, security applications, and broadband optical amplifiers. To develop NIR-luminescent materials, we have to overcome fatal bottlenecks; poor emission efficiency due to "energy gap law" and experimental difficulty in observations of photodynamics. Inspired by the fact that photosynthetic systems circumvent the energy gap law and attain excellent primary photosynthetic events in NIR wavelength region, our strategy employs glassy porphyrin assemblies to design the NIR-luminescent materials. Although the large planar porphyrin plane usually furnishes with a highly crystalline propensity, the elastic 3,4,5-tri((*S*)-3,7-dimethyloctyloxy)phenyl groups at the *meso*-positions impart a glassy nature to the porphyrin ring,[1] wherein the meso-ethynylene-conjugation enhances the intermolecular interaction and imparts unprecedented solid-state NIR-luminescent properties.[2] We developed an efficient synthetic protocol, trimethylsilanolate-promoted Hiyama cross-coupling, for the preparation of a systematic series of proquinoidal–ethynyl-conjugated porphyrin dimer $\mathbf{1}_{\pi}$.[3] The porphyrin dimers display the split of the Soret band and bathochromic shift of Q band due to exciton coupling in the J-type aggregates in solution and in thin films. It is found that the effect of the proquinoidal group on the thermodynamics of the solution-phase aggregations is classified into three families depending on the size and shape as well as the fluorine substitution based on the enthalpy–entropy compensation principle. Similarly, the size and shape of the proquinoidal group seem to be predominant in the crystalline arrangement in glassy films, as explored by glazing-incidence wide-angle X-ray diffraction (GIWAXD) experiments. Due to the steric repulsion of the high bulkiness of the 3,4,5-tri((*S*)-3,7-dimethyloctyloxy)phenyl groups, the porphyrin rings and the proquinoidal unit are cofacially located in close proximity. The red fluorescence of $\mathbf{1}_{\pi}$ bathochromically shifted due to excimer formation in solutions and further to the NIR in glassy films. Remarkable is that the NIR fluorescence maxima of $\mathbf{1}_{\mathbf{BDT}}$ and $\mathbf{1}_{\mathbf{Ant}}$ are shifted to 895 and 960 nm, respectively, in glassy films. The ultrafast NIR photodynamics of the glassy porphyrins were explored by a newly developed femtosecond fluorescence up-conversion technique. It has been revealed that the glassy porphyrin assemblies funnel excitons into the self-trapped excitons as the NIR-luminescent species.



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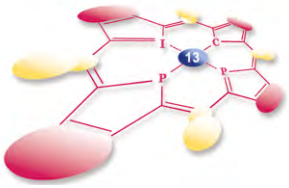

Excited State Intramolecular Proton Transfer and Excited State Aromaticity in Hemiporphyrazine

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Hemiporphyrazine is a phthalocyanine analogue consisting of two isoindole subunits and two pyridine subunits. In contrast to 18π-electron aromatic phthalocyanines, hemiporphyrazine can be regarded as a 20π-electron system [1]. Since the first report in 1952 [2], there have been many studies on the molecular and electronic structures of hemiporphyrazine in the ground state. However, those in the excited states are not well understood and remain controversial [3]. In this study, we have investigated the nature of the lowest singlet state of hemiporphyrazine by means of density functional theory calculations. Our calculations indicate that tautomer **1b** is more stable than tautomer **1a** upon excitation and tautomer **1b** has an aromatic character in the lowest singlet state (Figure 1). This implies that hemiporphyrazine satisfies Baird's rule and excited state intramolecular proton transfer (ESIPT) can occur [4]. We then synthesized several periphery-substituted hemiporphyrazines and measured their transient absorption spectra. Two transient components were observed for each compound, which experimentally supports the ESIPT process.

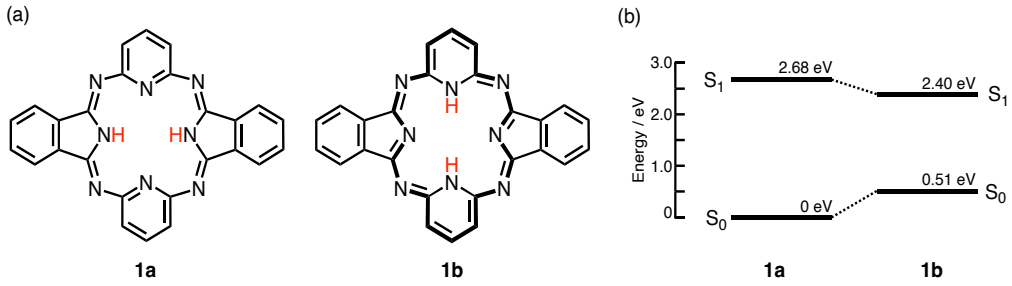

Figure 1. (a) Two tautomeric structures of hemiporphyrazine. Bold line indicates the 20π-conjugation pathway. (b) Energy levels of the ground state (S_0) and the lowest singlet state (S_1) of two tautomers calculated at the CAM-B3LYP/6-31G(d,p) level.

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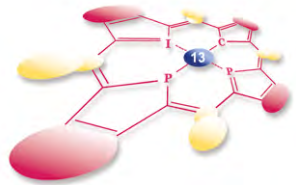

Developing model platforms for polariton photochemistry

Gloria Davidova[a], Suman Gunasekaran[a], Thomas Khazanov[a], Woojae Kim[b], Kelly Leiby[a], Rana Lomlu[a], Soham Mukherjee[a], Andrew J Musser[a]

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Polaritons hold great promise as a tool to 'rewrite' the functional behavior of molecular systems. Polaritons are mixed states formed from the hybridization of molecular transition dipoles with a confined electromagnetic field. Their formation can induce a host of exciting effects – enhanced energy and charge transport [1], changes to the selectivity or rate of chemical reactions, and modifications of spin physics – but not always, and not predictably. Though the field is increasingly adept at finding polaritonic effects, we lack a fundamental understanding of their underlying mechanisms [2]. How do we reconcile polariton (photo)chemistry with the fleetingly short polariton lifetime [3]? What is the impact of the vastly larger pool of intracavity dark states? How should our pictures of polariton physics evolve to capture the realistic levels of disorder and overlapping transitions seen in typical organic semiconductors [4]? To address these questions and lay a foundation for rational polariton photochemistry, we explore polariton dynamics in systematically controlled cavities based on model dye molecules. We consider how strong coupling alters intramolecular relaxation dynamics in porphyrins, long-range energy transport in BODIPY films, and donor-acceptor energy transfer mediated by rhodamine-6G polaritons.

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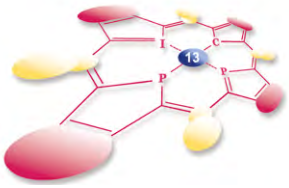

Oxidation of Möbius type Ni(II) and Pd(II) Hexaphyrin-Cyclodextrin complexes. The oak and the reeds fable.

Mickaël Ménand,[a,*] Syamasrit Dash,[b] Rajaa Benchouaia,[b] Ludovic Favereau,[b] Arnaud Fihey,[b] Corinne Lagrost,[b] Sébastien Blanchard,[a] and Stéphane Le Gac[b,*]

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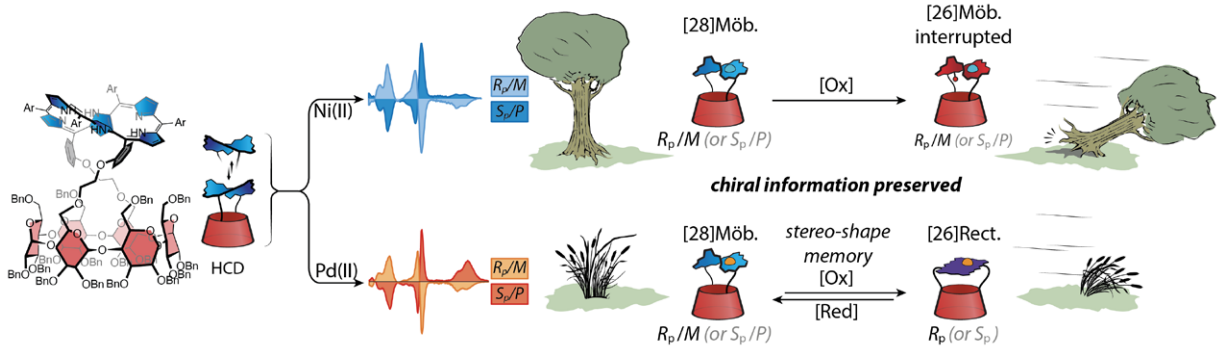
We have previously developed a family of hexaphyrin-cyclodextrin (HCD) [1] hybrids and in particular one that is doubly linked and incorporates specific chiral communications involving central, planar and Möbius chiralities. [2] The metalation of this latter with either Ni(II) or Pd(II) afforded two pairs of pseudo-enantiomers (R_p/*M* and S_p/*P*) featuring quasi-mirror ECD spectra. Chemical oxidation to [26] π systems led to behaviors reminiscent to "*The Oak and the Reeds*" fable, due to a stronger coordination of Ni(II) than that of Pd(II). Oxidation of the robust Ni(II) complexes ("*the Oak"*) interrupts the π-conjugation pathways but preserves the Möbius-like conformations which display marked ECD signatures. In contrast, oxidation of the more flexible Pd(II) complexes ("*the Reeds"*) converts the [28] aromatic Möbius systems into rectangular [26] aromatic ones losing their chiroptical intensities. However, the cyclodextrin linking pattern maintains a planar chiral environment (R_p or S_p), allowing the original Möbius configuration to be regenerated by reduction with a full chiral retention. These *stereo-shape-memory* processes will be disclosed in more detail in this communication.



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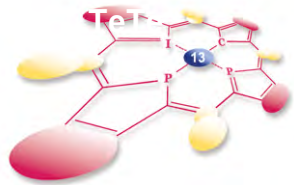

What do we learn from the chiral induced spin selectivity effect on electron transfer?

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Our studies of the chiral induced spin selectivity (CISS) effect explore the electrons' spin degree of freedom, in addition to the electrons' charge.[1] The additional information provides new insight on the mechanism of electron transfer through chiral molecules and demonstrates that several of the assumptions commonly made, when analysing electron transfer data, miss important ingredients of the transfer mechanism.

In my talk, the importance of electron-vibrations and electron-electron interactions will be demonstrated, as well as the role that the molecular polarizability plays in the electron transfer.[2]

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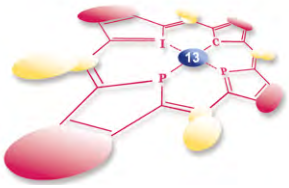

Old reactions and new compounds

Sara Nardis[a], Francesco Pizzoli[a], Alessandro Mita[a], Luca Prodi[b], Kevin M. Smith[c], Frank Fronczek[c], Roberto Paolesse[a]

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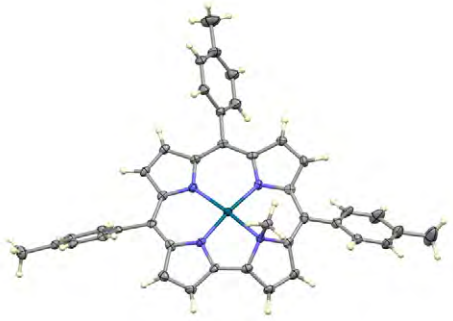
Pd(II) is frequently coordinated with porphyrins [1] to get oxygen sensing, photo upconversion, singlet oxygen generation and photocatalysis, while just a few examples of palladium corrole complexes have been reported until now [2, 3]. The alkylation of one of the inner core nitrogens is a possible approach to obtain dianionic corrole ligands, suitable for the coordination of divalent metal ions. For this reason, we have used an old procedure [4] to obtain the N-methyl derivative of the 5,10,15-tris(4-methylphenyl)corrole with CH_3I, optimizing it to limit the formation of the di-methylated by-product. Two regioisomers, the N-21 and the N-22 methyl derivatives are obtained from the reaction as a racemic mixture, with the first product achieved in a higher amount. The structural characterization of the reaction products evidenced the distortion induced by the inner core methyl groups, higher for N-22 than for the N-21 isomer. Further functionalization of the skeleton and reaction with different metals have been attempted. In particular, palladium [5] and copper insertion have been obtained in the case of monosubstituted arylcorroles, as confirmed by their X-ray characterization. Interestingly, the Pd complexes do not exhibit luminescence emission but are capable of producing singlet oxygen upon irradiation. Further research and exploration of the properties and applications of these complexes may provide valuable insights into their potential use in various fields.



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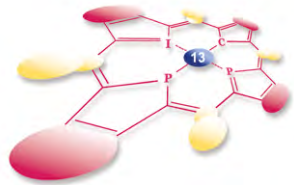

Charge-transfer spectroscopy of transition-metal phthalocyanines: correlation with Lever's E_L scale and TDDFT calculations

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Charge-transfer spectroscopy of the selected transition-metal phthalocyanines will be discussed in conjunction with their electrochemical properties. Specifically, UV-Vis and magnetic circular dichroism (MCD) spectra of the $PcFe(II)L_2$, $PcRu(II)L_2$, PcMn(III)LX, and PcCr(III)LX (L is a neutral and X is a monoanionic ligand) will be discussed in terms of their metal-to-ligand (MLCT) and ligand-to-metal (LMCT) charge-transfer spectroscopy determined by the experimental UV-Vis and MCD as well as theoretical (time-dependent density functional theory) methods. Lever's E_L scale was used to predict and correlate the MLCT and LMCT transitions in transition-metal phthalocyanines. The results are also correlated with the time-dependent density functional theory calculations.

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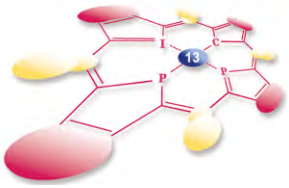

Resin-supported synthesis of phthalocyanines for fluorescent imaging and materials applications

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Phthalocyanines are among the most popular chromophores for imaging and luminescent materials applications. The bright luminescence in the near-IR spectral range along with high stability and countless possibilities for chemical functionalization make phthalocyanine chromophores an attractive choice for incorporating into various complex molecular systems. In many molecular designs, it is required to selectively synthesize phthalocyanine core with one reactive group for further chemical functionalization (i.e. asymmetrically substituted AB_3-type phthalocyanines). However, the most common practical method of synthesizing phthalocyanines involves the condensation of four phthalonitrile moieties, which delivers phthalocyanines with either four identical functional groups, or (when a mixture of two different phthalonitriles is used) a statistical distribution of six different products. The latter typically requires a tedious chromatographic separation, and isolation of the required AB_3 isomer is not always achievable [1]. In this presentation, we will discuss a simple and efficient method for the preparation of the single functional group substituted (i.e. AB_3-type) phthalocyanines using a resin-supported approach. This approach utilizes commercially available polymer resins and enables scaled-up preparation of the target phthalocyanine compounds. We used this approach to prepare selectively substituted phthalocyanines for the design of a series of novel near-IR fluorescent sensors for selective turn-on detection and quantification of specific biomacromolecular targets [2, 3] as well as hierarchically constructed fluorescent conjugated polymers for materials applications. The preparation and properties of these molecular systems will also be discussed in this presentation.

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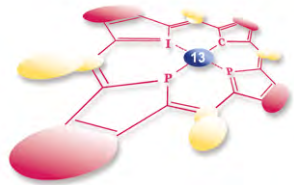

Phthalocyanines as imaging tools for the assessment of small-molecule inhibitors in live cells

Irina V. Nesterova[a], Evgueni E. Nesterov[a], Harouna Amadou[a], Haniyeh Jadidi[a], and Alan Calderon[a]

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As photostable and bright near-IR fluorophores, phthalocyanines have recently emerged as efficient *in vitro* and cellular imaging platforms that can be used to report on molecular events and environmental cues [1]. Thus, we have developed a new generation of phthalocyanine turn-on fluorescent sensors with high recognition selectivity for specific biomacromolecular targets [2-3]. Here, we discuss a new phthalocyanine-based fluorescent imaging approach for qualitative and quantitative assessment of inhibitor/receptor interactions *in vitro* and in live cells.

For the proof-of-concept model, we focus on small molecule inhibitors for epidermal growth factor receptor (EGFR) tyrosine kinase as a ubiquitous important target for anticancer therapeutic development [4-6]. The sensor consists of two domains: an anchor that specifically binds a target receptor (i.e. intracellular ATP binding pocket of EGFR kinase) and a near-IR fluorescent phthalocyanine reporter. Competitive binding of a small molecule inhibitor causes changes in the aggregation/deaggregation state of the phthalocyanine domain yielding a selective turn-on fluorescent readout.

We demonstrate that this simple single-fluorophore platform is capable of quantitatively assessing biomolecular target interaction with either covalently or non-covalently binding unmodified ligands. As small molecule fluorophores, the phthalocyanine-based sensors do not require genetic modifications and, as such, can operate in unmodified cells, are less likely to alter the structure and function of the target and off-target molecules, and can permeate through the cell membranes. All these characteristics are crucial for the assessment of ligand/receptor interactions in a range of formats including high throughput screening of native cells. Finally, the working principles of our sensing system are general and can extend toward a variety of other targets/binders in native environments.

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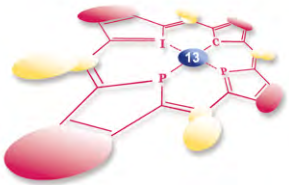

EPR Spectroscopy of Metalloporphenes

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ORALS

The recent advances in the preparation of porphyrin-based two-dimensional materials, porphenes, open wide opportunities in nanoelectronics, nanospintronics, and nanophotonics [1]. Porphenes electronic properties, and therefore magnetic, strongly depend on the metal ion [2]. Conventionally, the former is studied employing electrical transport measurements and the latter using electron paramagnetic resonance (EPR) spectroscopy. Under certain conditions, EPR spectroscopy performed at high magnetic fields and microwave frequencies (HFEPR) can accomplish both simultaneously [3, 4]. Here, we present our preliminary EPR results on Cu porphene. We chose Cu porphene because of its potential to serve as a model system due to the relatively simple behavior of spin ½ of Cu(II).

First, we performed EPR measurements at 10 GHz of monomeric frozen solutions (T = 77 K) in THF at the concentration of 400 µM to avoid broadening due to the dipolar or exchange interaction among neighboring molecules. We obtained an axial g tensor with $g_{\perp} = 2.04$ and $g_{\parallel} = 2.20$, and hyperfine couplings of ~20 mT for Cu and ~1.8 mT for N. The monomeric g factors and hyperfine coupling constants are an important reference for comparison with the EPR signals from the monolayer arrays.

Next, Cu porphene arrays were deposited on a gold-coated glass substrate (5 nm of Ti for better adhesion + 1.2 µm of Al for reflecting microwaves + 5 nm of Ti for better adhesion + 50 nm of Au) and performed initial HFEPR measurements in the 100 GHz frequency range. The spectra display a broad signal (~ 37 mT)) at $g \sim 2.01$ that vanishes below 170 K, indicating the presence of an antiferromagnetic coupling in the array. Additional narrow peaks (~ 1.2 mT) that increase in intensity with decreasing temperature were observed, following the behavior that we calculated for arrays of monomers with weakly antiferromagnetically coupled Cu ions with one spin per unit cell. These multiple peaks with different behaviors suggest that there are inhomogeneities in the sample where regions with different orientations and distribution of multilayered samples could coexist. Particularly, with an average interlayer distance between the metals of ~3.5 Å, a strong coupling is expected, exceeding the weak intralayer coupling by forming local Cu dimers or trimers [5]. To address this problem, we plan to switch to high-quality Si wafers and use magnetron sputtering for gold coating. This should result in a much more uniform and flatter surface improving the quality of the deposited monolayers. We are currently preparing measurements of both monolayered and multilayered samples, a procedure that will allow for a correct differentiation between the cases of interlayer and intralayer exchange couplings.

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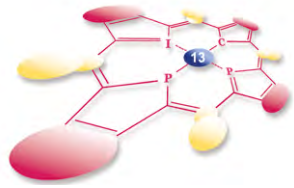

Laser Flash photolysis study of selected Metal free, Zn and Ga 5,10,15,20- tetrakis(4-phenylderivatives) porphyrins

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The use of dyes such as porphyrins, phthalocyanines, naphthalocyanines, chlorins, bacteriochlorins and texaphyrins as photosensitizers for photodynamic therapy (PDT) and photodynamic antimicrobial chemotherapy (PACT) investigations has been reported by many researchers working for the improvement of cancer treatment or antimicrobial activity [1-2]. These dyes are good targets because of their excellent physicochemical properties including photostability. Zn 5,10,15,20-tetrakis[4-(benzyloxy) phenyl]porphyrins, Ga 5,10,15,20-tetrakis(4-bromophenyl)porphyrin, meso-tetrakis(4-nitrophenyl)gallium porphyrins, meso-tetra(4-carboxyphenyl)porphyrin tetramethyl ester which are among the abovementioned compounds have been recently synthesized and tested for the PDT application [3-6]. In extension of knowing the photophysicochemical properties of the four selected porphyrins, in this work we used laser flash photolysis to generate in organic solvents different reactive intermediates taking place during the photoreaction in excited states, their transient absorption spectra and their lifetimes. The overall mechanism including the reactive pathway has been proposed.

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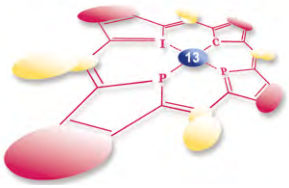

Porphyrin-based systems for CO_2 conversion

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The universal primary energy sources are fossil fuels such as natural gas, oil, and coal; however, their extensive utilization contributed to global warming and climate change [1]. As a result, there is an urgent need to establish a carbon-neutral and circular economy by converting CO_2 into valuable fuels and chemicals using renewable energy sources [2]. CO_2 can be converted into useful products such as formic acid, carbon monoxide, methane, methanol, ethanol, and ethylene [3]. To that end, several homogeneous, heterogeneous, and hybrid systems combining molecular catalysts and solid/heterogeneous elements have been investigated over the last few decades [4]. During this talk, two different approaches will be presented: i) electrocatalytic CO_2-to-ethylene conversion and ii) photocatalytic CO_2 reduction to CO. Concerning the first approach (**Figure 1**, left part), we have developed tandem CO_2 reduction schemes by combining molecular catalysts (Fe-porphyrins) with Cu-cubes. The Fe-porphyrin selectively converts CO_2-to-CO, and subsequently Cu-cubes are transforming CO into C_{2+} products, leading to the efficient and selective evolution of ethylene. Regarding our second approach (**Figure 1**, right part), we have developed dye-sensitized photocatalytic systems (DSPs) for CO_2 reduction based on noble metal-free photosensitizers (PS) and molecular catalysts (CAT). In these CO_2-to-CO DSPs, we have also incorporated an additional chromophore (An) to promote an antenna effect and boost the photocatalytic activity.

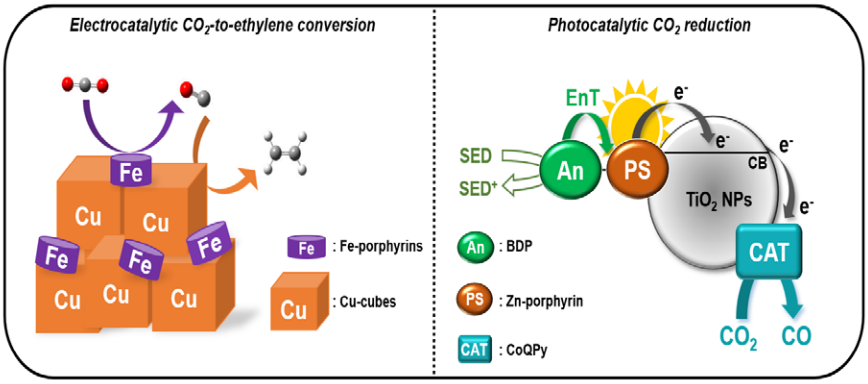

Figure 1. Overview of this work.

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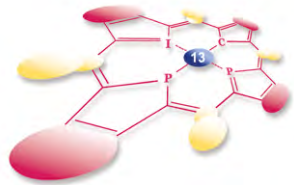

Nanobubbles in Cancer Therapy: Targeted Drug Delivery and Sonodynamic Advancements

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Gas-filled lipid nanoparticles, aka nanobubbles, demonstrate remarkable drug carrier and theranostic capabilities attributed to their submicron size, high compressibility, low density, and distinctive interactions with ultrasound (US). They have been used in the delivery of several therapeutic materials, including but not limited to chemotherapeutics agents. Our research focuses on their potential in cancer treatment, specifically in the context of liver tumors. Doxorubicin-loaded C_3F_8 nanobubbles (hDox-NBs) have shown promise in improving cancer treatment efficacy [1, 2]. In orthotopic liver tumors of immunocompetent rats, hDox-NBs, when combined with low-frequency ultrasound, effectively delivered tumor-specific, normal tissue-sparing, and highly lethal drug doses [3].

Additionally, we explored the application of nanobubbles in sonodynamic therapy (SDT), a minimally invasive cancer treatment derived from photodynamic therapy (PDT). Incorporating photosensitizing agents like Porphyrin or Iridium complex into nanobubbles allows for deep tissue activation of tumor-localized drug agents through acoustic cavitation. Photosensitizer-loaded nanobubble formulations demonstrated their potential as effective sonosensitizers for advancing SDT in cancer treatment [4, 5]. This engineered nano-system proves to be a promising tool for highly efficient SDT, capable of treating a broad range of deeper and less accessible tumors compared to PDT, with the added benefit of nanomedicine.

In summary, our work highlights the dual potential of nanobubbles in targeted drug delivery and sonodynamic therapy for enhanced cancer treatment. The efficacy demonstrated in liver tumors suggests broader applications in aggressive cancers, offering a promising avenue for more effective and minimally invasive approaches.

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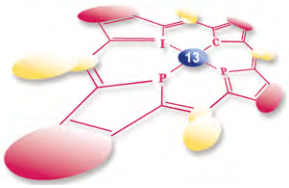

Si(IV) and Mg(II) as central atoms of tetrapyrazinoporphyrazines

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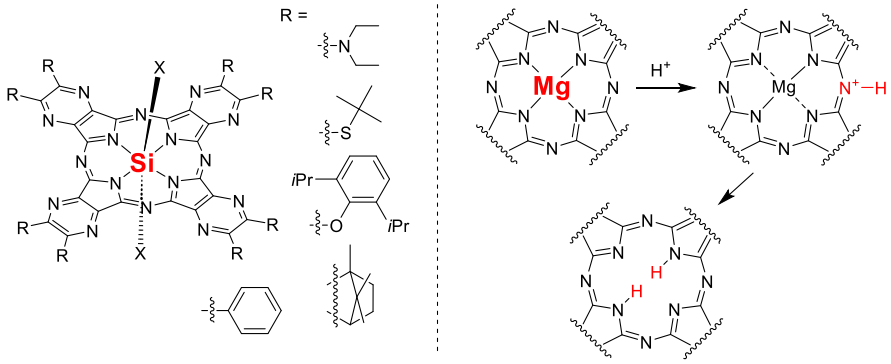
Tetrapyrazinoporphyrazines (TPyzPzs) are synthetic macrocyclic dyes composed of four isoindoline units. In comparison to phthalocyanines (Pcs), they have wider variability in precursor synthesis and have more electron-deficient cores, but suffer from hypsochromically shifted Q-band (620-650 nm) [1-2]. Thanks to their properties, TPyzPzs are widely investigated as fluorescence sensors, quenchers of fluorescence in oligodeoxynucleotide probes, or photosensitizers in photodynamic therapy [2, 3].
In the first part, we will focus on the synthesis of Si(IV) TPyzPzs and their axial modifications [4]. The complexation method starting from metal-free TPyzPzs will be compared to the template method employing diiminoisoindolines as the starting materials. The optimum reaction conditions for the coordination of Si(IV) to metal-free TPyzPzs in terms of peripheral groups, amount of trichlorosilane, and solvent used will be reviewed. Finally, the photophysical properties of target Si(IV) TPyzPzs will be discussed. The second part will be dedicated to Mg(II) TPyzPzs and Pcs and their (in)stability under acidic conditions. Mechanism-based on the protonation of azomethine nitrogens followed by demetallation will be discussed. Interestingly, we will show that microemulsions and liposomes may substantially protect these macrocycles from demetallation [5].



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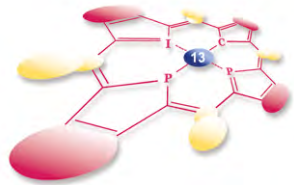

Self-delivering photoactivable nanoconstructs target and block the PD-L1 immune checkpoint in pancreatic cancer

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Desmoplasia in pancreatic ductal adenocarcinoma (PDAC) limits the penetration and efficacy of therapies, including nanomedicines and immune checkpoint inhibitors. Our prior work has shown that light-activated nanoconstructs remediate desmoplasia in PDAC to sensitize tumors to chemotherapy, thereby doubling survival.[1] In this study, we present PD-L1 immune checkpoint targeting and blocking nanoconstructs (containing benzoporphyrin derivative) that are capable of self-delivery through PDAC tumors.[2] They do so by modulating the tumor stroma upon 690 nm light activation by reducing the collagen density by 2.4-fold and fibroblast content by 39.4% in syngeneic CT1BA5 murine PDAC tumors. The nanoconstructs also block the PD-1/PD-L1 immune checkpoint more efficiently than free α-PD-L1 antibodies. Only a single sub-curative dose of activated nanoconstructs provides 54.1% tumor growth inhibition and prolongs overall survival in mice by 42.9%. Overall survival directly correlates with the degree of tumor self-delivery of the PD-L1 targeted nanoconstructs (Pearson's r=0.670, P=0.034), while no relationship was found for nanoconstructs containing the sham non-specific IgG. When applied over multiple cycles, as is typical for immune checkpoint therapy, treatment using these self-delivering immune checkpoint blocking nanoconstructs promises to offer durable tumor growth delay and significant survival benefits in PDAC patients, especially when used to promote self-delivery of integrated chemo-immunotherapy regimens.

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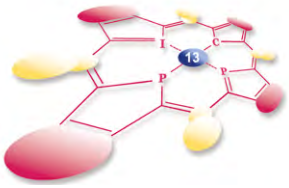

Gold Porphyrinoid-based Drugs with Anti-Cancer Activity

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The discovery of new chemotherapeutic agents against cancer represents an ongoing and important challenge to develop more efficient treatments. It was demonstrated for a long time, that some gold complexes are very active anticancer drugs, although the mechanism of action is still under debate.[1] In this study, we report the cytotoxic and phototoxic activity of a series of gold porphyrins and gold phthalocyanines (Figure). While gold porphyrins exhibit short-lived triplet excited states and thus very modest PDT activity,[2] we show in this work that the triplet excited state lifetime and singlet oxygen quantum yield of some gold phthalocyanines are significant. Moreover, the biological activity against four cancer lines (MCF-7, MDA-MB-231, Capan-2 and HCT116) indicates the real potential of gold phthalocyanines with lethal concentration (LC_{50}) in the range of few micromolar and even sub-micromolar for certain strains with very low toxicity against on healthy fibroblast cells (LC_{50} > 100 μM). Additionally, some gold phthalocyanines demonstrate some PDT activity on MCF-7 cancer cells upon light excitation. Overall, this study discloses the real potential of gold phthalocyanines as anticancer drugs.

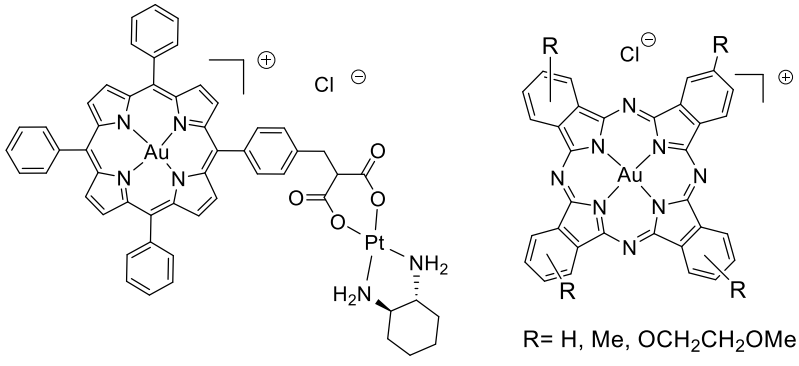

Figure. Structures of some gold porphyrins and gold phthalocyanines studied in this work.

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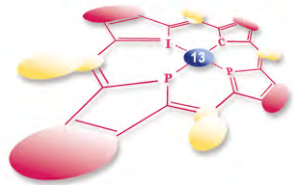

Excited-state Antiaromaticity in Metalloporphyrins and its Effect on Metal-Ligand Charge Transfer

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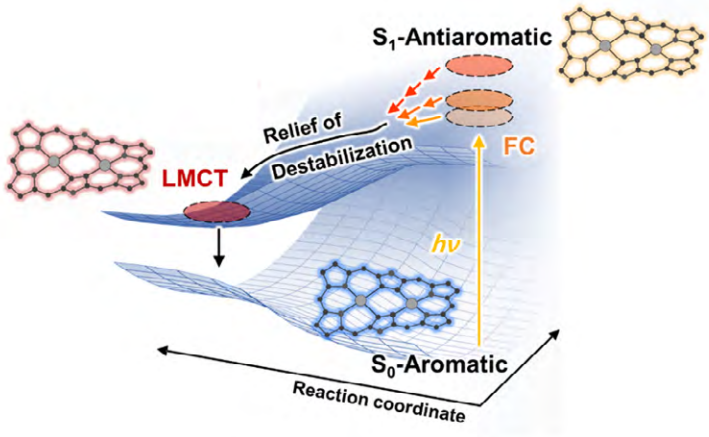
In recent times, excited-state aromaticity has emerged as a conceptual framework for describing excited-state behaviors. Referred to as Baird's rule, recent studies have rigorously confirmed that molecules exhibiting Hückel aromaticity in the ground state ([4n + 2]π) or antiaromaticity ([4n]π) undergo a reversal, transforming into Baird aromatic ([4n]π) or Baird antiaromatic ([4n + 2]π) configurations in excited states.[1] In these investigations, porphyrinoids have assumed pivotal roles in advancing our understanding of aromaticity reversal in excited states and its conceptual evolution. The distinctive structural and electronic characteristics of porphyrinoids, contingent upon their (anti)aromaticity, enable the direct observation of excited-state aromaticity reversal according to Baird's rule.[2] Explicit experimental demonstrations with porphyrinoids have significantly contributed to the conceptual development and application of Baird's rule in the realm of novel functional organic materials.[3] In this regard, we explored the effect of excited-state antiaromaticity on the ligand-to-metal charge transfer (LMCT) process of metallohexaphyrins. Due to the redox-like nature of charge transfer between the metal and ligand, the LMCT can be a means of avoiding energy destabilization from the excited-state antiaromaticity, which is demonstrated in our observation for a linear correlation between the ground-state aromaticity and time constant for the LMCT process.[4] These findings not only shed light on the influence of excited-state antiaromaticity on the behaviors of excited states but also offer valuable insights into the photochemistry of organic molecules.



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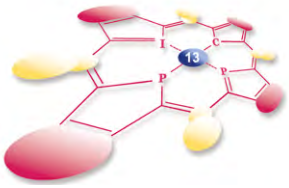

How anaerobic microbes use a nickel-tetrapyrrole to make and break methane: Mechanism of Methyl-Coenzyme M Reductase

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Abstract: One of the largest threats facing humanity is the increasing global concentration of greenhouse gases carbon dioxide and methane in the atmosphere, affecting rising sea levels, ocean acidification, and severe climate conditions. Methanogenic archaea are responsible for the production of 1 billion tons of methane per year and account for nearly all methane found on Earth. Methyl Coenzyme M Reductase (MCR), the key enzymatic catalyst in the anaerobic synthesis of methane (Equation 1), also catalyzes the reverse reaction - the anaerobic oxidation of methane (AOM). This protein is unique to methanogens and anaerobic methane oxidizers. MCR is one of the eight known Ni enzymes that catalyze the utilization and/or production of gases that play important roles in the global biological carbon cycle. MCR is the only enzyme containing a nickel tetrapyrrole (F430). It contains novel post-translational modifications in amino acid residues located at the surface of a 50 Å-long channel that accommodates the two substrates or the products. Spectroscopic and kinetic studies have demonstrated that the active state of the enzyme contains a low-valent and highly oxygen- and redox-sensitive Ni(I) state and that the metal ion appears to traverse three oxidation states (1+, 2+ and 3+) during catalysis. We will describe recent spectroscopic and structural studies that have identified a methyl radical at the transition state for methane synthesis. Other studies, including serial crystallography and X-ray spectroscopy, indicate that the active Ni(I) form of MCR exhibits significant active site rearrangements relative to the inactive Ni(II) form observed in all published structures. These results are leading to an enhanced understanding of how microbes make and break methane.

CH_3-SCoM + CoBSH → CH_4 + CoB-SS-CoM ΔG_0' = - 30 kJ/mol Equation.

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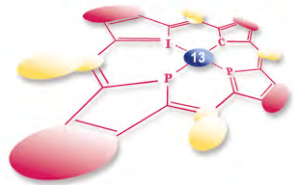

Near and short wave infrared microscopy and multimodal imaging to track biodistribution of photosensitizer nanocarriers, induce and visualize photodynamic action

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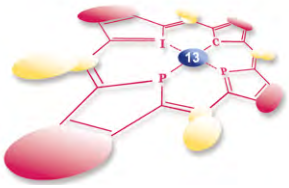
The use of near and short wave (NIR-SWIR) spectral regions opens new perspectives in the field of optical bioimaging due to a reduced attenuation of NIR-SWIR light by biological tissues and negligible autofluorescence in this range. Numerous bioimaging probes are being currently developed for NIR-SWIR imaging (e.g., fluorescence and photoacoustic imaging, FLI and PAI), delivering significantly improved imaging depth, resolution and signal-to-background ratio. A combination of a NIR-SWIR fluorescence/photoacoustic imaging contrast agent and photosensitiser (PS) on the same nanoplatform can allow for a "see-and-treat" approach with FLI/PAI guided photodynamic therapy (PDT) of cancer and other diseases. This talk will present our results on the applications of the nanoliposomal PS formulation equipped with NIR-SWIR FLI and PAI contrast agents, along with other medical imaging contrasts (i.e., computed tomography, CT, or magnetic resonance imaging, MRI) for multimodal microscopy imaging-guided, precisely localized vascular PDT in small animals (mice) in vivo. A microscale examination of photodynamic action, which also involved laser speckle contrast imaging (LSCI) of blood vessels, in addition to FLI and PAI, allowed us to assess an irradiation dose-dependent biological responses to PDT, including the vascular damage and self-healing, and reveal the irradiation-induced changes in the vessels morphology, volume and the blood flow rate. At the same time, the availability of MRI/CT imaging modalities provided us with the possibility to assess a whole body biodistribution at the macroscale. The developed approach allows for multimodal microscopy and imaging-guided, localized PDT; we employ it for theranostics of brain cancer and Alzheimer's disease in animal models.



Anion exchange of cyclo[8]pyrrole: polyoxometalate and phosphonate complexes

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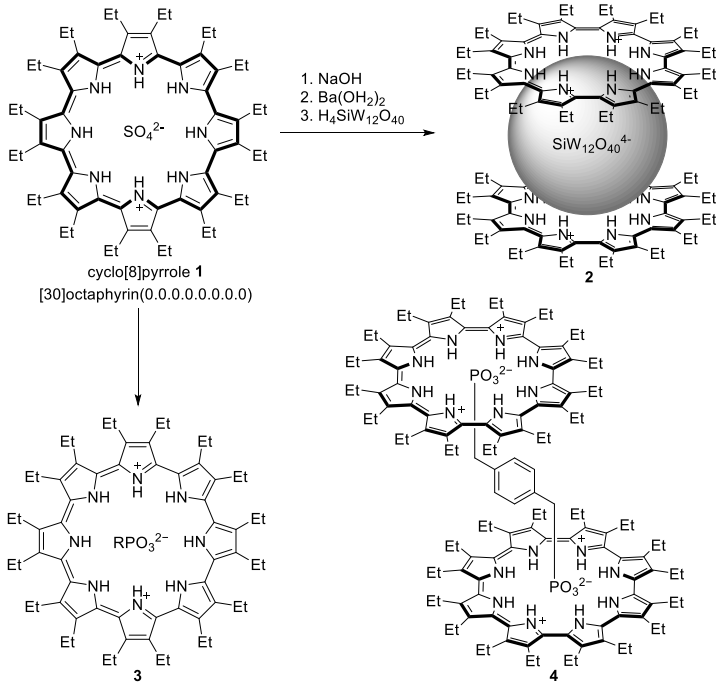
The first cyclo[n]pyrrole, a ring-expanded porphyrin without *meso*-bridges, was reported by Sessler in 2002.[1] Cyclo[8]pyrroles are usually synthesized via the oxidative coupling of 2,2'-bipyrrole with $FeCl_3$ and H_2SO_4, and isolated as sulfate salt. The absorption spectra show a weak B band at ca. 430 nm and a relatively intense L band at ca. 1100 nm. The photophysical, anion–binding, and liquid crystal properties of cyclo[8]pyrroles have been studied in-depth, along with their electronic structures. Dichloride salts of cyclo[8]pyrrole and smaller analogues can be isolated from oxidative coupling reactions in the presence of HCl.[2] Selective anion extraction from the aqueous layer, electron transfer, and kinetic analysis of the interaction of cyclo[8]pyrrole with anions have been reported, resulting from the unique anion-binding properties.[3] However, little is known about the isolation of the other anionic salts of cyclo[8]pyrrole.

We herein report the synthesis of the double-decker complex of cyclo[8]pyrrole coordinated with POM **2** and phosphonate complexes **3** and **4** based on the anion exchange method from sulfate **1**.[4] The POM and phosphate complexes **2**–**4** showed the B band at the visible region and the intense L band at the NIR region similar to **1**. The molecular structures were determined by the X-ray diffraction studies.



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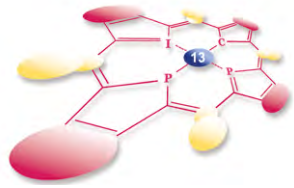

Unsymmetric Porphycene Synthesis: A Pathway to Novel Photofunctional Properties

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Porphycene is a unique functional dye that exhibits optical and redox properties different from those of porphyrins. [1] However, research into porphycenes is not as extensive as that into porphyrins, which is largely attributed to the complex and demanding multi-step synthesis required to produce porphycene.[2] Recognizing the importance of advanced synthetic studies of this compound, we are working on an approach that allows selective synthesis of unsymmetric porphycenes by successive intramolecular McMurry reactions using tetracarbonyl compounds as precursors (Figure 1).[3, 4] The substituents we are modifying include alkyl, cycloalkyl, phenyl, and thienyl groups. In this presentation, we will review our recent progress in the synthesis of unsymmetric porphycenes, exploring various tetracarbonyl precursors. We will also highlight the structural distortions induced by substituent modifications and discuss the resulting optical properties.

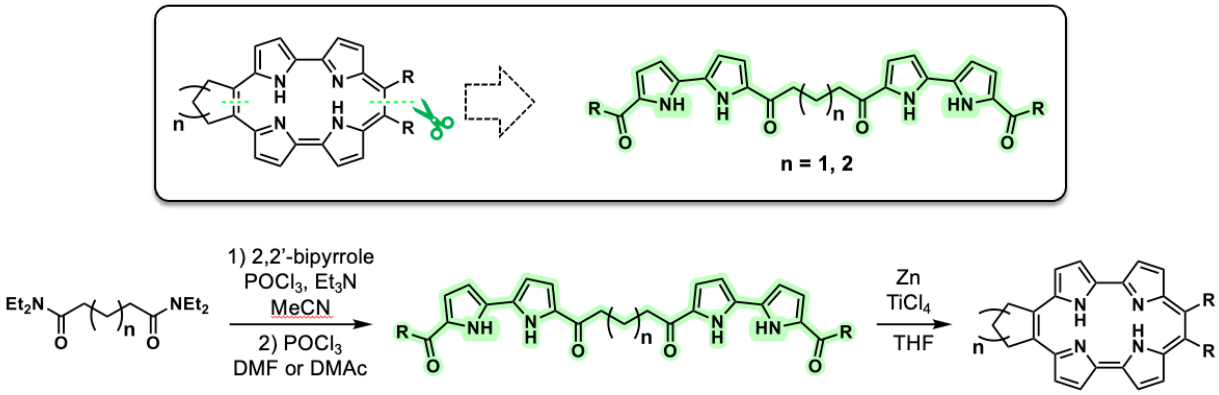

Figure 1. Synthesis of unsymmetric porphycene with tetracarbonyl compounds as precursors.

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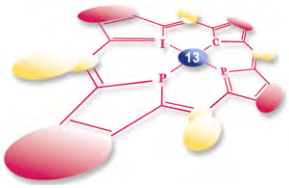

Redox tuning of reconstituted myoglobin with an artificial cofactor toward a highly reactive metal carbenoid species

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Hemoprotein is a useful scaffold to construct artificial metalloenzymes as well as natural enzyme models [1]. Our group previously demonstrated models of cobalamin-dependent methionine synthase by reconstitution of myoglobin with cobalt corrinoid cofactors [2]. The detailed investigation proposes the importance of redox potentials of metal centers toward both the formation and reactivity of the methyl complex as an intermediate in native catalysis. Recently, we have found a similar relationship in a metal carbenoid complex with porphyrinoid ligands toward olefin cyclopropanation [3].

Engineered hemoproteins are known to be promising catalysts for alkene cyclopropanation. However, most of them have little activity towards aliphatic alkenes due to the low reactivity of carbene species, an active intermediate. Here, we hypothesized that studies using myoglobins reconstituted with synthetic cofactors possessing various redox potentials would reveal a relationship between redox potential and cyclopropanation reactivity. In this work, iron porphyrins with two or one trifluoromethyl groups at the peripheral sites ($FePor(CF_3)_2$ and $FePorCF_3$, respectively), native heme and iron porphycene (FePc) were used as cofactors, and the range of Fe(II)/Fe(III) redox potentials of the four myoglobins exceeds 340 mV (Fig. 1). It was found that myoglobin with more positive redox potential shows higher reactivity toward inert alkenes. In particular, myoglobin reconstituted with $FePor(CF_3)_2$ ($rMb(FePor(CF_3)_2)$) exhibits a 165-fold higher turnover number for 1-octene cyclopropanation compared to native myoglobin. Mechanistic studies indicate that $rMb(FePor(CF_3)_2)$ generates an active species with a radical character. In contrast, myoglobin reconstituted with FePc provides a detectable iron–carbene species[2] with an electrophilic character. This work highlights the significance of the redox-focused design of the iron porphyrinoid cofactor in hemoproteins to enhance cyclopropanation reactivity.

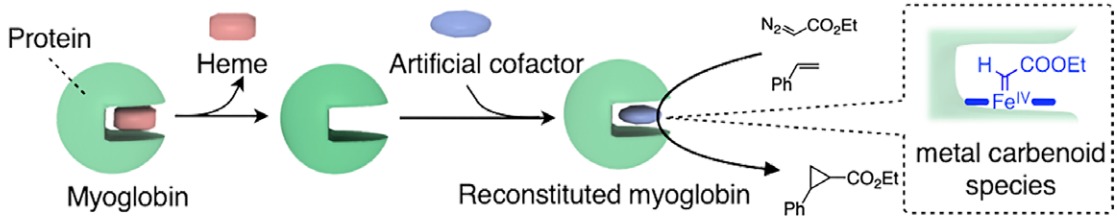

Figure 1. Catalytic cycropropanation via metal carbenoid species as an organometallic species in reconstituted myoglobin.

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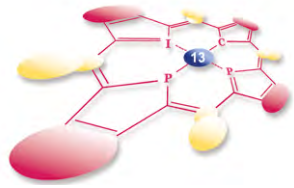

Flipping the Script on Hyperporphyrins: Spectroscopic and Electrochemical Evidence for Inverse Hypercorroles

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The four key frontier macrocycle-centered molecular orbitals (MOs) of porphyrins and corroles embodied by the Gouterman four-orbital model [1] are typically isolated from other metal-centered or substituent-centered π MOs and result in a classical porphyrin-type spectrum. However, when additional MOs fall within the energy range of these frontier orbitals, an atypical spectroscopic envelope is observed with additional NIR-absorptions and/or significant redshifts of the spectral bands. Gouterman [2] classified these systems as hyperporphyrins which he categorized into two distinct categories: p- and d-type whose spectral features stem from metal-to-ligand (MLCT) and ligand-to-metal (LMCT) charge transfer, respectively. As summarized in a recent account [3], Wamser later expanded on this by highlighting a third type of hyperporphyrin whose broad NIR bands stem from aryl-to-porphyrin, *i.e.*, ligand-to-ligand charge transfer (LLCT) transitions. In our recent work [4], a new hyper-spectra was defined as the antithesis of this behavior in which the broad, red-shifted spectral patterns are a result of *inverse* LLCT, *i.e.*, porphyrin-to-aryl charge transfers, observed more prominently in the case of trianionic corroles due to their electron-rich nature and ability to stabilize metals in higher oxidation states as compared to dianionic porphyrin ligands. This work will show this behavior depends not only on the electronic structure of the corrole (innocent *vs* noninnocent) but also on the position of the *meso*-substituents on the acceptor-type *meso*-phenyl rings and the number/type of axial ligands on various metallocorroles such as the one depicted Fig. 1.

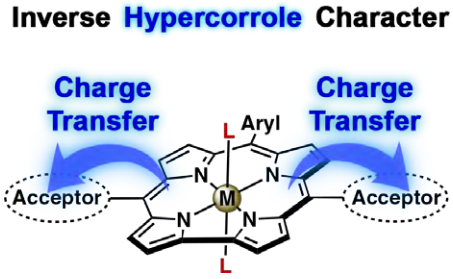

Fig. 1. Scheme depicting the inverse hypercorrole character for a general metallocorrole macrocycle.

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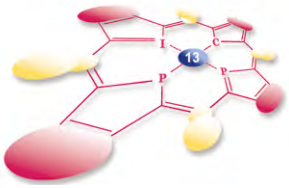

Coordination-Directed Assemblies of Porphyrins Bearing Coordination Sites

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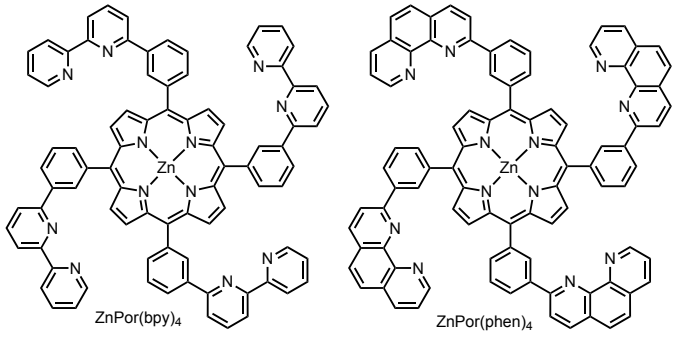
Porphyrins, when assembled into multi-porphyrin structures, not only exhibit altered spectroscopic and redox properties but also exhibit new properties and processes that are absent in individual porphyrins, such as energy transfer [1]. Among the various interactions employed for assembling, coordination interaction is notable as an effetive method for organizing porphyrins into well-organized supramolecular structures, mainly due to its inherent directionality and reversibility. There are two principal approaches to using coordination interactions for porphyrin assembly. The first involves the use of axial coordination to the central metal ions of metalloporphyrins. The second approach involves coordination between binding sites introduced into the periphery of the porphyrin and additional metal ions. Among the porphyrin assemblies constructed using the second approach, cofacial, face-to-face, dimers are partcularly interesting due to their potential applications as catalysts and host compounds [2]. In this study, we introduce a novel coordination-driven cofacial porphyrin dimer from a tetraphenylporphyrin derivative modifed with 2,2-bipyridine moieties at the meta positions of the phenyl groups (ZnPor(bpy)$_4$). Spectroscopic investigation has elucidated the binding processes and the structure in solution in detail. Initial zinc ion binding to the porphyrin hinders the subsequent zinc ion binding and the binding of the second porphyrin. However, once the dimer is formed, additional zinc ion binding is notably enhanced, resulting in a pronounced S-shaped binding curve. The detailed structure of the dimer in solution was established based on UV-vis spectroscopy, various ^{1}H NMR techniques and mass spectrometry. Notably, simulations of ring-current-induced chemical shift changes provided evidence for the face-to-face porphyrin structure with tetrahedral coordination of the bipyridine units. The stability of the dimer structure makes it promising for further exploration of this motif in developing new supramolecular structures and potential applications as host compounds and catalysts. We will also present results concerning related compounds, including ZnPor(phen)$_4$.



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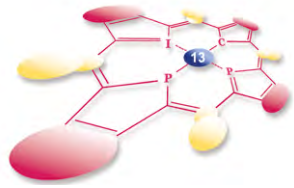

Photochemical lipid peroxidation: Targeting platinum resistance in ovarian cancer cells with distinct lipidomes

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Despite a favorable initial response, over 75% of ovarian cancer patients develop resistance to standard-of-care platinum-based chemotherapies and are consequently left with limited treatment options. Recent studies suggest that the same metabolic adaptations that drive chemoresistance can be leveraged to invoke ferroptosis — a regulated form of cell death driven by uncontrolled peroxidation of polyunsaturated fatty acids [1]. Despite the promise of this approach, existing ferroptosis inducers have unfavorable toxicity profiles and lack tumor selectivity, highlighting the need for alternative methods to induce ferroptosis and leverage its therapeutic capabilities. One such avenue may be in the form of photodynamic therapy (PDT). Peroxidation of lipids is an integral part of PDT mechanism and benzoporphyrin derivative (BPD)-enabled PDT has been recently shown to induce ferroptosis-like cell death [2]. This is relevant since intraperitoneal PDT is a promising adjunct modality for the post-surgical treatment of disseminated nodules in patients with advanced-stage ovarian cancer, and low-dose BPD-PDT has been shown to synergize with platinum-based chemotherapy [3]. Among the key areas that remain unexplored in the context of photochemical lipid peroxidation are (i) dependence on intrinsic cell lipid composition and (ii) relevance in photodynamic priming (PDP) to enhance platinum efficacy. This study investigates the potential of BPD-PDT to induce lipid peroxidation and enhance platinum efficacy in two human ovarian cancer cell lines: platinum-resistant OVCAR-3 and platinum-sensitive Caov-3 cells. An inverse relationship was found between susceptibility to platinum and ferroptosis: OVCAR-3 cells exhibited significantly higher sensitivity when treated with the pharmacological ferroptosis inducer ML210 compared to Caov-3 cells. Lipidomic profiling revealed that OVCAR-3 cells were enriched in phospholipids containing five to ten double bonds, whereas platinum-sensitive Caov-3 cells primarily contained phospholipids with zero to four double bonds. Intriguingly, BPD-PDT proved equally effective at inducing cell death and lipid peroxidation in both OVCAR-3 and Caov-3 cells suggesting it is agnostic to unsaturated lipid content. Finally, BPD-PDP re-sensitized OVCAR-3 cells to cisplatin in an *in vitro* perfusion model of platinum resistance, mimicking fluid shear stress of malignant ascites. These findings suggest that photochemical lipid peroxidation may be more ubiquitously applicable than canonical ferroptosis inducers and further exploration of its lipidomic signatures will inform the development of next-generation ferroptosis photoactive inducers to target platinum resistance.

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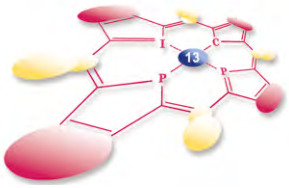

A New Spin on the Origin of Biological Homochirality

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Essential molecules of life—amino acids, nucleic acids, and sugars—are chiral; they exist in mirror-symmetrical pairs. However, biological systems exclusively use only one form of these pairs: right-handed sugars and nucleic acids, along with left-handed amino acids. This phenomenon characterizes life as homochiral. However, the origins of this asymmetry remain elusive, and it is this long-standing mystery that we address in our work. The chiral-induced spin selectivity (CISS) effect has established a strong coupling between electron spin and molecular chirality, and this coupling paves the way for breaking the chiral molecular symmetry by spin-selective processes [1]. Achiral magnetic surfaces, when spin-polarized, can function as chiral agents due to the CISS effect, serving as templates for the asymmetric crystallization of chiral molecules. We studied the spin-selective crystallization of racemic ribo-aminooxazoline (RAO), a central precursor of RNA, on magnetite surfaces—achieving homochirality in two crystallization steps [2]. Moreover, we have shown the chirality-induced avalanche magnetization of magnetite by RAO molecules, which verifies the reciprocal nature of the effect and allows for cooperative feedback between chiral molecules and magnetic surfaces [3]. Finally, based on empirical evidence, we propose a pathway through which the achieved homochirality in a single chiral compound, RAO, can efficiently propagate throughout the entire prebiotic network, starting from D-nucleic acids to L-peptides, and then to homochiral metabolites [4]. Our results demonstrate a prebiotically plausible way of achieving systems-level homochirality from completely racemic starting materials.

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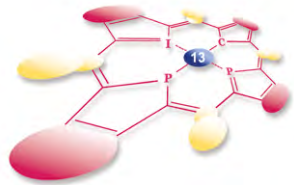

Metallaporphyrins – A young family of organometallic porphyrins

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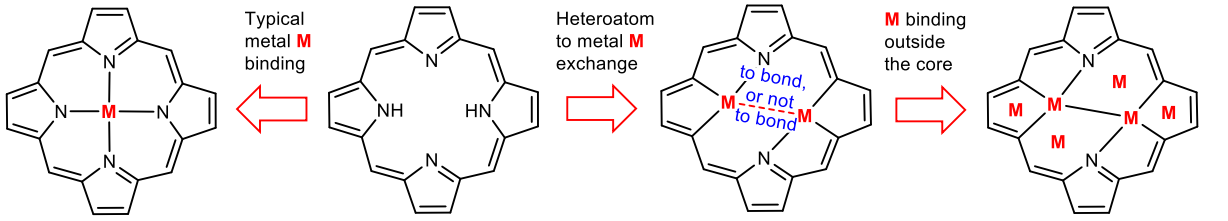
The idea of introducing transition metal atom(s) in place of the nitrogen atom(s) of the porphyrin core, instead of a typical metal ion coordination inside the 4N core, has led us to the creation of a family of metallaporphyrins[1-4]. The removal of two core donor atoms of a porphyrin allowed the accommodation of two transition metal ions, exemplified so far by the $Rh^{III}Rh^{III}$, $Rh^{III}Pt^{II}$, and $Rh^{III}Pt^{IV}$ pairs, in the center of the macrocyclic framework and practically within the porphyrin plane. The 18-π-electron aromatic circuit of a 21,23-dimetallaporphyrin plays a crucial role in the stabilization of the macrocycle and imposes the proximity of the two metal ions. The above metal ion pairs show different degrees of metal-metal interaction depending on the electronic structure of the central ions[4].

The specific coordination preferences of two metallic centers and their relatively large ionic radii impose a strong in-plane 21,23-dimetallaporphyrin deformation from the rectangular shape typical for 21,23-diheteroporphyrins with nonmetallic heteroatoms. The interplay between the macrocyclic constraints and the ion coordination preferences is reflected in the fluxional behaviour of 21,23-dimetallaporphyrins, involving alteration in the metal ion coordination sphere accompanied by changes in the macrocyclic skeleton conformation, studied in solution by ^{1}H NMR. The introduction of additional metal centers above and below the macrocyclic plane, bound by metal-metal and/or metal-π system interactions, leads to much more rigid and less aromatic, however, still very robust, multinuclear porphyrin-metal cluster hybrids.



Peripherial substituents and additional ligands at metal centers are not shown.

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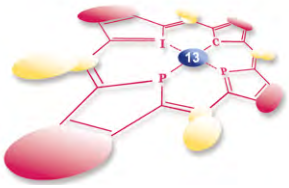

Engineering a novel dual-functioning protein complex for the treatment of hemolysis

Andre Francis Palmer

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Upon intravascular hemolysis (i.e. red blood cell lysis), cell-free hemoglobin (Hb) is released into the systemic circulation, which may subsequently release its iron-containing ligand – heme. Both cell-free Hb and heme are highly reactive and toxic species, that elicit vasoconstriction, systemic hypertension, and oxidative tissue injury. Under normal physiological conditions, the naturally occurring plasma proteins haptoglobin (Hp) and hemopexin (Hpx) scavenge and neutralize cell-free Hb and heme, respectively. Unfortunately, acute or chronic hemolytic conditions deplete these natural scavenger proteins, leading to harmful sequelae such as acute kidney injury and end-organ damage. In this talk, I will give an overview of techniques my lab has developed to purify Hp [1] and manufacture apohemoglobin (apoHb) [2], an analogue of Hpx generated by removing heme from Hb. Our purification strategies rely on simple observations that enable facile production of these proteins using tangential flow filtration, a scalable size-based separation system. I will then demonstrate how we can combine these two proteins – apoHb and Hp – to generate a single protein complex (apoHb-Hp) that can dually scavenge cell-free Hb and heme to treat hemolytic conditions [3-4].

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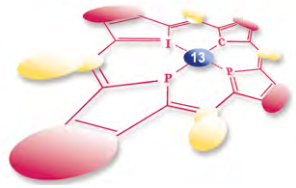

From organic chiral molecules to green energy

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Living organisms rely on chiral molecules, such as nucleic acids and proteins. A chiral molecule is not superimposable on its mirror image, also known as its enantiomer, just like our right hand cannot be superimposed on our left hand. Organisms contain only one enantiomeric form of a molecule, a selectivity that has prevailed through evolution. The chiral-induced spin selectivity (CISS) effect studied by us [1], can explain why enantiomeric purity might provide an advantage in biology [2]. CISS is an electronic phenomenon in which electron transmission through chiral molecules depends on the direction of the electron spin, a quantum mechanical property associated with its magnetic moment. Thus, charge displacement and transmission in chiral molecules generate a spin-polarized electron distribution. This effect: enhances electron transfer in proteins, enables nano-metric charge separation, and explains biorecognition [3].

The effect also explains the high efficiency of the multiple electrons process in biology (light harvesting and respiration). This understanding can be utilized to increase the employment of green energy by enhancing the efficiency and selectivity of the production process. Thus, improving in a significant way the efficiency of electrolyzers, fuel cells, batteries, and solar cells [4].

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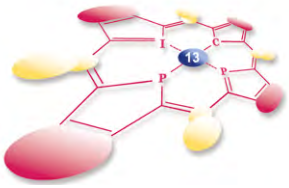

Photoluminescence metal-organic materials with multi-path photon conversion and energy transfer

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School of Chemistry, Sun Yat-Sen University

Taking advantage of multiple chromophore centers/origins combination in the metal-organic materials (MOMs), UV-OPA (one-photon absorption) or NIR-TPA (two-photon absorption) excited emissions with WLE (white light emitting), PLCT (photoluminescence color-tuning), or LPL (long persistent luminescence) attributes can be achieved. These PL properties are further coupled with structural transitions/deformations in coordination supramolecular matrices, resulting in controllable and multi-responsive thermo/solvato/rigido/piezo/mechano-fluorochromism, etc. Assembly and fabrication of these photo-functional MOMs into specific material morphologies or device models, various kinds of applications are implemented, including ultrasensitive water sensing, anti-counterfeiting, cell-imaging, and so on.

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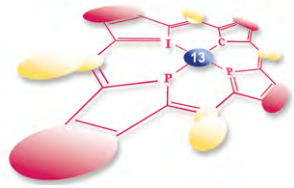

Design and Synthesis of New Functionalized Porphycenes & their Novel Complexation Chemistry

Anup Rana, Jodukathula Nagamaiah, Sameeta Sahoo, Katari Narmada, Arnab Dutta, Pradeepta K. Panda

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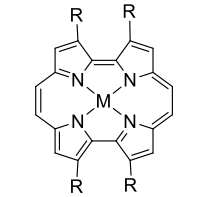
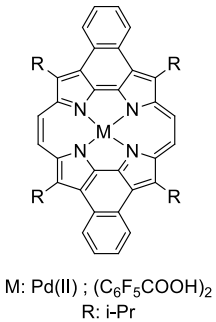
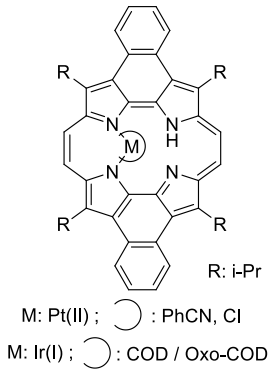
ORALS

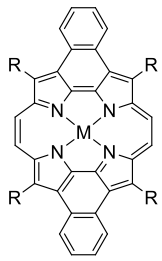
Porphycene is the first constitutional isomer of porphyrin to be reported by Vogel.[1] The presence of two bipyrrolic moieties, makes the macrocycle more sensitive to the effect of substituents at its periphery compared to its parent isomer porphyrin.[2] The synthetic difficulties associated with the preparation of bipyrroles limited the synthesis of porphycenes, conspicuous being the absence of 3,6,13,16-substituted analogues. We first employed the reductive dehalogenation approach to realize the first member of this series as 3,6,13,16-tetramethoxyporphycene.[3] Following its exciting chemistry, we developed a rational approach to synthesize the alkyl and aryl analogues.[4]

Separately, we found unusual out-of-plane *cis*-bimetallic and monometallic complexation in case of dinaphthoporphycene using palladium(II) salts.[5] This led us to explore the effect of substituents, metal ions, coligands and solvents in details.[6]









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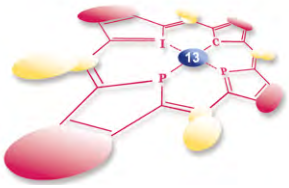

Photoacoustic Imaging and Photodynamic Therapy Efficacy of Polyacrylamide and Gold Nanoparticles Containing Near Infrared Photosensitizers

Kevin E. Siters[a], Farukh Durrani[b], Mykhaylo Dukh[b], Joseph Cacaccio[b], Steven G. Turowski[c], Joseph Spernyak[c] and Ravindra K Pandey[a,b]

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Magnetic resonance imaging (MRI), positron emission tomography (PET), X-ray and fluorescence are widely used in clinics for cancer imaging. These techniques offer several benefits; however, each technique suffers from certain limitations, including ionizing radiation, lack of depth penetration, and the ability to image tumors in real time.

We have developed certain nanoparticles that can be used for imaging tumors with non-invasive ultrasonic waves by Photoacoustic Tomography (PAT). Excitation of an endogenous or exogenous contrast agent can yield a detailed image with high spatial resolution and greater depth penetration if compared to ultrasound alone. Additionally, PAT provides imaging with real-time capabilities without the use of ionizing radiation. It is a non-invasive biomedical imaging modality, which generates ultrasonic waves by irradiating the material with a pulsed laser and reconstructs the image of light energy absorption distribution in the tissue. It could be a useful technology for imaging and photodynamic therapy of deeply seated tumors using long-wavelength photosensitizers.

In our laboratory, gold nanoparticles with and without photosensitizer conjugation have also been investigated as PAT contrast agents. In a preliminary study (*in vitro & in vivo*) both nanoparticles show promising imaging and therapy potential, and these results will be presented.

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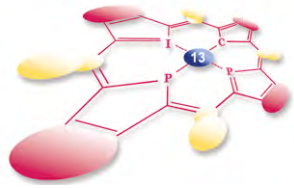

Chiral emissive thin films with phthalocyanines

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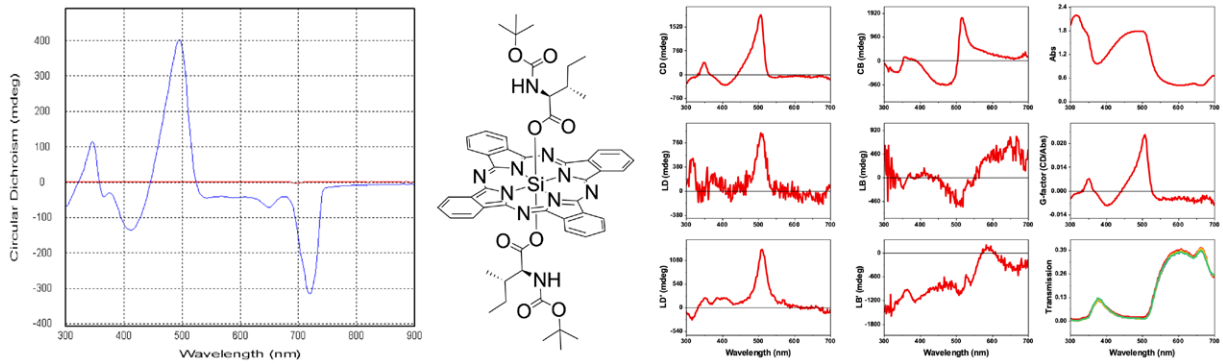
Chiral silicon phtalocyanines[1] have been used as dopants in the fabrication of chiral thin polymeric films using either inexpensive polystyrene or emissive F8BT as polymer substrates. The point chirality of the axial ligand of the silicon phthalocyanines leads to strong ellipticities observed on the phthalocyanine Q-band. These chiral phthalocyanines have been used in mixtures with polystyrene or F8BT (10-30% w/w dopants) to produce chiral thin films *via* spin-coating on fused silica plates. The film chirality has been investigated using benchtop spectrophotometers and CDi mapping to assess their homogeneity.[2] Mueller matrix polarimetry[3] has been used to dissect the contribution of linear dichroism and birefringence as well as circular birefringence and true circular dichroism in the observed response on conventional bench-top CD spectropolarimeters. The nature/size of the axial ligand and the solvent used to manufacture the thin films influence the chiroptical properties of these films. The F8BT films are emissive and display circular polarised luminescence with a large dissimetry factor.



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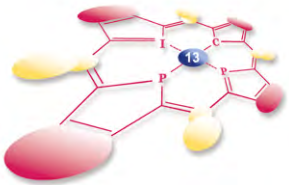

Visible-to-NIR Absorbing Phthalocyanine Derivatives for Optical, Electrochemical, and Photothermal Applications

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There has been a growing research interest in developing optical and optoelectronic devices based on organic macromolecules and their hybrid complexes. Particularly, substituted phthalocyanines (Pcs) have emerged as strong candidates, with remarkable chemical and thermal stability, distinct structural features, and unique coordination properties [1, 2]. In addition, they are well-known for outstanding spectral properties and fascinating electrochemical behaviors. Proper structural modification extended the long-wavelength absorption characteristics of Pc derivatives into the near-infrared (NIR) regions [3, 4]. Broad absorption in the visible-to-NIR ranges is significant because NIR-absorbing materials exhibited robust photothermal conversion behavior, garnering considerable attention for their versatile applications in photothermal control and energy conversion [5, 6].
Herein, we present an investigation of the spectral and electrochemical behaviors of substituted Pcs and their hybrid composite materials. The approach involves carefully designing and manipulating synthetic routes to yield peripherally and axially substituted Pc derivatives, either symmetrical or unsymmetrical. The strategic modification provides specific reaction sites, facilitating the formation of hybrid composites and thereby enhancing spectral and electrochemical performances. Moreover, the Pc's Q-band absorption is adjusted by introducing peripheral and non-peripheral substituents to the Pc aromatic rings and incorporating various transition metals in central core sites. The deliberate modification leads to a noticeable red shift in the Q-band, progressing toward the second near-infrared (NIR-II) region. The presentation elaborates on the synthesis and properties of Pcs and composite materials, providing an understanding of their optical, electrochemical, and photothermal applications.

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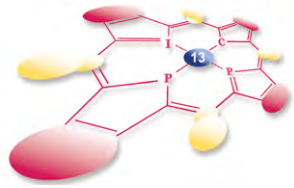

Switching Aromaticity in Doubly N-fused Bicyclic Expanded Porphyrins.

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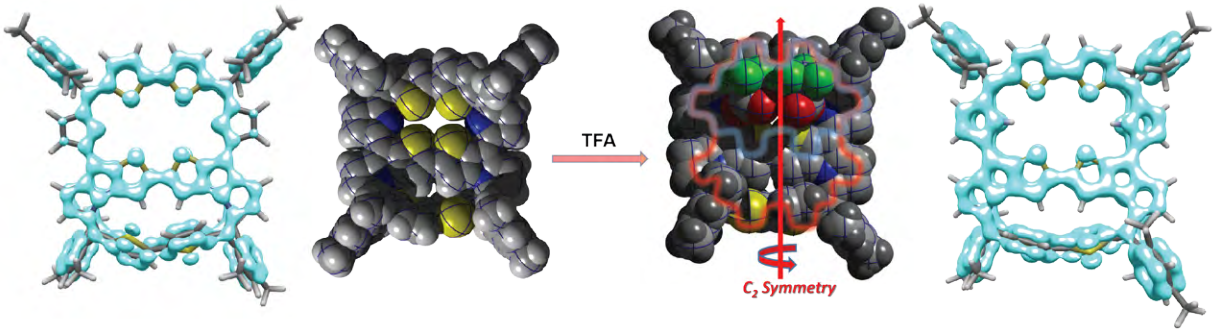
The notion of aromaticity has been one of the core concepts in organic chemistry for understanding and rationalizing the stability, structural, electronic, and magnetic properties of many cyclic π-electron delocalized systems and chemical reaction pathways. Among many molecular functional scaffolds, porphyrin and its analogues have been one of the prototypical systems to study the nature of aromaticity and related topics. For these materials, Hückel, Möbius, and/or Baird aromaticity rules have been mostly applied to rationalize their geometric, electronic, and magnetic features. Most of these systems in the literature have also been addressed as a monocyclic π-conjugated aromatic system, likely ascribed to one common criteria in the three aromaticity rules [1-5].

Here, we report the synthesis and characterization of doubly N-fused oligothiophene-bridged bicyclic expanded porphyrin derivatives. These derivatives possess unusual and interesting structural and electronic properties, including Möbius geometry and/or biradical spin states. Double N-fused bicyclic systems allow access to two or three different macrocyclic π-conjugated pathways. Controlling external stimuli including protonation, oxidation, and/or oxygen allows drastic changes in structural, electronic, and magnetic properties in comparison with the initial states. The nature and switching of aromaticity will be also addressed based on experimental results, including X-ray structural analyses, NMRs, EPR, optical absorption and emission properties as well as several quantum mechanical indices for aromaticity.



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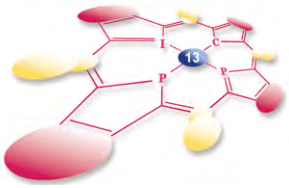

New Porphyrin- and Phthalocyanine-Based Dendrimers For Optics

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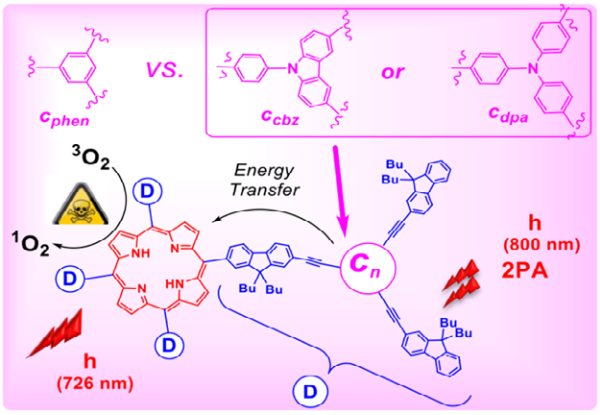
In 2004, we synthesised a porphyrin possessing four fluorenyl arms (**TFP**), with a remarkable high quantum yield (24%), compared to the reference **TPP**, demonstrating the capacity of the fluorenyl units to enhance quantum yields.[1] Then, to exploite this efficiency, a series of **Porphyrin Dendrimers** based on **TPP porphyrin core** and bearing, in a **non-conjugated** way, fluorenyl dendrons was prepared.[2-4] Different applications were exploited: as the fabrication of red Organic Light Emitting Diodes (OLEDs),[5-6] and supramolecular assemblies.[7] In 2016, a family of **conjugated** Porphyrin Dendrimers, still based on **TPP** was obtained.[8] More recently, a new family of conjugated porphyrin dendrimers based on promising **TFP-Bu** is tried.[9a,b] Last year, to improve light-harvesting, we explored new fluorene-based connectors in our dendrimers; the peripheral fluorenyl units are linked to the central tetrafluorenylporphyrin (**TFP**) core by original **fluorene-based connectors**[10] instead of the more classic 1,3,5-phenylene unit, and recently we tried **1,4-phenyl-{carbazol or diphenylamine}-based connectors.**[11] Very recently these **Dendrimers** were compared with **Star-shaped *meso*-substituted Porphyrins** with Fluorenyl-containing Arms. [12] All their detailed luminescence properties and selected photophysical properties are discussed in the frame of two-photon-induced theranostics.



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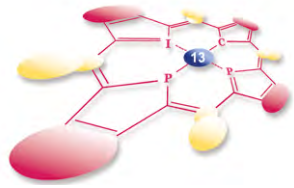

Synthesis of Porphyrins Through Continuous Flow Processes and Their Structural Effect on the Photoinactivation of Bacteria

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Nowadays bacterial infections are a global health concern, particularly due to the increasing resistance of microbes to currently available drugs. Multi-drug resistance (MDR) is a considerable challenge and novel approaches are needed to treat bacterial infections. Thus, novel molecules and therapeutic approaches are urgently needed. In this context, we highlight the use of porphyrins and their derivatives to photoinactive bacteria.[1]

Herein we describe a structure-activity study where a synergic effect, resulting from the combination of PDI with antimicrobial molecules like antibiotics or cinnamaldehyde, using a family of cationic di-imidazolyl porphyrins as photosensitizers, was observed.

We demonstrate that the combination of PDI with cinnamaldehyde known to alter bacteria cell membranes, offered synergic inactivation of *E. coli* (7 log CFU reduction), using just 50 nM of cationic di-imidazolyl with propyl-OH residues, (IP-H-OH^{2+}), and just 1.36 J/cm^2 light dose, Figure 1.

Additionally, new approaches for the development of photosensitive porphyrin-based antimicrobial materials for hospital applications like endotracheal tubes [2] will be discussed.

However, for *meso*-porphyrins to become ideal photosensitizers for clinical use in the future, large-scale synthetic processes need to be urgently developed. In this communication, we will revisit Lindsey and Pereira´s porphyrin synthetic methodologies [3,4] using continuous flow processes.

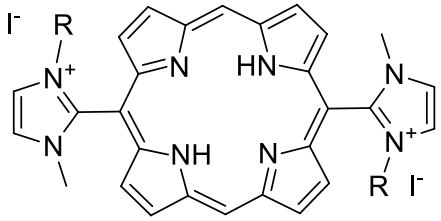

Figure 1: Photosensitizers for *E.coli* photoinactivation; R= CH_3; $CH_2CH_2CF_3$; $CH_2CH_2CH_2OH$ (IP-H-OH^{2+})

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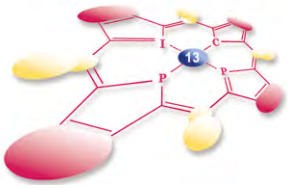

Antibody conjugates for cancer imaging and therapy

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Antibody modifications and labeling with porphyrinoids or positron emitters enable specific and selective fluorescent imaging or positron emission tomography (PET). Within the field of theranostics, these versatile agents find utility in both photodynamic therapy (porphyrinoid compounds) and systemic radionuclide therapy (endoradiotherapy). Despite their therapeutic potential, antibodies labeled with long-lived radioisotopes such as ^{89}Zr (t1/2 ~ 3.3 d) and ^{177}Lu (t1/2 ~ 6.6 d) pose a clinical challenge due to prolonged circulation times, resulting in elevated radiation doses to healthy tissues. This challenge is not exclusive to antibodies labelled with radioisotopes; antibodies directly conjugated with porphyrins also exhibit extended circulation times in the body. This presentation outlines strategies aimed at overcoming these limitations by leveraging pretargeted imaging and endoradiotherapeutic techniques [1, 2].

One promising strategy involves the inverse electron-demand Diels-Alder reaction between tetrazine (Tz) and trans-cyclooctene (TCO), which proves highly effective for *in vivo* pretargeting [3, 4]. Overall, the objective of *in vivo* pretargeted imaging and endoradiotherapy is to exploit the excellent tumor-targeting properties of immunoconjugates while mitigating the issues associated with their slow pharmacokinetics and high background doses. Pretargeting strategies decouple the targeting vector from the radioisotope at the time of injection.

In the case of Tz/TCO pretargeting, the TCO-labeled antibody is administered days before introducing a radiolabeled small molecule or a porphyrinoid. Only hours before imaging or endoradiotherapy, the radiolabeled small molecule or porphyrinoid rapidly circulates through the bloodstream, either forming a click chemistry bond with the TCO-labeled antibody or clearing from the living system. Pretargeted approaches offer the potential to achieve high activity uptake in tumors with minimal off-target radiation in non-target organs. This strategy holds promise for enhancing the therapeutic efficacy of both radioisotope and photodynamic therapies.

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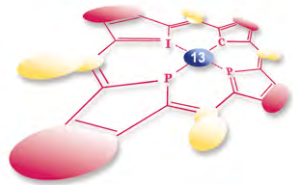

Use of Porphysomes for the accurate intra-operative detection of the primary tumour, lymph node metastases and intra-abdominal metastases in a model of endometrial cancer: A tool for image-guided resection

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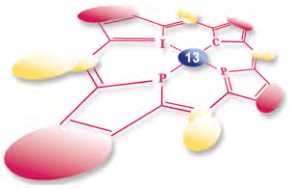
Objective: Establish the accuracy of intra-operative Porphysome fluorescence image-guided resection (PYRO-FGR) for the detection of uterine tumour, metastatic lymph nodes and abdominal metastases in a model of endometrial cancer.

Methods: Rabbits were inoculated with VX2 cells via intra-myometrial injection. At 30 days, Porphysomes were administered intravenously. At 24hrs the abdomen was imaged with a 675nm fluorescence endoscope. Fluorescent tissue was resected under image guidance (PYRO-FGR). Complete pelvic and para-aortic lymphadenectomies were performed after confirming remaining lymph node tissue was fluorescence negative. All resected tissue was examined for tumour by a gynecologic pathologist and histopathology including ultrastaging was used to detect VX2 cells in fluorescent tissue. Fluorescence signal to background intensity ratio (SBR) was calculated and VX2 (+) tissue was compared to VX2 (-) tissue. Biodistribution was calculated and fluorescent VX2 (+) tissue was compared to fluorescent VX2 (-) and non-fluorescent VX2 (-) tissue.

Results: 17 VX2 rabbits and 12 controls were used. 10 rabbits received a Porphysome dose of 4 mg/kg and 7 received 1mg/kg. 17 tumours, 76 lymph nodes (LN) and 50 abdominal metastases (AM) were fluorescence positive on PYRO-FGR and resected. Of these, 17 tumours, 60 LN and 45 AM were VX2 (+) and 16 LN and 5 AM were VX2 (-). 12 specimens were excluded from analysis due to incomplete assessment. 30 fluorescence-negative LN from lymphadenectomy specimens and 53 fluorescence-negative biopsies were resected. Two biopsies were VX2 (+) but no fluorescence-negative LN had identified tumour. Sensitivity and specificity of PYRO-FGR for VX2 (+) tissue for 1mg/kg was 96% / 84% for all tissue, 100% / 100% for uterine tumour, 100% / 67% for LN and 85% / 97% for AM respectively. For 4mg/kg the results were 100% / 75% for all tissues, 100% / 100% for uterine tumour, 100% / 63% for LN and 100% / 83% for AM respectively. Increased SBR was seen in all VX2 (+) tissue (p=0.041) and LN (p=0.032) in the 1mg/kg group when compared to the 4mg/kg group. Increased Porphysome uptake was seen in all fluorescent VX2 (+) in the 1mg/kg group (tumour (p=0.01) and LN (p=0.052)) when compared to the 4mg/kg group.

Conclusions: Porphysomes are a highly sensitive imaging agent for intra-operative fluorescence detection and resection of uterine tumour, metastatic lymph nodes and abdominal metastases. Low-dose administration improves specificity and decreases background fluorescence.



The Potential of Tetrapyrrolic Macrocycles as a Platform for Medical Imaging – From Mn(II/III) Redox Contrast Agents for MRI to Radiolabeled Contrast Agents for PET

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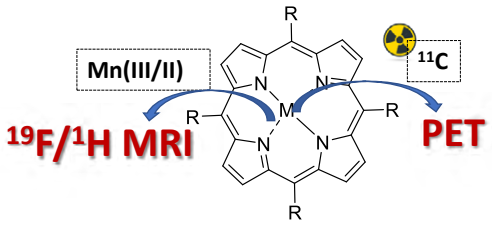

The World Health Organization (WHO) considers cancer as one the deadliest diseases worldwide. Thus, the development of effective therapies and early diagnostics is pivotal in combatting this threat. Indeed, early-stage diagnostics significantly enhance survival rates, enabling more efficient and cost-effective treatments. [1] We are deeply committed to advancing the field through the development of innovative tetrapyrrolic macrocycle-based probes.[2,3,4,5] These molecules showed promising properties for potential applications as redox-responsive MRI and PET Molecular Imaging probes. In this communication, we will present our recent findings regarding the synthesis of fluorinated imidazolyl porphyrins and their Mn(III/II) complexes as potential platforms for ^{19}F/^{1}H MRI and ^{11}C- PET. Mn(III/II) reduction studies by ascorbic acid, using UV-Vis spectroscopy, ^{19}F/^{1}H NMR, NMRD plots will be presented showing the potentiality for ^{19}F/^{1}H MRI. Also, the radiolabeling (^{11}C) synthesis of fluorinated imidazolyl porphyrins will be discussed.

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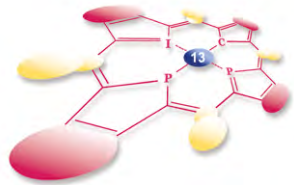

Redox properties of biological multiheme assemblies

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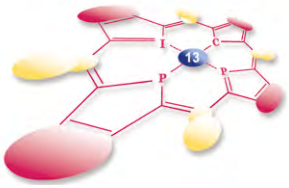
Multiheme proteins are important in energy conversion and biogeochemical cycles of nitrogen and sulfur. Redox properties of these assemblies depend not only on the ligands to the heme iron and how multiple hemes are arranged but also on the nature of the protein matrix surrounding them. A diheme cytochrome c_4 (c_4) was used as a model to elucidate the effects of the interdomain interface and charges on the protein surface on the redox properties of its two heme iron centers. Comparison of structural and redox properties of c_4 from different bacteria points to distinct scenarios in recognition of redox partners and roles in biological electron-transfer chains. Analyses of the isolated domains and similar monoheme proteins suggest that monoheme proteins arrange their polypeptides to enclose the heme edge. If this is not possible, the proteins dimerize. Affinity for dimerization depends on the oxidation state of the heme iron, reflecting the balance of hydrophobic and charged interactions at the interface. The potentials in c_4 proteins are tuned by heme solvent accessibility, interface properties, and surface charges. Phylogenetic analysis was used to identify polypeptide sequences that track the evolutionary relationship between two structurally similar c_4 proteins, one with apparent potentials of the two hemes being the same and the other with them being different by more than 100 mV. With this analysis, the effects of the polypeptide sequence on equalizing potentials are revealed. We present structural factors that tune potentials and cooperativity of metal centers in multiheme assemblies, important for multielectron delivery and guide redox-dependent complexation, important for unidirectional electron transfer.



Aluminum(III) Porphyrin Photosensitizers for Photosynthetic Reaction Center Models and Molecular Thermometer

Prashanth K. Poddutoori,[a] Stefan Charon,[a] Niloofar Zarrabi,[a] Jatan K. Sharma,[b] Paul A. Karr,[c] Art van der Est,[d] Francis D'Souza[b]

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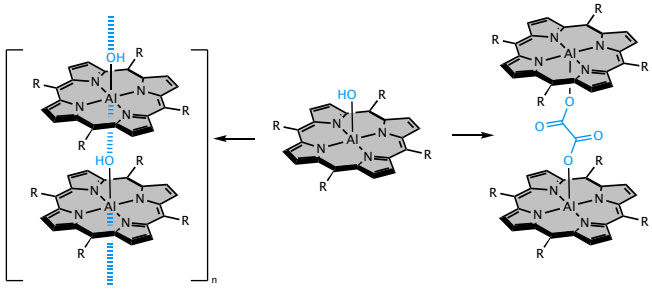
Aluminum(III) porphyrins are ideal candidates for the construction of multicomponent donor-acceptor systems.[1] Such systems can be easily assembled using the ability of the Al center to form axial covalent bonds with alcohols and carboxylic acids and using its Lewis acidity which allows coordination of Lewis bases.[2] Here we discuss some of our recent work on such systems, where AlPor can be utilized to form homodimers or multimers. The homodimer readily converted into donor-acceptor 'Homodimer-C_{60}' systems. Remarkably, this system mimics the primary photoinduced process of the photosynthetic systems which is electron transfer between chlorophyll special pair and pheophytin subunit. On the other hand, the same AlPors were also used to prepare multimer systems through a self-assembly strategy. Interestingly, these multimers exhibit strong aggregation-induced photophysical properties. Here, I will present some of these porphyrin systems and discuss their structural, redox, and remarkable photophysical properties.



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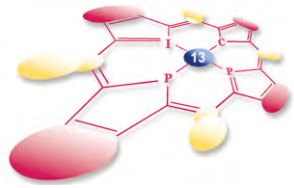

Preparation and biological evaluation of metallocorrole-bioconjugates for theranostic

Giuseppe Pomarico[a,c], Miriam Romano[b,c], Annalisa Radeghieri[b,c], Paolo Bergese[b,c], Federica Mandoj[d], Roberto Paolesse[d]

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The intense and tuneable interaction of porphyrinoids with visible light has enabled the use of tetrapyrrole derivatives as a diagnostic and therapeutic material.
Although lipophilic (and easily prepared) compounds usually have superior photophysical and cytotoxic characteristics, they suffer from limited solubility in aqueous systems. Some strategies can be pursued to overcome this limitation, making it possible to explore in biological fields luminescent phosphorus and silicon corrole complexes [1].
For example, the insertion of positively or negatively charged groups into the structure of macrocycles improves the affinity with water, but could also affect the biodistribution; alternatively, corrole/biomolecule bioconjugates can be proposed, based either on weak interactions or on covalent bonding, where the biosystem (proteins or nanoparticles) plays the role of the biocompatible shuttle system.
In the supramolecular approach, nanoaggregates composed of a core of P or Si complexes of tritolylcorrole coated with albumin layer(s) (the so-called protein corona) [2, 3] were prepared; albumin was chosen since it is the most abundant protein in the biological fluids. Bioconjugate stability, internalization mechanism, intracellular localization, and cytotoxicity toward cancerous and non-cancerous cell lines (A549 and MRC-5, respectively) were evaluated.

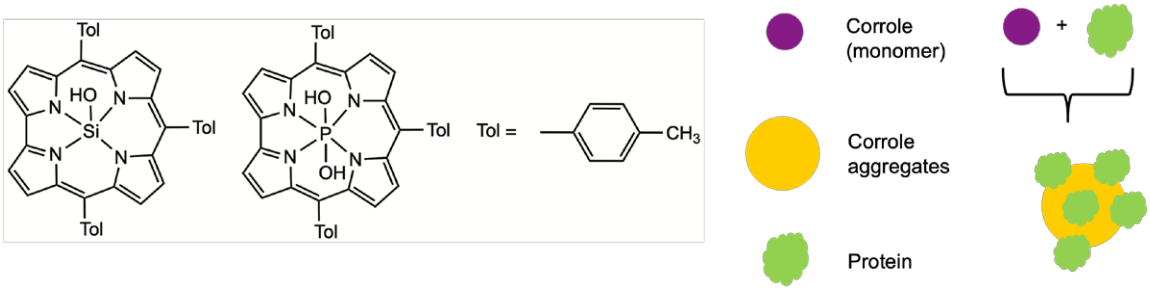

Figure 1. Structure of P and Si tritolylcorrole used in this work and procedure for nanoaggregates formation.

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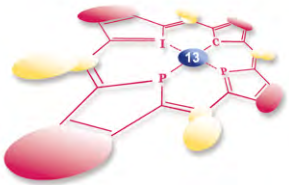

Supramolecular Assembly of Amphiphilic Dyes at the Air-Water Interface for the Synthesis of Quasi-two-dimensional Layers

Martin Presselt[a,b], **Sarah Jasmin Finkelmeyer**[a], **Anna Elmanova**[a,b], **Yisak Tsegazab**[a,b], **Maximilian Lutz Hupfer**[a]

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Supramolecular structures play a crucial role in defining the functionality of various thin films or membranes, which are applied in energy conversion or separation processes.[1, 2] It is often desirable that these structures exhibit a high degree of uniformity and a preferred orientation of their building blocks, thereby enhancing anisotropic charge, mass, or energy transport.[3, 4] In this talk, we will demonstrate that Langmuir-Blodgett and related techniques are exceptionally well-suited for fabricating such materials. Different dye classes[3, 5-7], *in situ* spectroscopy, photothermal deflection spectroscopy[8-11] and other methods will be discussed.

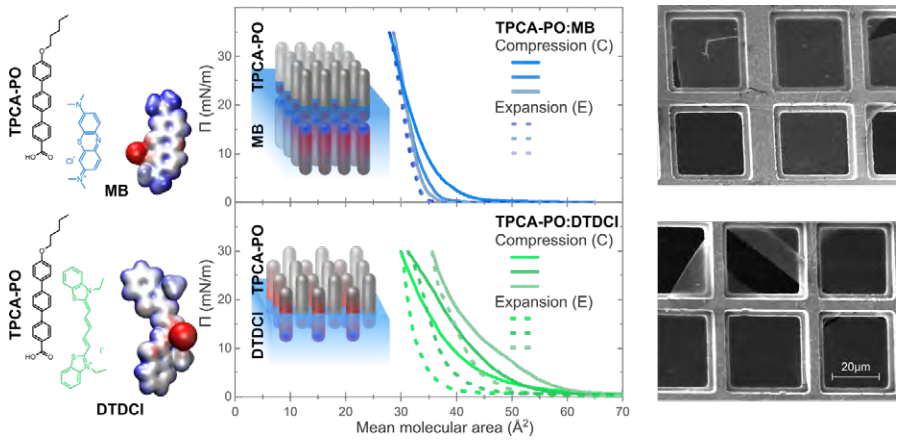

Fig. 1. Dyes, Langmuir isotherms, and scanning electron microscopy images of free-standing membranes

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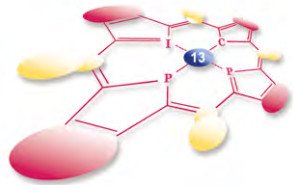


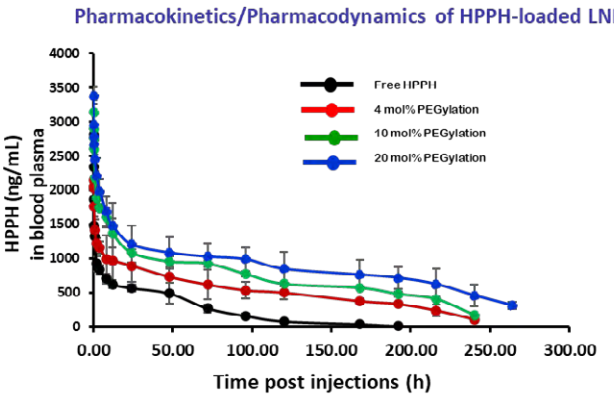
Tunable Lipid-based Nanomedicine for On-Demand Cancer Drug Delivery & NIH Funding Mechanisms Across the Career Path

Anu Puri

Center for Cancer Training, National Cancer Institute, National Institutes of Health, Rockville, MD 20850, USA.

ORALS

Cancer nanomedicine is a promising field for improved delivery of drugs and bioactive agents, including nucleic acids, and areas for further development for its clinical translation have been recognized [1]. Nanoparticles with desirable biodistribution characteristics, improved plasma stability as well as viable technologies for on-demand spatial and temporal release of loaded cargo from the nanoparticles are important for the clinical suitability of nanomedicine. Our research entails the development of tunable nanoparticles for site-specific cargo release by utilizing suitable light sources [2-4], and by designing novel cargo molecules [5]. The criteria include (i) selection of photosensitive molecules that can be activated by tissue-penetrating light sources with the preferred biological activity of their own, (ii) incorporation of these agents into nanoformulations without modifying their biophysical properties, (iii) minimization of off-target effects of the nanomedicine with no biological activity before photoactivation, and (iv) develop formulations with enhanced plasma stability, preferred tumor accumulation and enhanced tumor cure. These strategies and results will be discussed. Lastly, I will also provide a brief overview of various career development opportunities and programs available at the NCI, and NIH, which are geared to invite and enhance the participation of the next generation of cancer researchers. The broad objective of these programs is to enhance the impact on future scientific research to enable the cure of patients suffering from cancer



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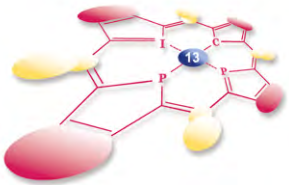

Silicon Oxide-Based Microchips Functionalized with Fluorescent Probes and Photosensitizers for Intracellular Sensing and Photodynamic Therapy Applications

Lluïsa Pérez-García[a,b,c], Saman Bagherpour[a,b], Gordon Bruce[c], Snow Stolnik[d], Marta Duch[e], Maribel Arjona[e], Jose Antonio Plaza[e], Consuelo González-Manchón[f], Patricia Vázquez[f], Mariano Redondo-Horcajo[f], Teresa Suárez[f]

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ORALS

Microparticles, such as biodegradable polymers or inhalable microparticles are emerging as versatile carriers for drug delivery, offering controlled release and targeted administration[1], and their functionalization makes them active for biosensing or therapeutical applications[2, 3]. We have prepared different BODIPY derivatives as glutathione (GSH) sensors, conjugated them to silicon oxide microchips, and monitored in real-time the intracellular GSH levels. Furthermore, an aminoporphyrin derivative was either supramolecularly encapsulated -using an imidazolium-gemini amphiphile- or conjugated to the surface of the microchips, to show enhanced cell internalization and phototoxicity using HeLa and Raw 264.7 cell lines.

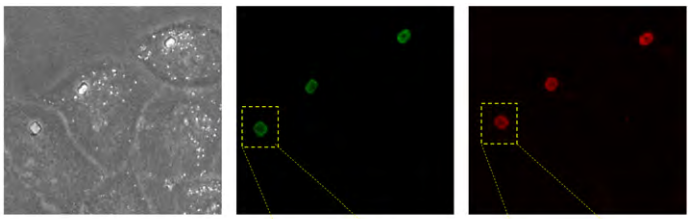

Figure: Silicon oxide microchips for intracellular GSH sensing.

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ORALS

Components of Bovis Calculus and neurological disorders: Evidence from the Mendelian Randomization study

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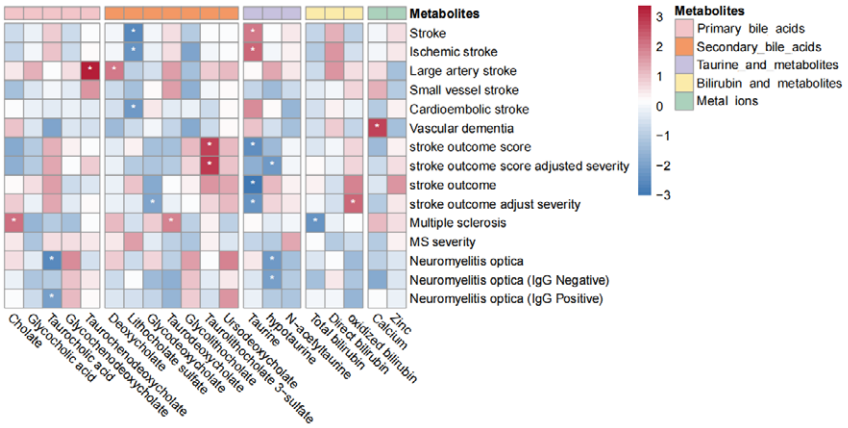
Bovis Calculus, a traditional Chinese medicine with complex components, such as bile acids, bilirubin and taurine, has been widely applied to treat various diseases, including stroke and epilepsy, among others for over 2000 years with unclear therapeutic mechanisms[1-2]. To identify specific roles of Bovis Calculus, we estimate the causal effects of 20 plasma metabolites it includes on various neurological disorders, as well as their causal relationships with brain structures in a two-sample Mendelian randomization framework. We found that higher plasma lithocholate sulfate level protects against stroke (OR, 0.960; 95%CI, 0.930-0.991), particularly ischemic (OR, 0.960; 95%CI, 0.927-0.993) and cardioembolic stroke (OR, 0.901; 95%CI, 0.821-0.990). Higher taurine (OR, 0.668; 95%CI, 0.514-0.869) and hypotaurine (OR, 0.723; 95%CI, 0.542-0.965) levels are associated with a reduction in the severity of stroke. Elevated bilirubin levels help to prevent multiple sclerosis (OR, 0.817; 95%CI, 0.688-0.967), and hypotaurine levels defend against neuromyelitis optica (OR, 0.504; 95%CI, 0.270-0.941). Conversely, Mendelian randomization supports cholate and taurochenodeoxycholic as risk factors for multiple sclerosis (OR, 1.189; 95%CI, 1.014-1.395) and large artery stroke (OR, 1.342; 95%CI, 1.131-1.592), respectively. Consistent with the relationship with neurological disorders, elevated concentration of lithocholate sulfate and bilirubin was identified to enhance the integrity of multiple white matter structures. While bile salts and taurochenodeoxycholic acid exhibit negative effects. Our results contribute to revealing the directionality of the causal relationship between the specific components of Bovis Calculus and neurological disorders, providing novel ideas for optimizing the composition and compatibility of artificial Bovis Calculus.



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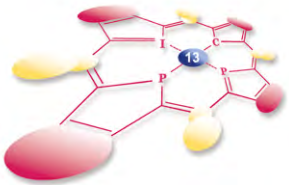

Photoactivatable BODIPYs for Bioimaging Applications

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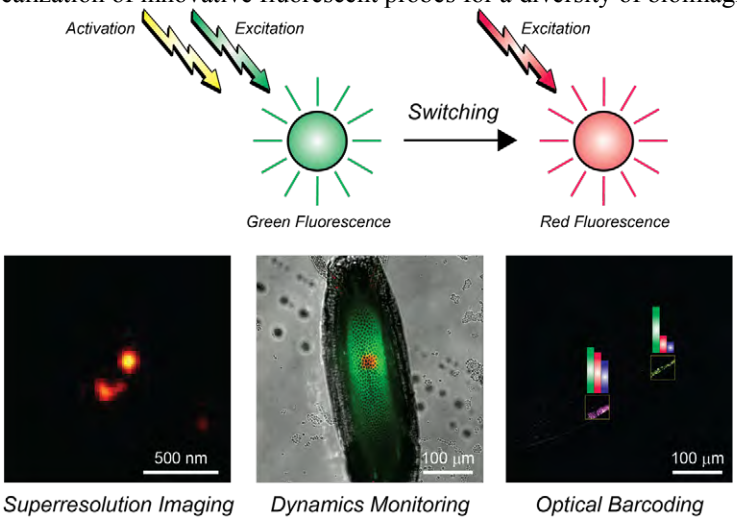
Laboratory for Molecular Photonics, Department of Chemistry, University of Miami

The goal of our research program is the identification of operating principles to switch fluorescence under optical control in order to develop photoactivatable fluorophores for bioimaging applications.[1–5] We design molecules capable of interconverting between states with distinct emission properties upon illumination at an appropriate activation wavelength. Their photochemical transformations enable the activation of fluorescence within a defined region of space at a specific interval of time in a given sample of interest. Such a level of spatiotemporal control provides the opportunity to overcome diffraction and reconstruct fluorescence images with spatial resolution at the nanoscale. It also permits the monitoring of dynamic events in real time with the sequential acquisition of fluorescence images. We are particularly interested in adapting these mechanisms for fluorescence photoswitching to allow the visualization of intracellular targets with nanoscaled resolution in live cells as well as the tracking of translocating species in live organisms. Thus, our fundamental investigations on molecular switches can eventually lead to the realization of innovative fluorescent probes for a diversity of bioimaging applications.



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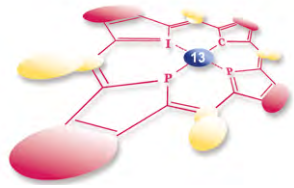

Parity-Forbidden Excited States in Zinc Tetraphenylporphyrin and Zinc Octaethylporphyrin Revisited by Fluorescence- and Nonlinear Absorption-Based Two-Photon Spectroscopy

Aleksander Rebane[a,b], Charles Stark[b], Aleksander Trummal[b], Merle Uudsemaa[b], Meelis-Mait Sildoja[b], Katrin Petritsenko[b] and Juri Pahapill[b]

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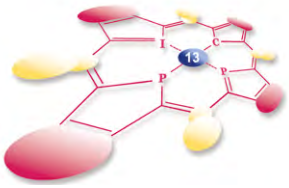
ORALS

Zinc tetraphenylporphin (ZnTPP) and zinc-octaethylporphin (ZnOEP) are ubiquitous natural pigments, which exhibit strong Soret band absorption in the blue range of spectrum coupled to high photochemical stability making them useful for various applications ranging from photovoltaics to photodynamic therapy. Due to the nominal inversion symmetry, the purely electronic transitions obey Laporte rule stating that one-photon and two-photon transitions are mutually exclusive due to parity considerations.

Even though in the past decades much interest has been devoted to both experimental and theoretical studies of two-photon transitions to gerade-parity excited energy levels located close- and above the Sortet band, reliable characterization of these important spectroscopic features has been lacking.

In our paper we present a detailed experimental study of the two-photon absorption spectra of ZnTPP and ZnOEP in a broad range of excitation wavelengths covering both the Soret region as well as the lower-energy Q-bands, using both the fluorescence excitation techniques as well as (non-fluorescence-based) nonlinear transmittance measurement. Our experimental results are corroborated by quantum-chemical calculations, thus allowing us to reliably quantify spectroscopic properties of two-photon allowed excited states in these two important model systems.



Heme Self Association and Stability of Heme:Protein Complexes

Kenton R. Rodgers, Olivia R. Stiller, Gudrun S. Lukat-Rodgers

North Dakota State University, Department of Chemistry & Biochemistry, Fargo, ND

Hemes are well-known to self-associate in aqueous solutions.[1, 2] The stabilities of their oligomers complicate the determination of stability constants for heme:protein complexes by the most widely used method, UV-visible spectrophotometric titration. Awareness of in-vivo heme distribution and heme trafficking has seen steep growth in recent decades and continues to emerge. Quantitative understanding of heme pathways and the interplay between them will rely on accurate and precise knowledge of the relative stabilities of heme complexes with proteins and enzymes involved in these pathways. In this presentation, kinetic and thermodynamic parameters relevant to the self-association of multiple hemes along with their impact on the formation and stabilities of heme:protein complexes will be discussed.

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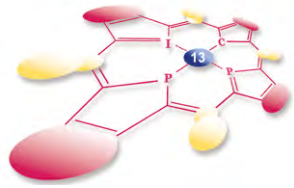

Porphyrin-Based Supramolecular Nanocapsules as Masks for Regioselective Functionalization of Fullerenes

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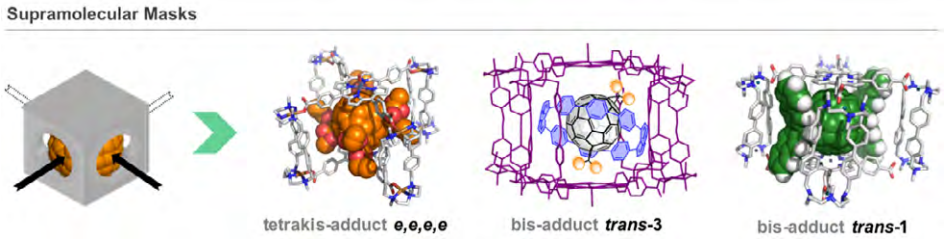
The regioselective functionalization of fullerenes and the control of the number of adducts is highly important to unbar the development of fullerene chemistry. Nowadays, easy-accessible C_{60} and C_{70} fullerene mono-adducts are mainly used in any application[1] due to the hampered accessibility to pure alternative fullerene poly-adduct derivatives. In a general basis, multi-adduct mixtures with uncontrolled regioselectivity (multi-isomers) are obtained, and chromatographic purification is too costly and time consuming to be used in the synthesis of multi-adduct fullerene species. Herein, porphyrin-based supramolecular nanocapsules[2,3] are used as supramolecular shadow masks to tame the over-reactivity of Bingel-Hirsch-type cyclopropanation reactions and, more importantly, to have full control on the equatorial regioselectivity and on the number of additions. Thus, exclusively equatorial bis-, tris- and tetrakis-C_{60} adducts using ethyl-bromomalonate are stepwise obtained and fully characterized (NMR, UV-vis and XRD). Furthermore, the regioselectivity control is finely tuned using a three-shell Matryoshka-like assembly towards the synthesis of a single *trans*-3 bis-Bingel-C_{60} for the first time.[4] Also, the mask strategy is extended to Diels Alder reactions with full control of the regiolectivity in the synthesis of *trans*-1 bis-pentacene-C_{60}.[5] These results, fully attributed to the confinement control imposed by the capsule's cavity, represent a novel and unique strategy to infer regio-control to the synthesis of fullerene multi-adducts. We envision that the described protocol will produce a plethora of derivatives for applications such as solar cells.



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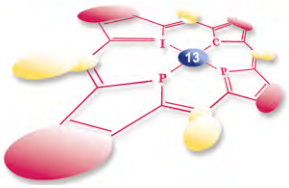
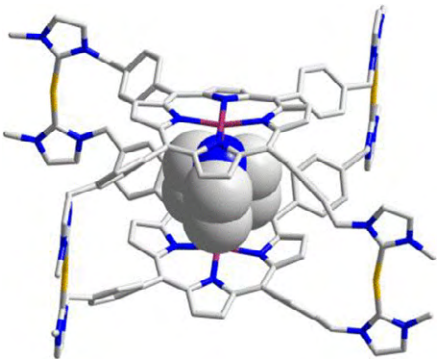


Porphyrin Cages Assembled from Carbene-Metal Bonds

Sébastien Richeter[a], Ludivine Poyac[a], Clémence Rose[a], Sébastien Clément[a],

[a]*Institut Charles Gerhardt Montpellier, University of Montpellier, CNRS, ENSCM, Montpellier, France*

N-heterocyclic carbenes (NHCs) and porphyrins have become ubiquitous ligands in the fields of organometallic chemistry and catalysis.[1] Over the last decade, NHCs have also emerged as promising ligands for the synthesis of metallosupramolecular architectures featuring M−C_{NHC} bonds.[2] For this purpose, numerous poly-NHC ligands were reported in the literature allowing the formation of discrete assemblies of various sizes and shapes. Here, we show that porphyrins equipped with imidazolium salts on the *para* positions of the four *meso* aryl groups can be used as NHC precursors for the synthesis of porphyrin cages assembled from eight M−C_{NHC} bonds.[3] Silver(I) was used to assemble metal ions because they form labile bonds with NHC ligands enabling the formation of thermodynamic products which are self-assembled porphyrin dimers with a face-to-face orientation. Moreover, the ability of Ag(I)−C_{NHC} bonds offers the possibility to generate new structures by transmetalation reactions forming more stable bonds like Au(I)−C_{NHC} with retention of the metallosupramolecular structures. Host-guest chemistry is feasible with porphyrin cages incorporating flexible linkers between porphyrins and NHC ligands. Indeed, the inner space between the two porphyrins of these cages expands enough to allow the encapsulation of guest molecules like water molecules or 1,4-diazabicyclo[2.2.2]octane (DABCO, see below).[4] The corresponding cages with Co(II) porphyrins were also synthesized because of performing the electrocatalytic O_2 reduction reaction (ORR).



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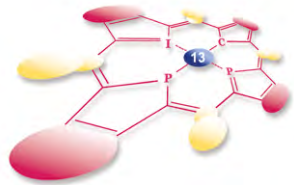

Interactions of Hydroxylamines and Aldoximes with Synthetic Metalloporphyrins

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ORALS

Heme enzymes are involved in the binding and metabolism of various RNHxOy compounds such as alky/arylhydroxylamines and oximes. The simplest hydroxylamine (NH_2OH) has been identified as an intermediate in enzymatic nitrite reduction and in hydrazine biosynthesis and is a substrate for the multiheme enzyme hydroxylamine oxidoreductase. The *N*-binding mode of NH_2OH appears to be the dominant feature of its binding to the Fe centers of the heme proteins, at least for the heme biomolecules studied to date. Alkylhydroxylamines such as *N*-hydroxyamphetamine (AmphNHOH) and arylhydroxylamines such as PhNHOH are biologically relevant species that have been shown to engage with heme Fe centers in various heme proteins. However, atomic-level structural information of their binding to heme has to a large degree remained elusive.

Oximes of the form RCH=NOH play important biological roles in the regulation of plant growth and defense, and in plant communication with the environment. The role of heme in oxime metabolism is gaining increased attention. In particular, a relatively new class of heme enzymes has been reported that catalyzes the dehydration of aldoximes to nitriles.

Our research laboratory has been interested in determining the structural and electronic factors that control the heme-enabled binding and activation of organo-NHxOy compounds. We reported the preparation and X-ray structural characterization of *N*-hydroxyamphetamine adducts of Fe porphyrins [1]. We determined that the AmphNHOH ligand displayed the expected *N*-binding mode to the Fe center. What was unexpected was the observation of an unprecedented intramolecular H-bond between the hydroxylamine-O*H* proton and a porphyrin N-atom. Density functional theory (DFT) calculations support the presence of this intramolecular H-bond in the optimized structure. We determined, using a natural bond order (NBO) analysis, that the intramolecular H-bond comprises a donor pi N=C (porphyrin) to acceptor sigma* O–H (hydroxylamine) interaction of 3.04 kcal/mol. We showed that this intramolecular H-bond was also present in a cobalt porphyrin analogue.

We have subsequently shown that such an intramolecular H-bond with a donor pi N=C (porphyrin) to acceptor sigma* O–H (hydroxylamine) interaction is also present in an X-ray crystal structure of an arylhydroxylamine (PhNHOH) complex containing a second-row transition metalloporphyrin, specifically (TPP)Rh(PhNHOH)(C_6H_4Cl) [2], raising the possibility that such intramolecular H-bonds may be common in the absence of competing H-bond interactions (e.g., distal pocket H-bonding residues). Interestingly, we also show by DFT calculations that these internal H-bonds are feasible for biologically relevant and synthetic aldoximes such as butyraldoxime. We have since shown by X-ray crystallography that the intramolecular H-bond may be present in some oxime adducts of metalloporphyrins but not others. The relevance of these observations to the metabolism of RNHxOy compounds will be discussed. [Funded by the U.S. NSF; grants CHE-2154603, -2102071, -1900181]

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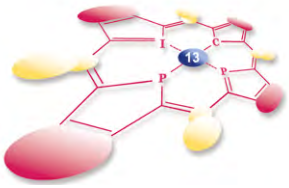

The mobilization of iron stored in bacterioferritin requires heme, which is indispensable for metabolic homeostasis in bacteria

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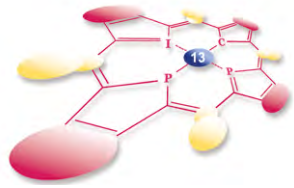
A key component of iron metabolism is the compartmentalization of Fe^{3+} in bacterioferritin and its subsequent mobilization as Fe^{2+} to satisfy metabolic requirements. In *P. aeruginosa*, Fe^{3+} is compartmentalized in bacterioferritin (Bfr). Its mobilization to the cytosol requires the binding of a ferredoxin (Bfd) to reduce the stored Fe^{3+} and release the soluble Fe^{2+}. This presentation will discuss evidence demonstrating that blocking the Bfr-Bfd complex in *P. aeruginosa* by deletion of the *bfd* gene triggers an irreversible accumulation of Fe^{3+} in Bfr, concomitant cytosolic iron deficient, metabolic dysregulation, and impaired biofilm development. It will also discuss results from a structure-guided campaign that enabled the discovery of small molecule inhibitors of the BfrB-Bfd complex. Studies conducted with surface-attached biofilms grown in flow cells, or with pellicle biofilms grown at the air-liquid interface showed that the inhibitors are bactericidal to *P. aeruginosa* cells in mature biofilms. These findings expose a rare weakness of *P. aeruginosa* biofilms, and the conservation in the Bfr and Bfd amino acid sequences from *P. aeruginosa*, *Acinetobacter baumannii*, and *Klebsiella pneumoniae* suggest the inhibitors may also be active against these pathogens.



Catalytic reduction of CO_2 beyond 2 electrons with molecular complexes

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Reduction of carbon dioxide has as its main objective the production of useful organic compounds and fuels - *renewable fuels* - in which solar energy would be stored. Molecular catalysts can be employed to reach this goal, either in photochemical or electrochemical (or combined) contexts. They may in particular provide excellent selectivity thanks to easy tuning of the electronic properties at the metal and of the ligand second and third coordination sphere. Recently we have shown that such molecular catalysts may also be tuned for generating highly reduced products such as formaldehyde, methanol and methane, leading to new exciting advancements. [1-5] Obtaining C-C coupling products is an additional intriguing possibility. Our recent results will be discussed, using earth-abundant metal (Fe, Co) porphyrins and phthalocyanines as well as related complexes as catalysts.

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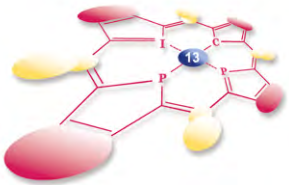

Subporphyrazine-based photoswitches and extended-conjugated systems

M. Salomé Rodríguez Morgade[a,b], **Elena Cañizares-Espada**[a], **Gema Pérez de Bustos**[a], **Tomás Torres**[a,b]

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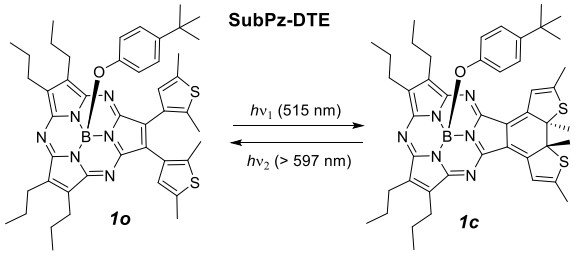
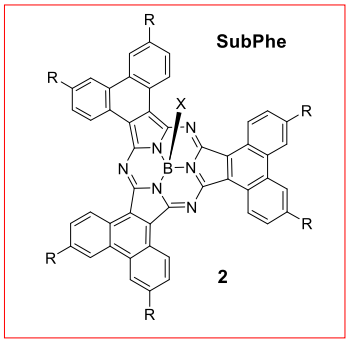
Subporphyrazines (SubPzs) are a class of curved, aromatic macrocycles that consist of three pyrrole subunits connected through their 2,5-positions by *aza*-bridges.[1] As for all the other subporphyrinoids, SubPzs are cone-shaped, contain a 14 π-electron aromatic circuit and exclusively coordinate boron(III).[2] As distinctive features, these dyes show exceptional electronic tunability by peripheral functionalization, arising from an unusually strong influence of the directly attached peripheral substituents on the SubPz π-system. Besides, SubPzs contain a quasi-isolated C_β=C_β bond that is not included in the 14 π-electron circuit. This feature provides an additional tool to chemically manipulate these macrocycles and design chromophores with properties that are virtually inaccessible within macrocycles bearing fused rings. Taking advantage of this structural peculiarity, we are developing photo-responsive SubPzs that behave as molecular switches activated by >500 nm visible light. These devices consist in blended subporphyrazine-dithienylethene systems (**SubPz-DTE**) wherein the DTE can reversibly switch near infrared SubPz absorbance through a photochemically driven electrocyclic ring closure involving the SubPz quasi-isolated double bond.[3]





In addition, we have prepared a new family of subporphyrinoids that we have called Subphenantrenocyanines (**SubPhe**, **2**), which contain a 9,10-phenantrene system fused to the SubPz ring. Our recent advances in these SubPz derivatives are discussed.

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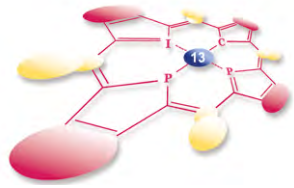

Electronic Structure and Magnetic Properties of Metalloporphenes

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Two-dimensional (2-D) materials attract high interest because of their remarkable mechanical, electronic, and magnetic properties. These properties can be fine-tuned through controlled functionalization, which is difficult to achieve in the case of archetypal 2-D materials such as graphene or hexagonal boron nitride.[1] In contrast, porphene is a recently prepared 2-D material composed of fully fused porphyrins which may be easily tuned by changing the embedded metal.[2] Here, we use density functional theory to show how the electronic structure of metalloporphenes is determined by (a) the extent of the Peierls distortion from an antiaromatic square planar shape and (b) the number of π electrons in their unit cell.[3]

In zinc porphene (**Zn(II)P**) and many other metalloporphenes there is no electron transfer between the π backbone and the metal *d* electrons, resulting in an electronic structure determined by the extent of the Peierls distortion of the unit cell from square to rectangular, which can also be understood as an antiaromaticity relief of the cyclooctatetraene unit. When this distortion is absent or small (e.g. **Ti(IV)Cl$_2$P**), the metalloporphene will display metallic conductivity. If the distortion is sufficiently large (e.g. **Zn(II)P**), it will open a band gap and the resulting metalloporphene will be a semiconductor.

In the case of metalloporphenes such as **Ti(IV)P**, electrons are injected into or removed from the metalloporphene π system. Changing the number of π electrons by two results in a high-symmetry geometry and a large band gap, which may be understood as an aromaticity recovery. Removing or adding a single electron usually results in a single conducting spin channel, which may be useful for spin filtering.

Our results also suggest that some metalloporphenes may undergo an insulator-to-metal transition with the application of an external magnetic field. In the absence of a magnetic field, metalloporphenes such as **Cu(II)P** or **Fe(III)ClP** adopt antiferromagnetic or paramagnetic configurations, which are predicted to be non-conducting. A sufficiently strong (~10 T) magnetic field will induce ferromagnetic ordering, increasing the electric conductivity by several orders of magnitude.

Acknowledgments: This work was supported by grants from the NSF (CHE-2247956), USARO (23-05-0007), and GACR (20-03691X).

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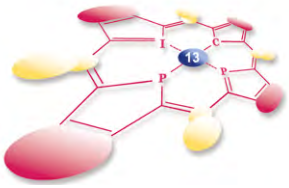

Structure of oxidized cytochrome *c* oxidase

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Cytochrome *c* oxidase (C*c*O) is the terminal enzyme in the electron transfer chain in the inner mitochondrial membrane. It serves a dual role of (*i*) maintaining electron flow for oxidative phosphorylation, by catalyzing the four-electron reduction of oxygen (O_2) to H_2O, and (*ii*) creating an electrochemical proton gradient to generate ATP, by coupling the oxygen reduction chemistry to proton translocation. The oxygen chemistry takes place in a binuclear center (BNC) consisting of heme a_3 and Cu_B, in which the metals are separated by only 5Å. Although many studies of the structure and function of C*c*O have been carried out, many questions remain unresolved [1]. One of the most controversial issues is the ligand structure of the BNC in the fully oxidized resting enzyme, **O,** which does not support proton translocation upon reduction, in contrast to the oxidized enzyme formed during turnover, $\mathbf{O_H}$, which does support proton translocation upon reduction. To address this question, we made resonance Raman measurements of the resting enzyme in solution and serial femtosecond X-ray crystallography (SFX) diffraction measurements of microcrystals of the enzyme by using an X-ray free electron laser. In the resonance Raman spectrum, we detected an oxygen-isotope sensitive line at 451 cm^{-1}, which we assigned as a Fe-OH stretching mode, just as in the oxidized enzyme formed during turnover, $\mathbf{O_H}$ [2]. With the SFX measurements, we confirmed that the heme a_3 iron atom is coordinated by a hydroxide ion and Cu_B is coordinated by a water molecule, indicating that the ligand structure of **O** and $\mathbf{O_H}$ are identical [3]. However, we found that the protonation state of Y244, which is post-translationally linked to one of the Cu_B ligands, differs between **O** and $\mathbf{O_H}$, accounting for the functional difference between these two states of the enzyme.

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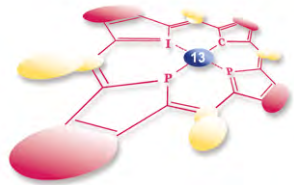

Conformationally Locked and Protonation Induced Helical Chirality in Cyclo[2]dipyrrins Linked with Anthracene Subunits

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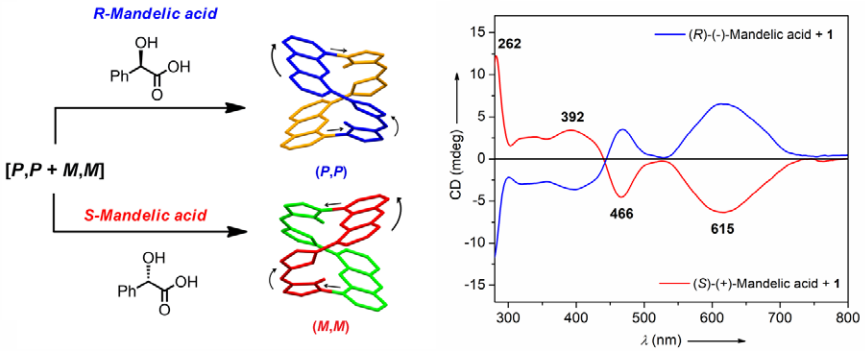
Chirality in porphyrinoids is an emerging field recently realized with large and flexible macrocycles with appropriate linking subunits. Expanded porphyrinoids with a minimum of eight cyclic units reduce their bond angle strain by undergoing two half twists (T20) i.e., figure of eight structure, and exhibit helical chirality [1]. The optical resolution of these macrocycles is often difficult to achieve owing to their dynamic interconversion between two conformers [2]. In this talk, I will present the synthesis, structure, and chiroptical properties of a conformationally stable, helically locked, and twisted Cyclo[2]Dipyrrins **1** containing two dipyrrin units linked with 1,5-anthracene subunits [3]. We have prepared a non-planar building block, 1,5-dipyrrylanthracene (1,5-DPA) for the first time, which was subjected to acid-catalyzed condensation with 2,3,4,5,6-Pentafluorobenzaldehyde. Macrocycle **1** turned out to be a non-planar structure and crystallized as a racemic mixture as revealed from X-ray crystallographic analysis. High racemization energy barrier enabled facile optical resolution. The (*P*,*P*) and (*M*,*M*) enantiomers show moderate chiroptical properties, such as absorption dissymmetry factors in the order of 10^{-3} and luminescence dissymmetry factors of 3.8 x 10^{-3} and 2.9 x 10^{-3} at 702 nm respectively. On the contrary, a conformationally flexible and enantiomerically switchable Cyclo[2]dipyrrins and its *bis*-BF_2 complex were prepared using the 1,8-dipyrrylanthracene (1,8-DPA). Herein, we were unable to separate the chiral enantiomers as (*P*,*P*) and (*M*,*M*) due to their low racemization barriers. However, upon protonation, the chirality was induced using chiral mandelic acid [4].



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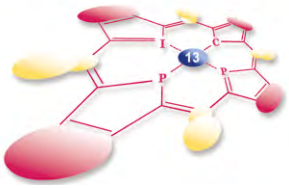
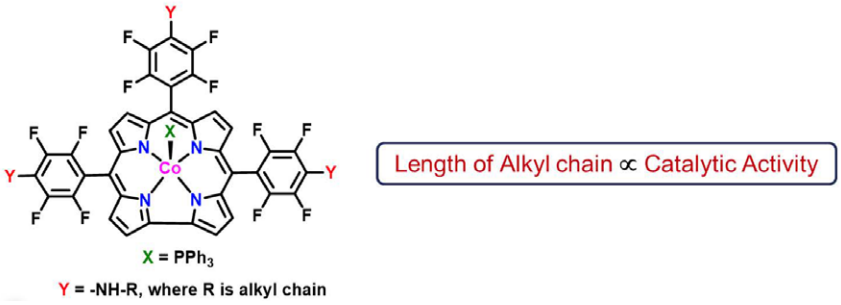


Investigating the Influence of Polymer-Catalyst Interaction on Water Electrolysis in Alkaline Environment using Bifunctional Cobalt Corroles

Sameeta Sahoo[a], **Elizabeth Johnson**[a], **Charles W Machan**[a]

[a]*University of Virginia*

Hydrogen is a possible option for renewable energy storage in chemical bonds for later use in fuel cells to generate electricity[1]. Water electrolyzers using electrical energy from renewable sources would be an ideal source of this hydrogen fuel. Hydroxide exchange membrane electrolyzers (HEMEL) have recently gained attention due to the possible use of cost-effective electrocatalysts and their ability to operate in pH 14 or pure water[2]. Catalysts based on molecular complexes offer potential advantages in understanding and optimizing the active site, however, the development of compounds with sufficient catalytic activity and stability is an ongoing challenge. Metallocorroles have previously been explored for their electrocatalytic activity in water-splitting electrolyzers[3]. The synthesis and electrocatalytic testing of a series of Co(III) corroles with varying aminoakyl chain substitution on the *meso* position is reported and compared. All complexes were observed to be bifunctional water-splitting catalysts at pH 14. The presence, as well as chain length of the alkyl amines functional groups, were found to be of significance to the aggregation of the complexes as well as their interactions with the polymer support, altering mass transport during electrocatalysis.



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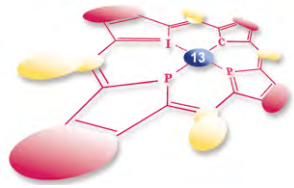

Structural Modulation on Corroles for Optical and Magnetic Applications

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Corroles are fast becoming popular tetrapyrrolic macrocycles to address some of the long-standing challenges in porphyrin chemistry. Recently, these ligands are suitable for catalysis, light harvesting and understanding modern coordination chemistry. In this regard, we have been working on perturbing the electronic structure of the corroles to investigate the intricacies in reactivity and photophysical characteristics. Peripheral modification of corroles leads to often molecules with interesting photophysical and magnetic properties. In the current talk, we shall be discussing an example of an internally coordinating N5-corrole unit that will impart intriguing photophysical and magnetic properties. Further, an unexpected dimerization in the solid state of the derivative will also be highlighted. Additionally, the innocence and noninnocence of the derivative towards metallation will be discussed.

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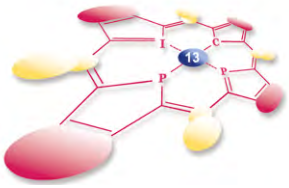

Synthesis of N-Confused Porphyrin Metal Complexes and Their Applications in Catalysis and PDT

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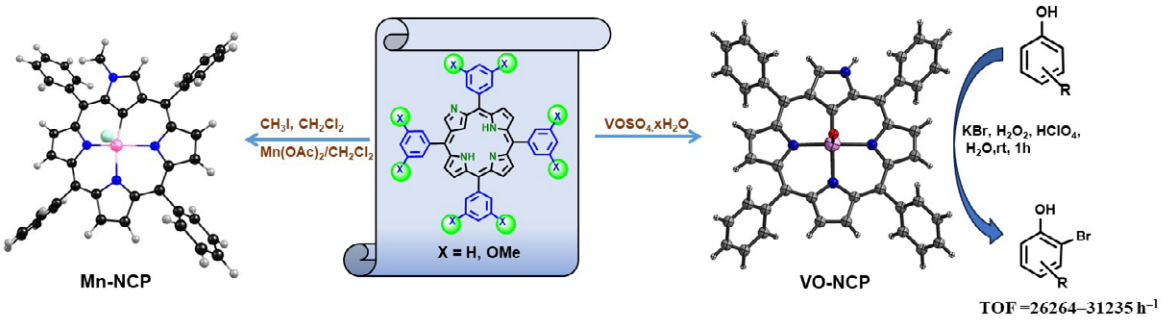
N-confused porphyrin (NCP) is an analog of regular porphyrin having one of the four pyrrole nitrogen atoms positioned at the periphery. NCP was first synthesized independently by Furuta [1a] and Latos-Grazynski [1b] in the year 1994. Over the past three decades, there has been ample progress in the expansion of N-confused porphyrins for diverse applications.[2] However, vanadyl complexes of NCP and their catalytic activities have not been explored to date. Herein, we synthesized VONCTPP and VONCP(OMe)$_8$ and characterized them by various spectroscopic techniques and SCXRD (Scheme 1). They exhibited a red shift in the Soret band ($\Delta\lambda_{max}$ = 14–17 nm) as well as Q bands ($\Delta\lambda_{max}$ = 10–28 nm) in comparison to their respective free base NCP. EPR studies revealed a +4 oxidation state of vanadium metal having an axial compression with d_{xy}^1 configuration. Catalytic potential for *bromoperoxidases*-like activity has been explored for both complexes for the first time. Both the catalysts have demonstrated excellent TOF values (26 264 - 31 235 h^{-1}) using KBr as a source of bromine and H_2O_2 as a green oxidant in an aqueous medium at 298 K. Notably, both the catalysts show excellent recyclability, and their recyclability was tested up to five cycles.[3a] Further, we have also synthesized Sn(IV) NCP which exhibits one of the Q bands in the NIR region. By keeping this in mind, we investigated their antimicrobial photodynamic therapy (a-PDT) against *Escherichia coli* and *Staphylococcus aureus* bacteria as well as PDT activity against MCF-7 cells.[3b] Recently, we have synthesized N-methylated Mn(III) NCPs to explore their catalytic activities (Scheme 1). In this presentation, the facile synthesis and characterization of metal complexes of NCP and their applications in catalysis and photodynamic therapy in detail.



Scheme 1. Synthesis of N-methylated MnNCPs and VONCPs and the catalytic activity of VONCP.

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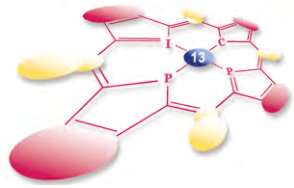

Phthalocyanines Dimers as Hole Transporting Agents and as Potent G-quadruplex DNA Binders

Ángela Sastre-Santos,[a] Lydia Ferrer, [a] Adrián Hernandez, [a] Ariadna Gil-Martínez, Desiré Molina,[a] Jorge Follana-Berná, [a] Félix Manjón, Javier Ortiz [a]

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Recently, significant progress has been achieved in the fabrication of highly efficient perovskite solar cells, while major challenges, such as the commercial viability of exotic materials and their instability, remain an obstacle. Hole transporting materials (HTMs) represent a tricky choice for the fabrication of efficient solar cells and the cost-effective Spiro-OMeTAD continues to be so far the most obvious candidate. Semiconductor molecules, such as metallophthalocyanines (MPcs) [1] appeared as a promising class of p-type material since they are less expensive and more stable.

A large number of G-quadruplexes (G4s) binders have been intensely studied as promising anticancer agents. Most recently, an interesting approach to tackle cancer has emerged combining G4 binding and the photosensitization of the G4 ligand, which can then generate reactive oxygen species (ROS) and the resulting breakage of the G4 DNA/RNA structures and other nearby biomolecules. In this context, MPcs have the suitable structure to interact via π–π stacking with the external tetrads of G4s and also to act as photosensitizers in photodynamic therapy.[2]

In this communication, we will present the synthesis of novel MPcs as efficient, stable, and low-cost HTMs in PSCs (Fig. 1a). [3] Also, we will report the synthesis of MPcs and their capacities to bind G4 (Fig. 1b) [4] with a large number of biologically relevant G4 forming sequences by UV-Vis/fluorescence spectroscopies and FRET melting assays.

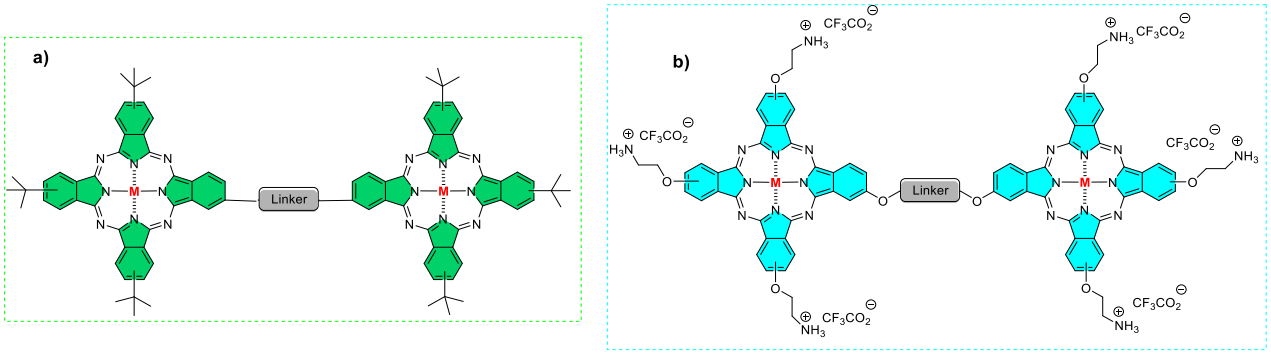

Figure 1. MPcs structures a) HTMs in PSCs and b) G4s binders

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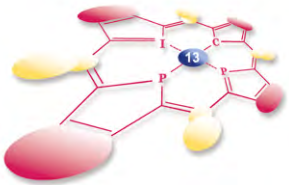

Aza-dipyrromethene-based complexes as electron acceptors for organic solar cells

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Azadipyrromethenes are pi-conjugated bidentate ligands very similar to dipyrromethenes except that the meso carbon is replaced with nitrogen, resulting in a red shift in the absorption spectra and a higher electron affinity than the dipyrromethene analogues. As a result, complexes of azadipyrromethenes are excellent visible to NIR absorbers and great candidates as electron acceptors for solar energy conversion applications. Their optoelectronic properties can be tuned via substitution and chelation. We have demonstrated that zinc(II) complexes of tetraphenyl azadipyromethenes are promising solution-processable electron acceptors for organic solar cells due to their non-planar geometry which promotes favorable film morphology when blended with regioregular poly(3-hexylthiophene) (P3HT) as the electron donor [1, 2]. Here we present structure-propertiy studies to tune their crystallinity, molecular packing, and charge carrier mobility, with the goal of improving their performance in organic solar cells. To summarize, we find that installing phenylethynyl groups at the pyrrolic positions ($Zn(WS3)_2$) increases the conjugation length and electron affinity of ADP-based Zn(II) complexes. Replacing the pyrrolic groups to 1-naphthylethynyls and adding hexyl solubilitizing groups increase crystallinity and performance in OPVs ($Zn(L2)_2$) [3]. Strategic fluorination of $Zn(L2)_2$ promotes cofacial pi-pi stacking between arylethynyl groups of adjacent molecules and increases both electron an hole mobilities in diodes by an order of magnitude [4]. Further, we show that modifying the nature and placement of solubilizing groups on $Zn(WS3)_2$ can also tune the electrical properties of these non-planar molecules. To develop electron acceptors with higher electron affinity and charge carrier mobility, we are now turning to the BF_2^+ chelates, or aza-BODIPYs. While aza-BODIPYs originally did not perform well in organic solar cells when blended with P3HT, we have since discovered that their properties could be improved with side chain modifications. Here, I will present new aza-BODIPYs with good charge transport properties that are promising candidates for organic solar cell and photodetector applications.

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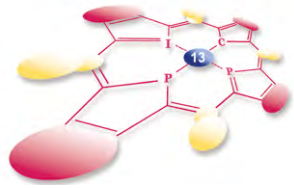

On-surface synthesis of porphyrin-graphene nanoribbons and porphyrin polymers

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Graphene nanoribbons (GNRs) possess fascinating electronic properties with the potential for application within (opto)electronic devices [1], and therefore there is significant interest in achieving doped and heterostructured GNRs to facilitate bandgap and fermi-level engineering. Studies of GNRs often focus on the on-surface synthesis of extended graphitic polymers formed from the Ullmann-type coupling of halogen-functionalised bianthracene units [2], and in common with many on-surface synthesis protocols, the initial, intermediate and product states can be studied by scanning tunneling microscopy (STM) and atomic force microscopy (AFM) to provide sub-molecular insights into reaction pathways and resultant structures [3].

While an on-surface synthesis approach to the formation of GNRs has allowed polymers with a range of structures to be fabricated, there are still significant challenges relating to the selectivity and efficiency of such on-surface reactions. Our proposed methodology is to utilise the atomic precision of solution-phase chemistry to form highly regular polymeric precursor species, and to employ on-surface protocols to enable reaction steps that are not often facile in solution (e.g. the dehydrogenative-cyclisation reaction step required to produce conjugated graphitic materials). Our focus is on the inclusion of porphyrin species within the graphene nanoribbons; giving rise to porphyrin-fused graphene nanoribbons (PGNRs).

Here I will detail the use of electrospray-based deposition (ESD) to deposit a polymeric precursor species onto a Au(111) substrate held under ultra-high vacuum (UHV) condition (utilising methodologies from our previous work [4-7]) and characterise the on-surface synthesis of a porphryin-graphene nanoribbon using a combination of scanning tunnelling microscopy (STM) and photoelectron spectroscopy-based techniques (including XPS, NEXAFS, and NIXSW).

In addition, I will present results from low-temperature UHV-STM studies of functionalised tetraphenyl porphyrin species on metal (111) surfaces. Multiple steps within an on-surface reaction are observed; including dehalogenation, formation of metal-organic frameworks, ring-opening, ring-closing, self-metalation, and covalent coupling. A systematic, temperature-controlled, investigation reveals the step-wise evolution of the reaction with a combination of STM, XPS and NEXAFS providing insight into the mechanisms and energetics of the on-surface reactions.

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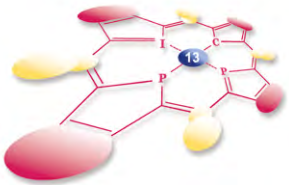

Sub-molecular fluorescence microscopy of Phthalocyanine molecules with STM

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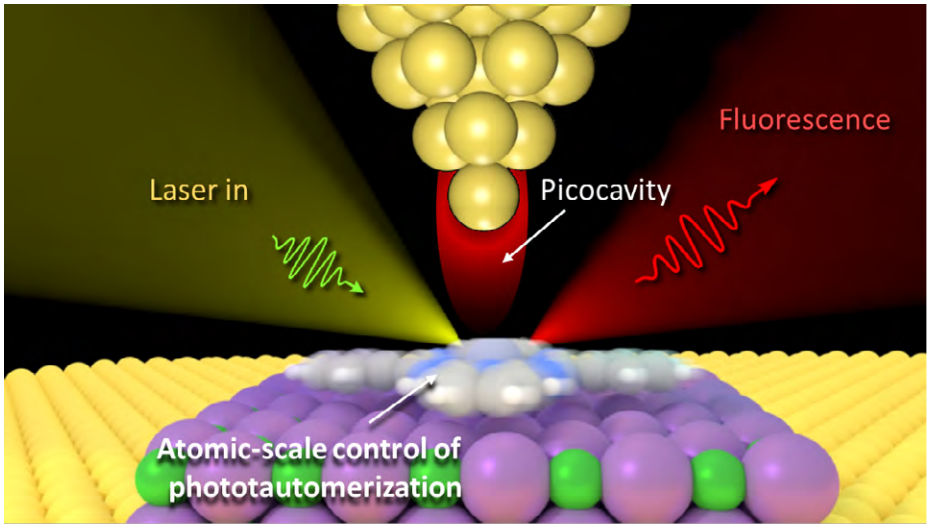
The electric current traversing the junction of a scanning tunneling microscope (STM) may lead to a local emission of light that can be used to generate sub-molecularly resolved fluorescence maps of individual molecules. Combined with spectral selection and time-correlated measurements, this hyper-resolved fluorescence microscopy approach allowed us to characterize the photonics properties of individual [1, 2], or interacting phthalocyanine molecules [3]. The presentation will describe the underlying mechanisms giving rise to sub-molecular resolution in STM-induced fluorescence [4, 5] and discuss more recent observations of atomic-scale control of phototautomerization in free-based Phthalocyanine.



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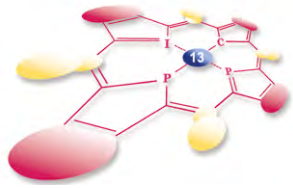

Tuning π-Conjugated Corroles for Heterogeneous Catalysis

Wolfgang Schöfberger[a], Houssein Awada[a], Luyang Song[a], He Sun[a], Adrian Dorniak[a], Farzaneh Yari[a].

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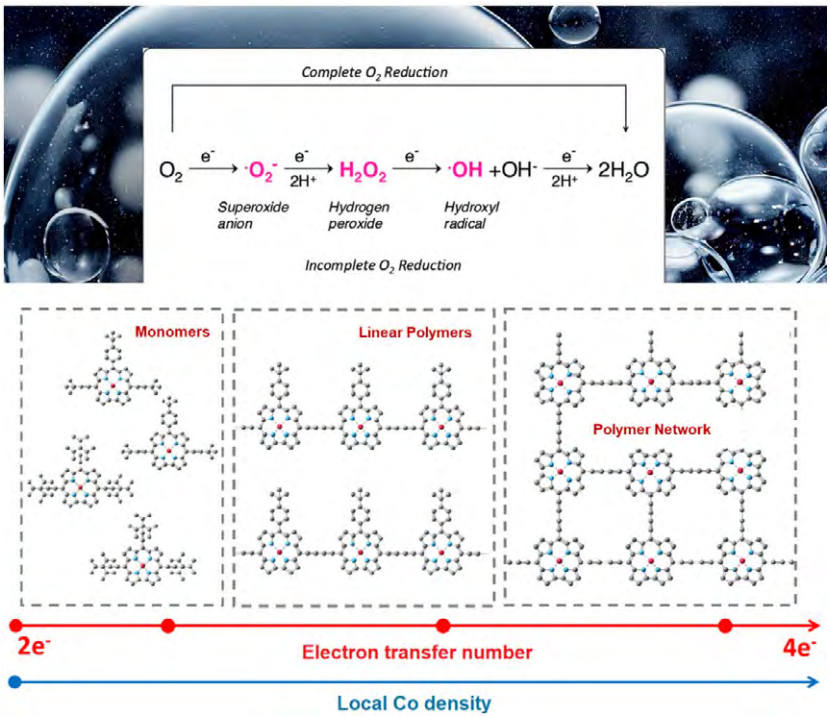
In this talk, we demonstrate a method to tune OER/ORR selectivity by adjusting the local metal density through simple oligo-/polymerization of novel π-conjugated metal A_2B and A_3-corroles to linear and two-dimensional matrix structures. [1] These heterogeneous catalysts exhibit remarkable physicochemical properties, fast charge transfer kinetics, electrochemical reversibility, and high durability. As an example, unselective three-electron transfer kinetics with n = 2.5–2.9 in between -0.20 V and +0.40 V vs. RHE are detected with the π-conjugated cobalt(III) A_2B- corrole polymers. Highly selective four-electron kinetics with n = 3.7 in between -0.20 V and +0.40 V vs. RHE are detected by employing the cobalt A_3-corrole oligomers during the ORR catalysis.



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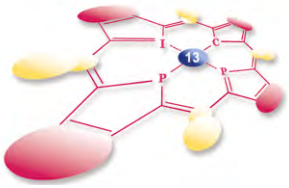

From Shape to Function – Conformational Engineering of Porphyrins

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Porphyrins are nature's cofactors par excellence. Next to oxygen transport and storage, their role in electron transport and as photosynthetic pigments, they catalyze a multitude of chemical reactions. All these catalytic functions depend on the presence of a central metal which is intricately involved in the catalytic processes. However, upon appropriate manipulation of the porphyrin macrocycle conformation, the core nitrogen atoms in free-base porphyrins can be involved in organocatalysis as well, exemplifying a mode of catalytic action for porphyrins that does not require a central metal ion [1]. In addition, similar concepts of molecular engineering the molecular shape of porphyrins can be used to develop switchable porphyrin receptors for the detection of analytes and removal of pollutants [2].

Further engineering of functional porphyrin materials is possible through the control of peripheral substituents in porphyrin atropisomers [3] and picket fence porphyrins [4] and the logical spatial construction of 1D, 2D, and 3D arrays. The latter involves the use of porphyrinoids as photoactive components together with rigid hydrocarbon linker groups such as cubane or bicyclo[1.1.1]pentane either in solution [5], the solid state [6], or interfaces [7,8] and in novel macrocycles [9].

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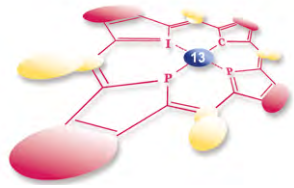

Proton Coupled Electron Transfer Aromaticity Switching

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Considerable interest is focused on porphyrin analogues that can exist in several different electronic states. In collaboration with several groups, whose contributions are gratefully acknowledged, an emphasis has been made lately to develop expanded porphyrins that can be switched between formal aromatic, non-aromatic, antiaromatic, and semiaromatic or open shell and forms via so-called proton-coupled electron transfer reactions. Early efforts along these lines involved the study of rosarins, but have lately been extended to include other hexapyrrolic macrocycles, various fused, and cage-type systems. Lately, an effort has been made to explore how changes in electronic states can be used to switch on potentially useful biomedical properties, including those associated with photodynamic therapy, photothermal therapy, and photoacoustic imaging.

Acknowledgments: The authors are grateful to a number of collaborators, including Dongho Kim, Juwon Oh, Masatoshi Ishida, Xian-Sheng Ke, Zhan Zhang, Jong Sung Kim, Changhee Lee, Zahid Siddik, Rick Finch, Zhengrong Cui, Dani Gibson, and Zhao-Xi Wang, Adam Sedgwick, Chengbo Liu, and Jingqin Chen. Current research support for the work in Austin is provided by the Robert A. Welch Foundation and the National Science Foundation.

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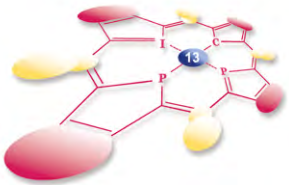

Photoredox catalysis of B_{12} derivative in green organic synthesis

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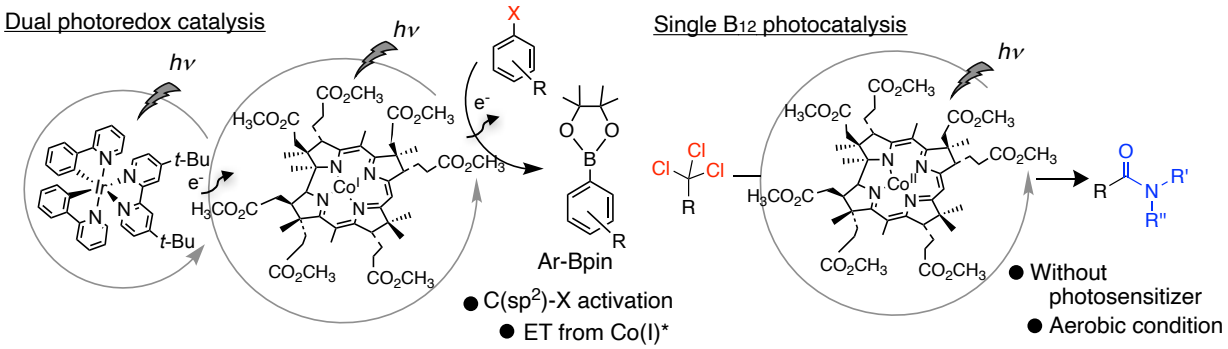
The combined use of bio-related metal complex such as cobalamin derivative with photochemical technique has been developed in green organic synthesis due to its efficient and non-toxic reaction system [1]. We report a reductive dehalogenation of aryl halides by the photo-excited B_{12} complex, heptamethyl cobyrinate, with the labile Co(I) oxidation state [2]. This reaction pathway could overcome the substrate limitations during conventional catalysis of the B_{12} cobalt complex which could not applied to Ar-X with the C(sp^2)-X bond. Based on this finding, we develop the new catalytic reaction of the B_{12} derivative for the borylation of Ar-X with the combined use of photosenzitizer based on a dual photoredox strategy by visible light irradiation [3]. The excited Co(I) species ($^*Co^I$) species of heptamethyl cobyrinate acted as a reductant for the Ar-X reduction and an arylboronate was formed in the presence of bis(pinacolato)diboron (B_2pin_2) as the radical trapping reagent. The reaction proceeded with a very low amount of catalyst loading of 0.025 mol% towards the substrate and the highest 3,880 TON was achieved at room temperature. The dual photoredox system provides advantages for the reaction under mild conditions, a small amount of catalyst loading, and simple procedure.

Furthermore, we discovered the single photocatalytic system of B_{12} derivative without additional photosensitizer [4]. As advanced to this reaction, one-pot synthesis of amide from trichloromethylated organic compounds under aerobic condition is developed.



Applications of B_{12} derivative in light-driven organic synthesis will be reported.

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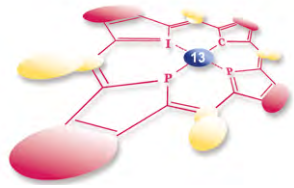

Creation of NIR aza-aBODIPY Analogues Based on a Schiff Base Forming Reactions

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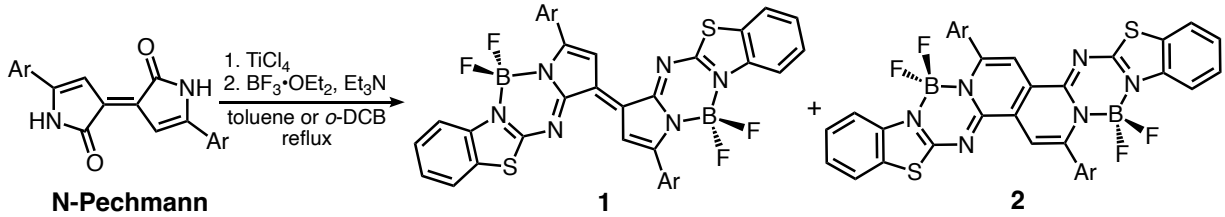
In recent years, near-infrared (NIR) chromophores have been attracting attention, especially in the fields of bioimaging and phototherapy because of the high penetration of the NIR light into biological tissue, less autofluorescence, and low scattering, which enable medical diagnosis and therapies deep in tissue. Owing to the intense absorption and fluorescence in the far-red region, aza-borondipyrromethene (aza-BODIPY) has been regarded as a fundamental chromophore structure to target optical properties in the NIR region. Therefore, the synthesis of aza-BODIPY and its analogues has been intensively investigated, and three main synthetic methods have been developed.[1–3] However, those conventional syntheses have a limitation in the available aza-BODIPY structures. Recently, as a new synthetic method of aza-BODIPY, we have developed a Schiff base forming reaction of lactam and azaarylamine.[4] Because this synthetic method is highly applicable to lactams and azaarylamines, various kinds of novel aza-BODIPY analogues were reported.[5]

In this study, to develop NIR chromophores toward applications in photoacoustic imaging and photothermal therapy, we focused on a N-Pechmann dye as a precursory lactam structure. The target aza-BODIPY analogue (**1**) was successfully synthesized from the Schiff base-forming reaction (Scheme 1). To our surprise, owing to the thermal isomerization of the N-Pechmann dye, an aza-BODIPY analogue bearing 6,6-membered ring units (**2**) was also obtained. After optimizing the reaction conditions, two compounds were selectively synthesized by changing the solvents and reaction temperatures. Both compounds exhibit redshifts of the absorption from the starting lactam compounds. **2** exhibits intense fluorescence at 522 nm with a high fluorescence quantum yield of 0.54, whereas the fluorescence of **1** is virtually quenched. The non-emissive nature and the NIR absorption of **1** up to 900 nm are beneficial for developing photoacoustic imaging and photothermal therapy agents.

In this presentation, the synthesis and optical properties of the novel aza-BODIPY analogues will be reported.



Scheme 1. Synthesis of aza-BODIPY analogues from a N-Pechmann dye.

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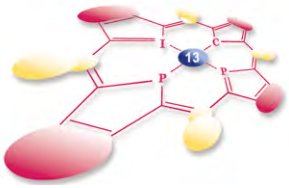

Secondary dual-ion batteries with porphyrinoid electrodes

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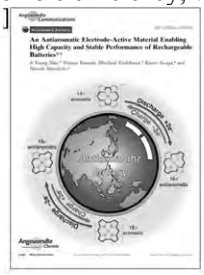
Rechargeable batteries have been the heart of energy-storage technologies, for which many scientists and engineers have attempted to exploit sufficient electrode and electrolyte materials for practical and sustainable secondary batteries. In terms of low environmental footprint and high safety, endurable organic molecules have captivated the next generation of rechargeable batteries, and organic/organometallic-based cathode materials, such as porphyrins with delocalized π-conjugation stems which are capable of stabilizing different redox states over the π-electron delocalization, has been pondered as competitive candidates for electrode materials requiring high power densities. It is delightful to explore highly tunable organic molecules inducing excellent cyclability, fading the organic molecular dissolution, multi-redox state capability providing appropriate electronic contributions, and charming permeability for the electrolyte kinesis. Nickel(II) norcorrole (NiNc) exhibiting sufficient chemical stability along its multi-redox processes with the advantageous chemical property of antiaromatic nature has been engaged to the organic electrode material in secondary batteries, which exposed efficient long-term charge-discharge performances with superb Coulombic efficiency [1]. Investigation of dual ionic modulations in liquid electrolytes essentially improved the battery capacity and practical efficiencies [2], and the facile redox conversions of the electrode material and their relative mechanical processes were then fully comprehended by examining in-situ XRD and ex-situ Raman spectroscopy and monitoring dual-ion behaviors of three-electrode cells [3]. More extended π-delocalized expanded porphyrinoids were also investigated as practical secondary organic batteries, cooperating with Li and Na [4,5]. Moreover, sufficiently enriched dual-ion batteries were invented with novel ferrocenyl-substituted NiNc and structurally parallel Nickel(II) porphyrin, providing enhanced battery behaviors, quick and durable charge-discharge performances, superior battery capacity, and Coulombic efficiency, whose overall system successively manipulates pseudocapacitive processes [6].

[1] 

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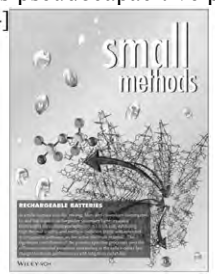
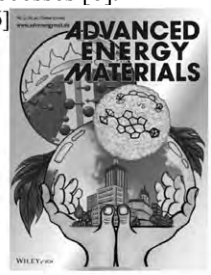
[4] 

[6] 

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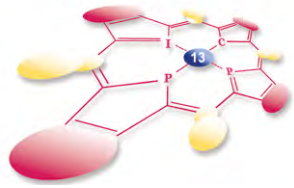

Metallaantiaromaticity of 10-Platinacorrole Complexes

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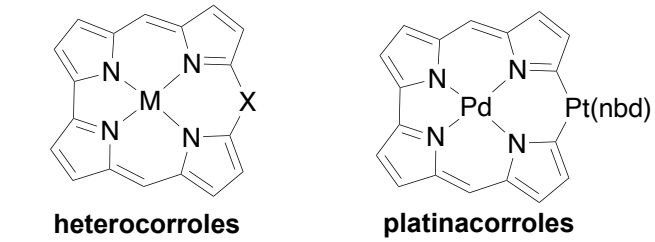
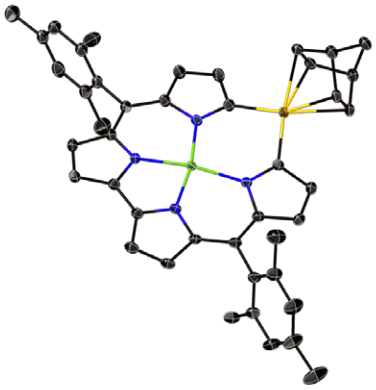
Metallaaromaticity is the aromaticity of cyclic π-conjugated organometallic compounds. Metallacycles such as metallabenzenes and metallapentalenes have been actively explored to elucidate the existence of cyclic π-conjugation involving the *d* electrons of transition metals.[1]

The properties of various 10-heterocorroles have been examined.[2] The aromaticity and antiaromaticity are sensitive to the heteroatoms incorporated at the 10-position. The property of the heteroatoms is critical for the macrocyclic π-conjugation.

Recently, we have succeeded in the synthesis of Pd(II) 10-platinacorrole complexes with cyclooctadiene (COD) and norbornadiene (NBD) ligands.[3] The 10-platinacorrole COD complex adopted a distorted structure, which resulted in the lack of the macrocyclic π-conjugation. In contrast, the 10-platinacorrole NBD complex exhibited an antiaromatic character due to its planar conformation. DFT calculations revealed that two *d* orbitals are involved in the macrocyclic π-conjugation. We also revealed that Craig–Möbius antiaromaticity is not involved in the case of the 10-platinacorrole NBD complex.





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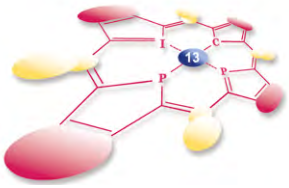

Revolutionizing Methane Transformation: Pioneering Catalytic Hydroxylation by Cytochrome P450BM3

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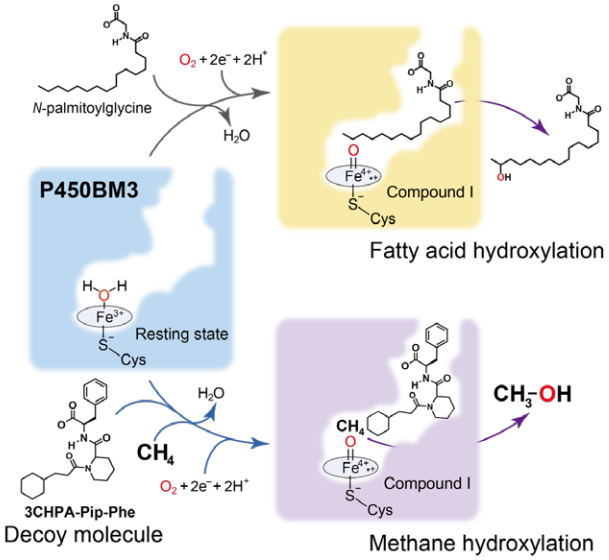

The utilization of biological methane oxidation represents an exceedingly sought-after approach for converting natural gas into a liquid state. This method addresses the escalating demands for fuel and chemical feedstock, simultaneously mitigating the potent greenhouse effects of methane emissions. Until recently, the prevailing assumption, stemming from the absence of naturally occurring hemoenzymes capable of catalyzing methane-to-methanol conversion, suggested that hemoenzymes, including cytochrome P450s (P450s), were incapable of facilitating the oxidative conversion of methane. In a groundbreaking revelation, we are pleased to announce the successful catalytic methane oxidation by wild-type P450BM3. Notably, this achievement was realized without resorting to any mutagenesis and was conducted under the influence of chemically evolved dummy substrates (decoy molecules)[1] at high-pressure methane conditions of 10 MPa. Our extensive investigations unveil a compelling narrative in which methane undergoes catalytic conversion into methanol at ambient temperatures, showcasing an impressive total turnover number of 4.0 ± 0.4.[2] The cocrystal structure of P450BM3 with 3CHPA-Pip-Phe, the best decoy molecule for $^{13}CH_4$ hydroxylation, solved at 1.54 Å resolution showed that 3CHPA-Pip-Phe binds similarly to the native substrate *N*-palmitoylglycine, with the pipecolic acid moiety at the center of 3CHPA-Pip-Phe inducing a "curved" conformation akin to *N*-palmitoylglycine. The *N*-terminal cyclohexyl group occupies the space above the heme, blocking the channel connecting the active site and the outside of the protein to form an isolated pocket for methane binding. The volume of P450BM3 with 3CHPA-Pip-Phe is too large for binding a single methane molecule with a diameter of 3.8 Å. Docking simulations revealed enough space at the active site to simultaneously accommodate at least two methane molecules.

This discovery not only challenges previously held beliefs regarding the catalytic potential of hemoenzymes but also paves the way for advancing our understanding of methane transformation processes. Essentially, this breakthrough holds great promise for addressing the dual imperatives of sustainable energy production and environmental stewardship. It marks a pivotal stride in our ongoing quest for innovative solutions to pressing global challenges.

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Photoinduced Ground State Electron Spin Polarization of Different Organic Radicals

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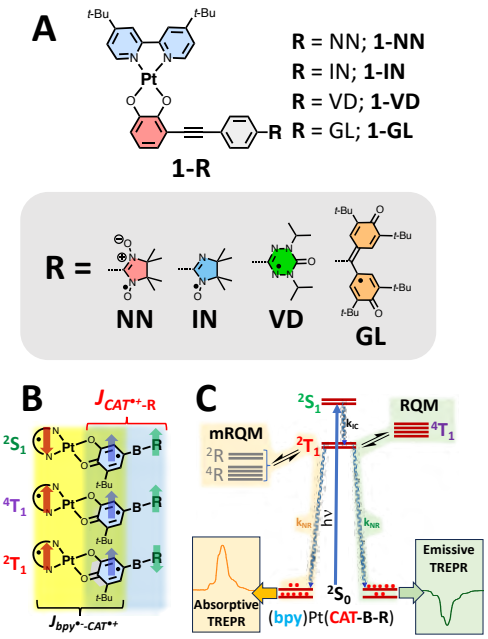
Stable spin-½ radicals covalently attached to various chromophores are an important class of open-shell molecules for demonstrating a variety of properties and structure-property relationships related to quantum information science. Our efforts have focused on square-planar, d^8 platinum(II) complexes of catecholate (CAT) donor- and bipyridine (bpy) acceptor ligands in which a nitronyl nitroxide radical is attached to the CAT ligand via an organic bridge fragment (*e.g.*, **1-NN**, *Figure A*).[1, 2] These complexes exhibit a CAT → bpy, ligand-to-ligand charge transfer (LL'CT) LL'CT electronic absorption band in the visible regions of the spectrum. When a stable radical is attached to the LL'CT chromophore, photoexcitation of the LL'CT band results in a radical-chromophore coupled excited state manifold comprised of $^2S_1$ (sing-doub), $^2T_1$ (trip-doub), and $^4T_1$ (quartet) states, *Figure B,C*. In the absence of a stable radical, these LL'CT complexes undergo rapid charge recombination back to the ground state in under 1 ns. Covalent attachment of a stable radical is also accompanied by fast charge recombination to the ground state, but not before enhanced intersystem crossing from the vertical $^2S_1$ to $^2T_1$, followed by equilibration of $^2T_1$ with $^4T_1$ and/or localized radical excited states (*Figure C*). Equilibration pathways are enabled by zero-field splitting, energy transfer, or spin-vibronic coupling, and result in non-Boltzmann populations ("spin polarization") of the $^2T_1$ m_s-levels. Since the $^2T_1$ lifetimes are all shorter than the spin-lattice relation times of the stable radical, charge recombination delivers the spin polarization to the ground state where it can be recorded using transient EPR spectroscopy, *Figure C*. This talk will show evidence of the general utility of our chromophore for polarizing a variety of stable radicals, *Figure A*.



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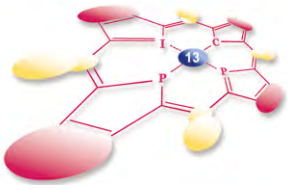

Reflections on PDT experiences involving David Kessel

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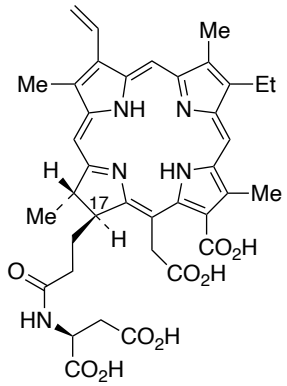
The presentation involves the author's first major interaction with David Kessel, already a major figure in PDT, at the 1984 Gordon Research Conference on the Chemistry and Biology of Tetyrapyrroles, through to the present day. In particular, David pushed my research group and myself to investigate differing proposals for the chemical structure of mono-aspartylchlorin-e_6 (NPe-6, Talaporfin, LS-11), a promising second-generation chlorin photosensitizer. The original patent [1] assigned structure (**1**) to the sensitizer, but when an alternate proposal, regioisomer (**2**), surfaced [2] and was mostly ignored, David insisted that *someone* had to solve the conundrum! In a series of 5 publications [3-7] over 10 years, we did exactly that. The presentation will show how.



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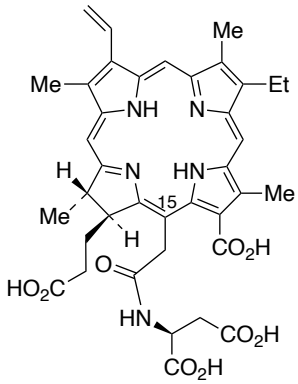

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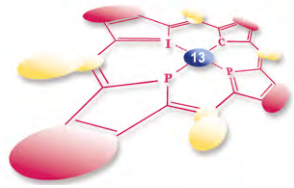

Highlighting the enzymatic mechanism of coproporphyrin ferrochelatases of the Firmicute *Listeria monocytogenes.*

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The discovery in 2015 of the coproporphyrin-dependent heme biosynthetic pathway, used almost exclusively by monoderm bacteria, by Dailey and coworkers [1] evidenced that the heme *b* metabolism in many dangerous pathogens markedly differs from that of humans. Ferrochelatases are enzymes that insert ferrous iron into a porphyrin macrocycle, being the coproporphyrin III (cpIII) in gram-positive bacteria and the protoporphyrin IX (ppIX) in humans. In the final step of the coproporphyrin-dependent biosynthetic process, the protein-bound ferric coproheme is eventually decarboxylated to yield heme *b* by the coproheme decarboxylase enzyme [1]. The active site of coproporphyrin ferrochelatase of the Firmicute *Listeria monocytogenes* (*Lm*CpfC) has been characterized by biophysical and biochemical investigation using the physiological substrate cpIII, which, in contrast to ppIX, has four propionate substituents and no vinyl groups. The characterization of selected variants within the active site allowed us to uncover the role of H-bonding interactions between specific residue side chains and the porphyrin propionates. All four propionate side chains are essential requirements for the correct orientation and stabilization of cpIII inside the active site, confirming the substrate specificity of *Lm*CpfC towards the four propionates [2, 3]. Moreover, by following the metal titration with resonance Raman spectroscopy and X-ray crystallography, we proved that upon metalation a saddling distortion becomes predominant both in the crystal and in solution. This is a consequence of the readjustment of hydrogen bond interactions of the propionates with the protein scaffold during enzymatic catalysis. Once the propionates have established the interactions typical of the coproheme complex, the distortion slowly decreases, to reach the almost planar final product [4]. The results all together provide significant, new and intriguing information on the catalytic reaction pathway. The understanding of the structure-function correlation of enzymatic mechanisms in heme biosynthesis is essential for the development of new therapeutic strategies.

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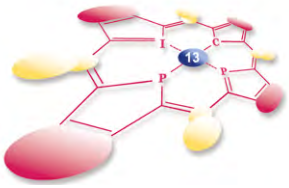

Xylans based cross-linked hydrogel for antimicrobial photodynamic therapy.

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Photodynamic Antimicrobial Chemotherapy (PACT) is a promising treatment that could overcome the challenge of multidrug-resistant bacteria. However, the use of most existing photosensitizers has been severely hampered, due to their poor water solubility, severe self-quenching effect, lack of selectivity against bacterial cells, and possible damage to the surrounding tissues. The use of hydrogels may overcome some of these limitations. We herein report a simple strategy to synthesize a cross-linked hydrogel from beech xylan [1]. The hydrogel showed good mechanical integrity and an interconnected porous structure, and a high swelling ratio. Different photosensitizers (PS) were encapsulated or grafted inside or into the hydrogel. PS-loaded hydrogel showed a photocytotoxic effect against *Escherichia coli, Pseudomonas aeruginosa, Bacillus cereus* and *Staphylococcus aureus* strains, while no cytotoxicity was observed in the dark [2, 3].

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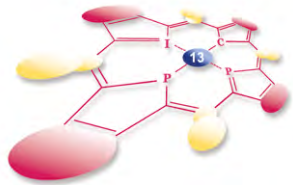

Prolinated Porphyrins in Chiral Systems Development

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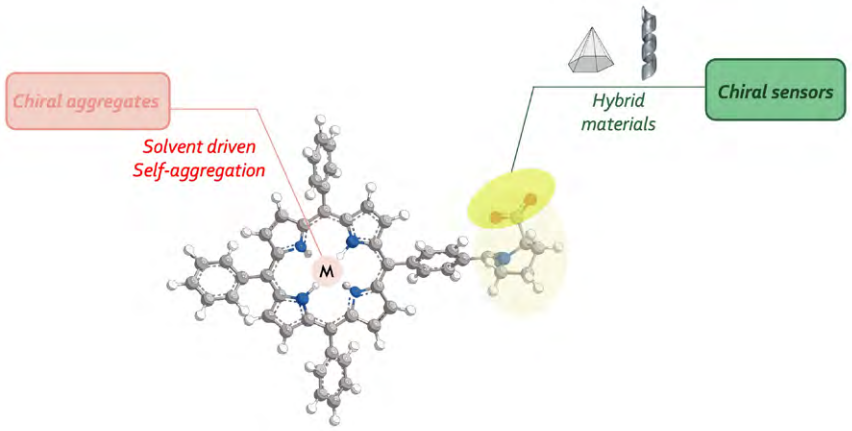
The self-assembly of porphyrin chromophores in sophisticated, size and shape-controlled suprastructures often significantly boosts the potentialities of these macrocycles, leading to advanced functional materials with improved properties. Accordingly, the achievement of these soft materials with desired functions represents an ongoing challenge for many researchers. Over the years, we focused on the building up of chiral porphyrin systems by using derivatives functionalized with proline moieties, both in solution and at the solid state [1,2]. This contribution will illustrate the huge potentialities offered by the prolinated porphyrin molecular scaffold to construct supramolecular architectures with distinctive chiroptical and morphological features by, among others, changing the metal coordinated [i.e. Zn(II), Pd(II), Co(II) and Co(III)] (Figure 1). In addition, the possibility to anchor these macrocycles with inorganic nanostructures as ZnO nanoparticles or SiO2 nanohelices allows the development of chiral solid films that can be exploited in chiral recognition applications [3].



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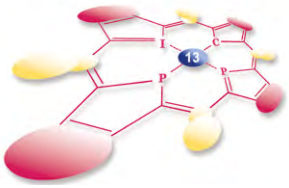

Donor–Acceptor Oligopyrroles: Functional Aromatics via Naphthalimide Fusion

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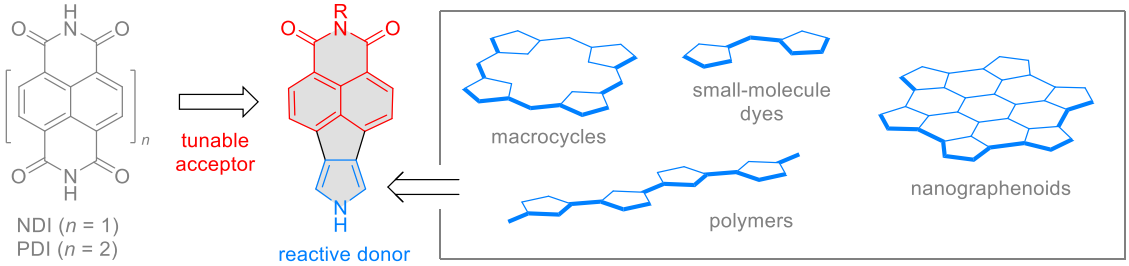
Systematic tuning of electronic energy gaps in organic molecules can be achieved by homologation (oligomerization) of linear π-conjugated motifs, by ring expansion of π-conjugated macrocycles, or by extension of fused ring systems in two dimensions. A complementary approach relies on combining donor and acceptor (D–A) moieties, with diverse recent applications in small-molecule and polymer chemistry. The D–A paradigm is particularly suitable for the development of tunable building blocks, which can be constructed by judicious merging of existing electron-deficient and electron-rich motifs. A simple and potentially productive design of such a hybrid structure is achieved by combining naphthalenemonoimide (NMI, red) and pyrrole (blue), as shown below [1]. We will discuss the application of these and similar pyrroles as building blocks for the synthesis of diverse polycyclic aromatics, including macrocycles [1,2], heteroatom-doped nanocarbons [3,4], and small-molecule dyes [5]. These systems reveal rich redox chemistry, spanning multiple oxidation levels, tunable optical signatures extending into the near-infrared, and an ability to form complex supramolecular assemblies. We will also discuss our efforts to extend the concept of NMI fusion to non-pyrrolic heterocycles and carbocycles.



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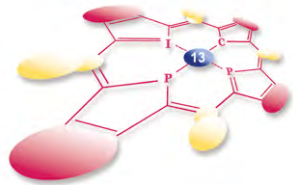

DNA-templated multi-porphyrin systems

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DNA has become very attractive as a scaffold for functional molecules on the nanometre scale. The sequence-specific insertion of modified nucleotides using automated DNA synthesis allows for the creation of 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 multi-porphyrin arrays.[1,2] The spectroscopic data and structure calculations indicate the formation of a stable helical array in the porphyrin-DNA but also reveal intermolecular interactions giving discrete assemblies. The π-stack of the porphyrins leads to strong electronic interaction between the chromophores.

The porphyrin-modified DNA is now being used in several applications, spanning optics, electronics, medicinal chemistry and sensors. We will present our latest research in these fields with several selected examples:

a) DNA-based molecular rulers enable scientists to determine important parameters across biology, from the measurement of protein binding interactions to the study of membrane dynamics in cells. However, existing rulers can suffer from poor nanometre resolution due to the flexible nature of linkers used to tether to the DNA framework. We aimed to overcome this problem using zinc and free-base porphyrin chromophores attached via short and rigid acetylene linkers.[3] This connectivity enables the distance and angle between the porphyrins to be fine-tuned along the DNA scaffold. The porphyrins undergo favorable energy transfer and chiral exciton coupling interactions to act as highly sensitive molecular ruler probes. To validate the system, we monitored the detection of small changes in DNA structure upon intercalation of ethidium bromide. CD spectroscopy showed the porphyrins undergo highly sensitive changes in excitation coupling to facilitate the base pair resolution of the novel system.

b) The use of azide-alkyne cycloaddition (“click chemistry”), both Cu-catalysed and Cu-free, was probed to attach different porphyrins onto oligodeoxynucleotides (ODNs), and the efficiency was compared to amide coupling reaction. Terminal attachment using the different methodologies provides porphyrin-ODNs in varying yields, and the porphyrin-ODNs can be transformed into multiporphyrin arrays using DNA-templated assembly.[4] These arrays show exciton coupling between the porphyrin units and thus demonstrate an efficient and alternative route to multiporphyrin assemblies.

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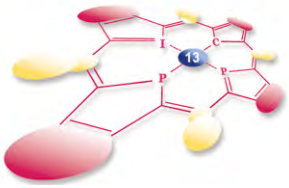

Halogenated subporphyrazines: Synthesis and some unusual transformations

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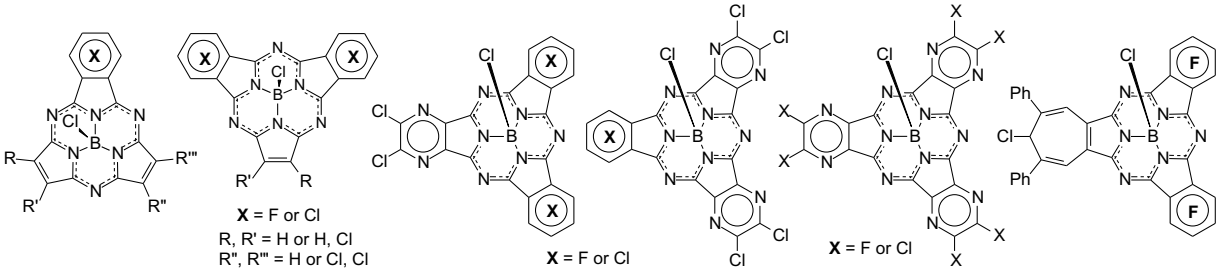
To tune the electronic and spectral properties of subphthalocyanine type-dyes we have prepared the series of halogenated benzo, pyrazine and 1,4-diazepine fused subporphyrazines differing in the dimension of the π-system, number and position of the fluorine or chlorine atoms [1-4]. Subporphyrazines were prepared starting from commercially available dinitriles (fumaronitrile, tetrafluoro- and tetrachlorophthalonitrile, 5,6-dichloropyrazine-2,3-dicarbonitrile) which were cyclotrimerized or cocyclotrimerized in the presence of boron trichloride in *p*-xylene or *o*-dichlorobenzene upon reflux. Fluorine atoms in pyrazine rings were introduced in chlorinated derivatives by nucleophilic substitution, while pyrrole and 1,4-diazepine rings were halogenated by electrophilic substitution in the course of macrocyclization.



The position of the long-wave Q band maximum in this series can be varied from 500 to 590 nm, and for perchlorinated tripyrazinosubporphyrazine, the highest electron affinity among subphthalocyanine-type dyes was achieved (1st reduction at -0.13 V vs Ag/AgCl in CH_2Cl_2) [1,2]. For some of the halogenated subporphyrazines hydrolytic cleavage of the macrocycle can occur leading to deborylation and formation of diazatripyrrine derivatives. Hydrolytic cleavage of fused 1,4-diazepine ring affords aminobenzamide substituted subporphyrazine [4].

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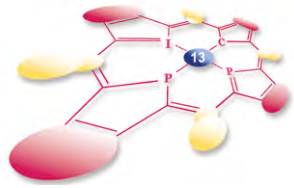

Anisotropic spin relaxation time in chiral assemblies of π-conjugated polymers

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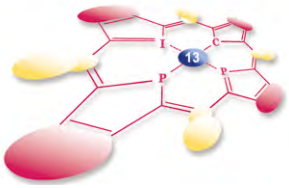
Coupling of spin and charge currents from structural chirality in non-magnetic materials, referred to as the chirality-induced spin selectivity (CISS) effect, has shown promising applications for spintronic devices at room temperature. Here we report the observation of the uniaxial anisotropic spin relaxation time in chiral assemblies of π-conjugated polymers. By widely tuning conductivities and supramolecular chiral structures via the printing method, we found an unprecedently long spin relaxation time of up to ~6 nanoseconds parallel to the chiral axis, whereas the spin relaxation time perpendicular to the chiral axis remains short. The demonstration of the anisotropy of spin relaxation opens possibilities for elucidating the puzzling interplay of spin and chirality, manifesting a new paradigm for spintronic applications using printable chiral assemblies.

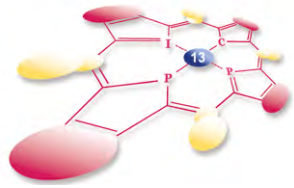


Monitoring light-triggering of chemo-phototherapy drug release in vivo by quantitative fluorescence imaging

Ulas Sunar

SUNY Empire Innovation. Department of Biomedical Engineering. Stony Brook University. USA.

In this talk, I will present an imaging technique that combines reflectance and fluorescence imaging. This tool is designed to enhance the diagnosis and treatment of advanced ovarian cancer, which often involves small tumor nodules within the abdominal cavity. The endoscope is particularly useful for administering and monitoring the concentration of chemotherapy drugs at the site of the tumor. The drug used, Liposomal Doxorubicin, has fluorescent properties that enable its in vivo quantification through fluorescence imaging. The developed endoscope has novel features like Near-Infrared (NIR) light-triggered drug release and can improve detection with enhanced fluorescence contrast. It offers quantitative imaging over large areas and can be used in two modes: imaging and treatment. The endoscope's ability to monitor the precise local concentration of the drug as it is released by light has been demonstrated in a mouse model of ovarian cancer. I will demonstrate that such a tool could improve the delivery of drugs to tumors while minimizing the side effects of systemic chemotherapy.



Magnetically Induced Current-Density Susceptibilities and Ring Currents in Porphyrinoids

Dage Sundholm[a], Qian Wang[a]

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The aromatic nature of metal-containing porphyrinoids[1,2], Möbius-twisted porphyrinoids[3,4], stacked porphyrinoids[5,6] and novel porphyrinoids[7] have been analyzed by calculating magnetically induced current density susceptibilities (MICD), current-density pathways (CDP) and ring-current strengths using our GIMIC approach[8,9]. To understand the complicated CDPs, we developed a method for separating diatropic and paratropic contributions to the MICD, which were analyzed and visualized separately[3]. The approach has been used for determining the aromatic pathways of platinum-containing porphyrinoids[2] and figure-eight-shaped octaphyrins[3,4]. A method for calculating spatial contributions to nuclear magnetic resonance (NMR) shielding constants has been developed[10,11] and used for studying ring-current contributions to the nuclear magnetic shielding constants of the inner hydrogen atoms of lemniscular porphyrinoids[4] and free-base porphyrin[10]. Calculations on dimers consisting of stacked antiaromatic porphyrinoids show that the dimer becomes aromatic when the interactions between the two molecules are strong enough[5,6]. Calculations at density functional theory (DFT) levels as well as at ab initio correlation levels such as second-order Møller-Plesset (MP2) and large-scale complete-active-space self-consistent-field (CASSCF) calculations[6] yielded NMR shielding constants in close agreement with measured ones. The calculated MICD confirms the aromatic nature of the dimer of Ni(II) bis(pentafluorophenyl)norcorrole[5].

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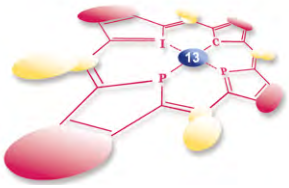

Synthesis of Spiro-Fluorene-Embedded Calix[4]phyrins by Utilizing Scrambled Dipyrromethanes

Masaaki Suzuki[a], **Eisuke Tsurumi**[b], **Yuto Taketa**[b], **and Kyosuke Nakamura**[b]

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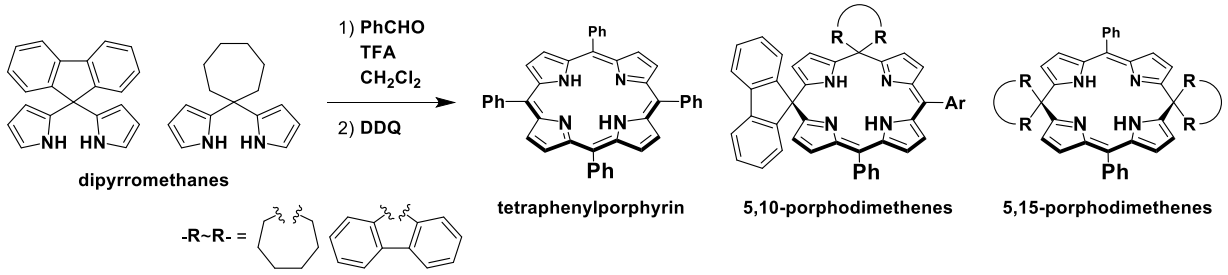
Among calix[4]phyrins, porphodimethenes possess two sp^3 hybridized carbons at their *meso*-positions. We synthesized spiro-cylcloalkyl-bound 5,15-porphodimethenes by condensation of spiro-cycloalkyl dipyrromethanes with benzaldehyde in the presence of a catalytic amount of trifluoroacetic acid (TFA) and the subsequent oxidation using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), affording a mixture of 5,15-porphodimethenes bearing spiro-cyclopentyl and/or spiro-cycloheptyl side chains at the *meso*-positions.[1] As the next step, employing a similar protocol, we attempted to introduce a 9-fluorenyl subunit onto a porphodimethene framework in a spiro manner. Such a three-dimensional linkage of π-systems is expected to give the molecule robustness by a stable connection through multiple saturated bonds as well as a potentially expansive π-electronic network *via* spiro-conjugation.

When two dipyrromethenes bearing spiro-fluorenyl or spiro-cycloheptyl moieties, respectively, were simultaneously treated with benzaldehyde (Scheme 1), not only the presumable 5,15-porphodimethenes (-R~R- = 2,2'-biphenylene and/or hexamethylene) but also 5,10-porphodimethenes (-R~R- = 2,2'-biphenylene or hexamethylene), and tetraphenylporphyrin, which were thought to be derived from the scrambling of dipyrromethanes, were also obtained. Since the reactions of sole spiro-fluorenyl dipyrromethane with mesitaldehyde or pentafluorobenzaldehyde instead of benzaldehyde also gave the corresponding porphyrin (only for mesitaldehyde), 5,10-porphodimethene, and 5,15-porphodimethene, thus such scrambling side reaction of dipyrromethene was supposed to be sufficiently reproducible in the case of acid catalyzed tetrapyrrolic annulations. In addition to a similar formation of a 5,10-derivative given by the suggested scrambling of *meso*-phenyldipyrromethane reported very recently,[2] such a strategy formally can be regarded as a synthesis of tripyrrin due to the fully conjugated tripyrrolic partial structure.[3]



Scheme 1. Synthesis of spiro-fluorene-embedded porphodimethenes by scrambling of dipyrromethanes.

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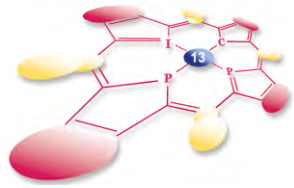

Iminopyrrole-based self-assembly: towards mechanically interlocked pseudoporphyrinoids

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The construction of a supramolecular architecture through a subcomponent self-assembly approach employs the pyridine-based dialdehyde reacting with the amine, generating a respective diiminopyridine.[1] The replacement of the latter with iminopyrrole synthon was envisaged to allow for the construction of coordinationally dynamic entities, providing a new group of mechanically interlocked molecules. Iminopyrrole synthons were previously exploited for the construction of macrocycles and molecular cages.[2,3] The use of diformylpyrrole in the reactions targeting mechanically interlocked molecules proved that the iminopyrrole synthons can be treated as a full-fledged replacement of iminopyridines for the construction of metal-stabilised architectures[4], which revealed new properties, such as intramolecular dynamics and allowed the observation of novel coordination modes of the introduced metal nodes. The use of this synthetic strategy allowed for the construction of a new class of metal-stabilized mechanically interlocked architectures resembling porphyrinoid macrocycles.

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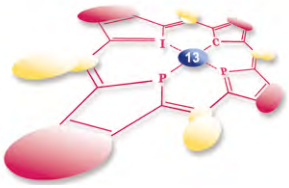

Chirality in chlorophylls and their derivatives

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Chlorophylls (Chls) are the most abundant pigments in phototrophs and function in light-harvesting and energy-migrating antennas and electron-transferring reaction centers. Chl molecules are stereochemically pure compounds within photosynthetic organisms [1,2]. Specifically, Chl-*a* is found in oxygenic phototrophs including higher plants, algae, and cyanobacteria, and its molecular structure is illustrated in the left drawing of Fig. 1. In the core part of a Chl-*a* molecule, three asymmetric carbons are at the 13^2-, 17-, and 18-positions, whose stereochemical orientations are confirmed to be *R*-, *S*-, and *S*-configurations, respectively. Chl-*a* possesses two more asymmetric carbons in the phytyl group as the esterifying group in the 17-propionate residue. In photosynthetically active proteins, Chl-*a* molecules are always fixed by the axial coordination at the central magnesium atom with any species, such as a histidyl imidazolyl group and a water molecule. The magnesium complexes axially coordinated from either the upper or lower side of the cyclic tetrapyrrole plane bearing unsymmetrically peripheral substituents provide additional chirality at the five-coordinated magnesium atom. These *C*- and *Mg*-centered chiralities are observed for all the Chl-*a* molecules in natural systems.

Here, we report chirality in naturally occurring Chls and their synthetic derivatives, including pheophorbides-*a* possessing asymmetric carbon atoms at the 3^1-, 7-, 8-, and 13^2-positions, nitrogen atom at the 22-position, and metal atoms at the central position as well as rotationally restricted C3/C5/C20-substituents around the C3–$C3^1$/C5–$C5^1$/C20–$C20^1$ single bonds (Fig. 1, right) [3–7].

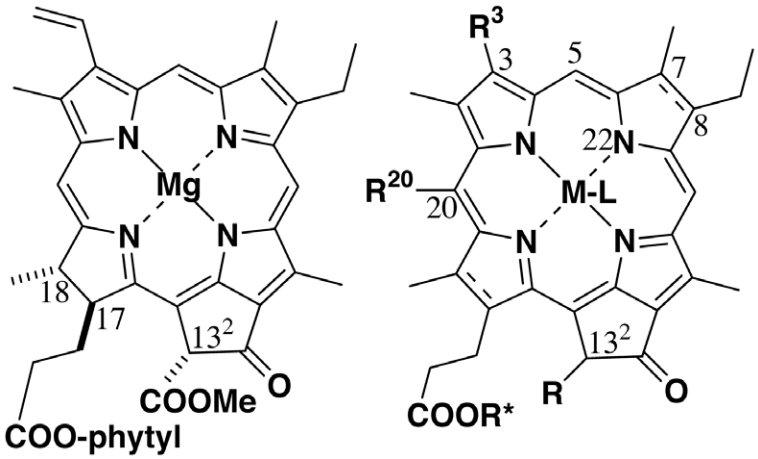

Fig. 1. Molecular structures of Chl-*a* (left) and pheophorbides-*a* (right).

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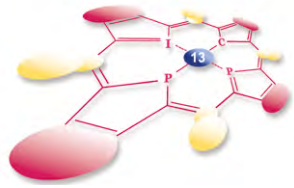

Nanoporous Liquid Crystals for Guest Molecule Arrays

Kentaro Tanaka

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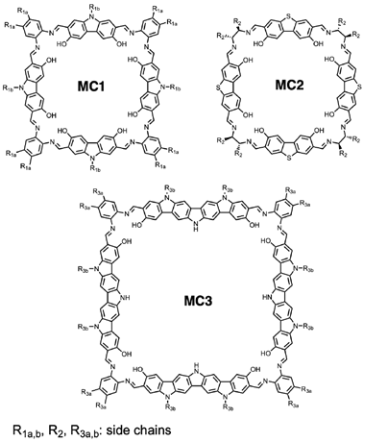
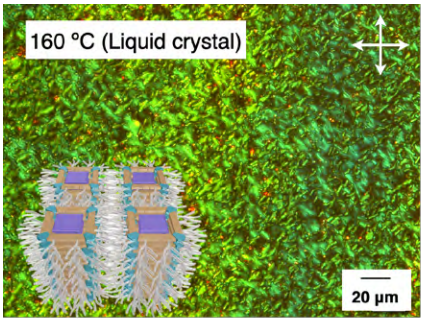
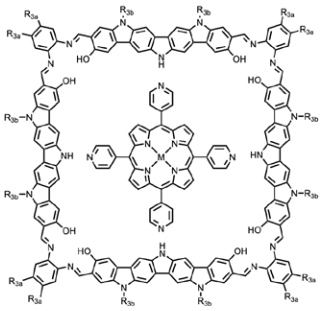
Structurally well-defined macrocyclic molecules have great potential to accommodate specific guest molecules in the cavity. Recently, we have reported a series of macrocycles composed of four carbazoles linked to four salphen ligands [1], four dibenzothiophenes linked to four salphen ligands [2], or four diindrocarbazoles linked to four salphen ligands [3] (**MC1**, **MC2**, and **MC3**, respectively). The macrocycles with appropriate peripheral alkyl chains and their tetranuclear metal complexes with square planar metal ions exhibited thermotropic columnar liquid crystalline properties [1-2]. These macrocycles stack up to form columns in the fluid materials, and nanochannels are formed in the center of the columns [4]. The nanochannels would be nanospaces for arranging guest molecules in the highly oriented fluid materials. In particular, the giant macrocycle **MC3** contained a square cavity with a diagonal of 2.5 nm. This giant macrocycle has the largest internal cavity of any known discrete shape-persistent macrocycle exhibiting thermotropic LC properties. The size and shape of the hollow structure make it interesting for molecular inclusion applications. For example, the **MC3** molecule can accommodate a tetrapyridylporphyrin inside the cavity to yield a planar conjugate, and the conjugate showed liquid crystalline behavior.



Liquid Crystalline Macrocycles





Columnar Liquid Crystal of TPyP@MC3

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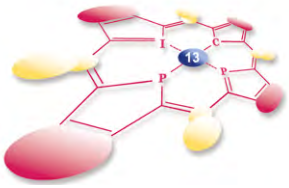

Antiaromaticity of 8,10-Fused Iminoisocorroles

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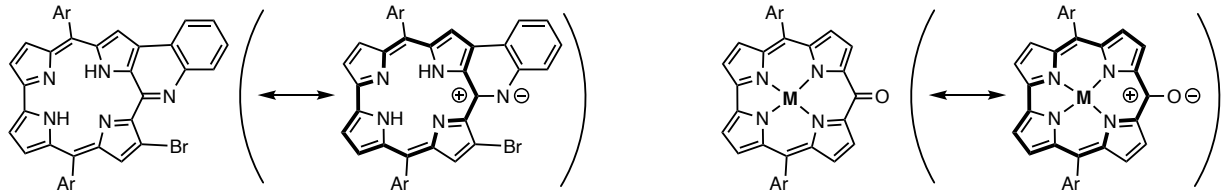
Antiaromatic molecules are usually unstable due to the intrinsic instability arising from their cyclic 4nπ-electronic conjugation systems. However, thermodynamically or kinetically stabilized antiaromatic porphyrinoids have recently emerged and are attracting increasing interest in applications such as OFETs, organic ambipolar batteries, and highly conductive single-molecule wires. While norcorrole complexes have recently been extensively studied as strong 16π antiaromatic ring-contracted porphyrinoids, the parent corrole features essentially 18π aromatic characteristics, hardly altered by peripheral substituents. For long time, *β*-functionalization of *meso*-triarylcorroles has been reported, while *meso*-functionalization of corroles has been left behind the *β*-functionalized counterparts because of the difficult access to *meso*-unsubstituted corroles stable enough to be allowed for further transformation. In 2015, we reported a scalable and reliable synthetic method of *meso*-unsubstituted corroles (*i.e.*, *meso*-free corroles), which opened up a new avenue of peripheral functionalization chemistry based on corroles.[1,2] Along this line, the aromaticity switch by peripheral modification of corrole is a forefront topic.

Herein, we report 8,10-fused iminoisocorrole **1** as a rare example of corrole derivatives featuring antiaromatic resonance contribution.[3] Iminoisocorrole **1** was synthesized from 5,15-diaryl-8,12-dibromocorrole as a useful synthon for new *β*-functionalized corroles in 4 steps including Ag(III) metalation, Suzuki-coupling with 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline, demetallation with $NaBH_4$, and oxidation with MnO_2. The antiaromatic characters of **1** was probled by ^{1}H NMR spectrum, UV/vis absorption spectra, cyclic voltammetry, NICS and ACID calculations. From these results, it was considered that the weak antiaromaticity derives from the C(+)–N(–) polarized resonance contribution that can be indeed mapped by ESP. The degree of the antiaromatic contribution is smaller than that of *meso*-oxoisocorroles **2M** we previously reported.[4] In the case of *meso*-oxoisocorroles, the central metal ions play an important role to attenuate the conjugation. In addition, Lewis-acid-promoted antiaromaticity enhancement has been experimentally observed. Thus, we here demonstrate that changing the *meso*-substituted heteroatoms as well as the fused structure also play a pivotal role to alter the contribution of the polarized resonance state.



1 16π antiaromatic **2M (M = 2H, Zn, Ni, Pd)** 16π antiaromatic

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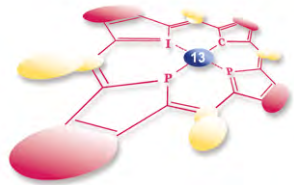

Chiral Metal-Organic Frameworks as Catalysts for the Oxygen Evolution Reaction

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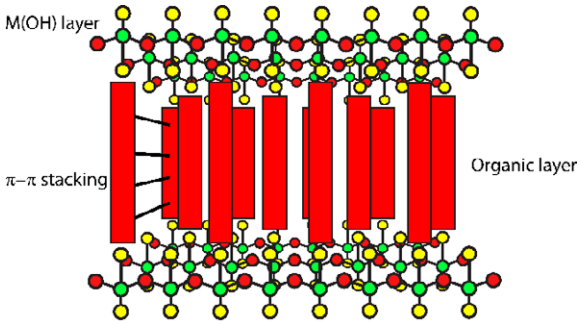
The important positive effect that spin-polarized currents have on reducing the overpotential required for the Oxygen Evolution Reaction (OER), and on improving the overall efficiency of the water-splitting process, has been reported recently by several groups [1–4]. Chiral materials can create spin-currents without external electromagnetic fields thanks to the so-called Chiral Induced Spin Selectivity (CISS) effect [5, 6].
The research on metal-organic frameworks (MOFs) as electrocatalysts for the OER has seen several contributions in recent years showing the great potential of this class of materials [7, 8]. However, the possibility of exploiting a chiral MOF to take advantage of the CISS effect in electrocatalysis has still to be explored [9].
In this work, we report the investigation of nanostructured chiral metal hydroxide-organic frameworks based on transition metals as catalysts for the OER, and we show the improved efficiency of a chiral catalytic system compared to the achiral analogue.



Model structure of the metal hydroxide-organic frameworks used in this study

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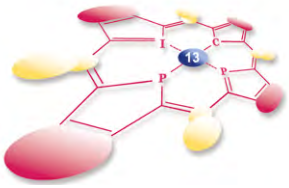

Ultrafast Photoinduced Coherent Proton-Coupled Electron Transfer Reactions

Rui Liu[a], Zachary X. W. Widel[a], Jarrett P. Mansergh[a], Jiaqi Zhu[a], Aubrey R. Caplin[a], Nicholas F. Polizzi[a,b], Samuel I. Mann[b], Kassandra J. Pinnock[a], Peng Zhang[a], William F. DeGrado[b], David N. Beratan[a] and Michael J. Therien[a]

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Nature's bioenergetic proton-coupled electron transfer (PCET) reactions exploit intricate coupling of electron (e^-) and H^+ movement. PCET underpins photosynthesis and respiration, as well as nitrogen and carbon dioxide fixation in the biosphere.[1] Nature evolved a wide range of PCET reactions, from sequential ET and proton transfer (PT), to concerted transfers, with a continuum of intermediate regimes; this richness continues to prompt the development of approaches to better understand their mechanisms [1-4]. Yet, the coordinated motion of the humble e^- and H^+ is poorly understood in homogeneous media. Here we describe ultrafast photoinduced PCET and hole transfer reactions that oxidize tyrosine and tryptophan analogues at unit quantum yield that rely on powerful rylene- and porphyrin-based photooxidants. These systems manifest ultrafast photoinduced PCET charge separation (CS) reactions ($\tau_{CS} \sim 400$ fs) at unit quantum. This work illuminates ultrafast dynamics of ET and PT via time-resolved pump–probe transient absorption experiments that concomitantly monitor the vis-NIR and IR spectral regions. These compositions and transient dynamical experiments provide a roadmap for distinguishing concerted ETPT reactions and stepwise yet ultrafast ET-PT processes, as well as opportunities for studying the driving force and solvent dependences of PCET reactions.

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Photoactive Bioconjugates and (nano)Materials for Targeted and Enhanced Cancer Photodynamic Therapy

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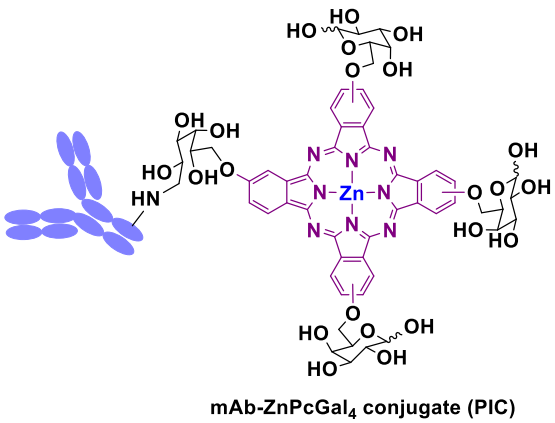
Cancer photodynamic therapy (PDT) has had an enormous development with newly approved photosensitizers (PSs). However, the currently approved ones suffer from low selectivity and unsatisfactory photochemical properties, which limit their therapeutic effectiveness. Therefore, the research community believes that more selective and powerful PSs are still needed to extend conventional PDT to a broader clinical use for cancer treatment. Having this in mind, photoactive bioconjugates and nanoformulations are interesting strategies to surpass some of PSs' limitations, and more and more targeted PDT (tPDT) has emerged as a better alternative. Actually, it is expected that these novel molecular-targeted PSs and nanoformulations will push forward PDT into a robust therapeutic solution for the treatment of different tumors. Some of the rational strategies to enhance cancer PDT include photoactive glycoconjugates, immunoconjugates and (nano)formulations. In this context, the decoration of the periphery of porphyrins, and similar macrocycles, with different (bio)motifs, such as carbohydrates and monoclonal antibodies opens the possibility of fine-tuning, not only the PSs' physicochemical properties but also the nanomaterials' functions.

In this talk, some of our recent work on photoactive bioconjugates and silica nanoformulations will be highlighted, presenting their synthetic strategies and their main photochemical and photobiological results on cancer treatments [1-3].



Photoimmunoconjugate for colorectal cancer PDT

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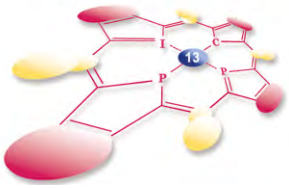

Subphthalocyanine-Based Molecular Materials: From Singlet Fission and Molecular Photovoltaics to Chirality and Supramolecular Organization.

Tomás Torres[a,b,c], Jorge Labella[a], Giulia Lavarda[a], Elisa López-Serrano[a], Marta Gómez-Gómez[a], Juan Laforga-Martín[a], Adriana Agramunt[a,b], Daniel Holgado[a]

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Due to their exceptional structural and photophysical properties, such as pronounced absorption and/or emission in the UV-vis and near-infrared (NIR) spectrum, superior charge transport characteristics, and broad chemical adaptability, **Subphthalocyanines** (**SubPcs**; Figure 1a) occupy a distinguished position among the most widely explored and versatile porphyrinoids [1]. These aromatic macrocycles, characterized by their distinctive non-planar structure, exhibit significant potential across various cutting-edge applications. These applications include the creation of polar superstructures, the development of thermotropic and lyotropic liquid crystals, the utilization as non-fullerene acceptors, and as materials for singlet fission.

Herein, we unveil pivotal aspects within SubPc chemistry that are ushering in a new era in the conception, synthesis, and utilization of these macrocycles [2]. We will elucidate how SubPcs can be harnessed in molecular photovoltaics, serving as materials for singlet fission, and explore their enantiopure versions in chiral technologies (Figure 1b-d) [3]. Additionally, we will present the synthesis and characterization of SubPc columnar materials. Depending on the molecular design, these materials can function as either lyotropic or thermotropic liquid crystals, form columnar polymers in solution, or organize into polar assemblies in the solid state. The unconventional behaviours governing such phenomena are scrutinized through a combination of various experimental techniques.

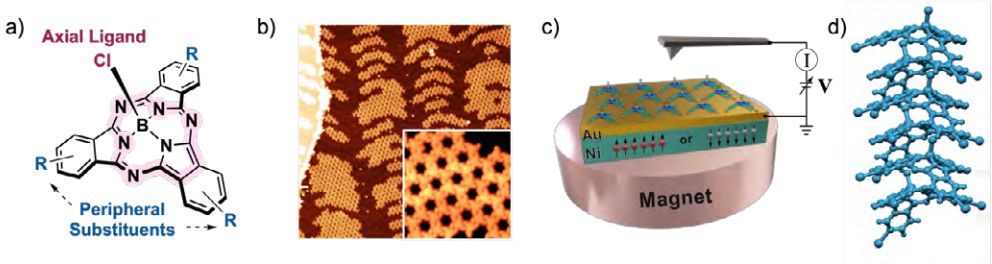

Figure 1. a) The molecular structure of SubPcs. b) An example of a self-organized network composed of SubPcs absorbed on Au (111). c) A SubPc-based spintronic device. d) A columnar array based on SubPcs interacting in a head-to-tail fashion at a solid state.

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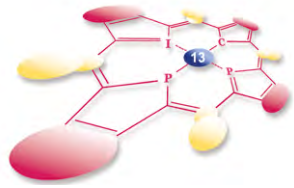

Trapping of reaction intermediates of nitric oxide reductase by cryo-photolysis of caged substrate

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ORALS

As active centers of metalloenzymes, heme participates in a variety of physiological processes. To understand the action of heme in biology, the reaction mechanism of heme-containing enzymes needs to be clarified. Because time-resolved spectroscopic (TR) techniques are very powerful for the characterization of the reaction intermediates in heme enzymes, we have developed the TR method with a photo-sensitive caged substrate and showed its great potential for studies on heme enzymes through the characterization of the short-lived reaction intermediate of fungal nitric oxide (NO) reductase [1-2]. Here, we tried to further develop the method using a caged substrate and applied this technique to elucidate the reaction mechanism of membrane-integrated NO reductase (NOR).

NOR catalyzes the reductive coupling of two NO molecules to nitrous oxide (N_2O) using two protons and reducing equivalents ($2NO + 2H^+ + 2e^- \rightarrow N_2O + H_2O$) at a heme/non-heme Fe binuclear center. Because this reaction contains fundamental elements for chemical reactions such as the N-N bond formation and the N-O bond cleavage, the reaction mechanism will provide how the metal center effectively proceeds with the chemical reaction. To follow the catalytic reaction of NOR, the TR-visible absorption spectra for NOR were measured using caged NO, which produces NO upon UV illumination, as a reaction trigger. The TR data indicated the following mechanism [3]. One NO molecule binds to reduced NOR to form *intermediate 1* in ~5 μs, followed by the formation of *intermediate 2* without protonation and the second NO biding at ~100 μs. Finally, the binding of the second NO and the protonation to *intermediate 2* yield N_2O in ~ms. To get further insights into the structure of the intermediates, we aimed to trap the reaction intermediates by the photolysis of caged NO under cryogenic temperature (cryo-photolysis) and following thermal annealing. The cryo-photolysis of caged NO with reduced NOR and subsequent annealing at ~160 K produced a species showing g = ~4 signal in EPR spectroscopy [4]. Taken together with the fact that the NO stretching mode was detected at 1683 cm^{-1} by the TR-IR measurement with caged NO at 5 μs, *intermediate 1* is a non-heme Fe-NO species [4]. Based on the data obtained by the method using caged NO, more details on the catalytic mechanism in NOR will be discussed.

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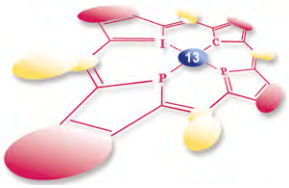

MRI Contrast Agents Based on Porphyrin Complexes

Eva Toth[a]

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Thanks to its excellent spatial resolution and the lack of ionizing radiation, Magnetic Resonance Imaging (MRI) has become the most prominent full-body imaging modality in clinics. In MRI, paramagnetic chelates can substantially enhance the contrast. We have investigated Gd-complexes conjugated to porphyrin derivatives as theranostic agents combining MRI with photodynamic therapy where we could show that the presence of the porphyrin platform can be beneficial for the MRI efficiency of the Gd^{3+} chelate [1]. Porphyrin derivatives have been also explored for Gd3+ complexation [2]. Following recent safety and ecological concerns related to the use of gadolinium, other paramagnetic metal ion alternatives are intensively investigated, expected to provide a better safety profile and biocompatibility. The most obvious choices are high spin Mn^{2+} (S = 5/2) and Mn^{3+} (S = 2). Manganese is an essential element that alleviates the toxicity concerns related to the use of its complexes as exogenous imaging probes. Porphyrin ligands can be excellent chelators for both Mn^{3+} and Mn^{2+}. After some early reports, Mn-porphyrins are increasingly attracting attention in the context of MRI. Mn^{3+} porphyrin complexes can provide interesting relaxation properties, in particular with improved efficiency at higher magnetic fields. Also, the redox properties of manganese can be exploited for the design of MRI probes with the capability to detect the redox state of tissues, which is considered as an important biomarker for various pathologies [3]. Further, the introduction of ^{19}F atoms on the molecules opens novel opportunities for detection not only in classical ^{1}H, but also in ^{19}F MRI with the advantage of eliminating any background signal [4]. Several examples will be presented to illustrate these developments.

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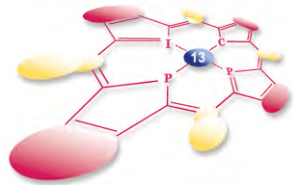

Development of Oxidative Dimerization of Alkaloids Using Iron Phthalocyanine Catalyst

Hirofumi Ueda[a], Soichiro Sato[a], Kenta Noda[a], Kosuke Okada[a], Ken-ichi Ojima[a], Nagao Kobayashi[b,c], Hidetoshi Tokuyama[a]

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From nature, numerous dimeric compounds, demonstrating a variety of biological activities, with potential applications in pharmaceuticals, fragrances, and agrochemicals, have been isolated.[1] For example, microorganisms, such as bacteria and fungi, produce dimeric alkaloids via enzyme-mediated oxidative dimerization of monomer units. However, in a flask, oxidative dimerization of nitrogen-containing polyfunctional compounds is challenging due to the high reactivity of nitrogen functional groups towards oxidizing agents. We have recently developed a novel biomimetic oxidation using an iron phthalocyanine catalyst, inspired by the cytochrome P450 mediated oxidation. Among various iron catalysts examined, including porphyrins, phthalocyanines, and non-heme iron complexes, we found that a combination of a carboxylated iron phthalocyanine complex[2] with oxygen as a bulk oxidant effectively facilitates the oxidative dimerization of structurally complex alkaloids. By application of this methodology, we have successfully achieved the total synthesis of pharmaceutically valuable dimeric alkaloids [3-4], which will be discussed in detail.

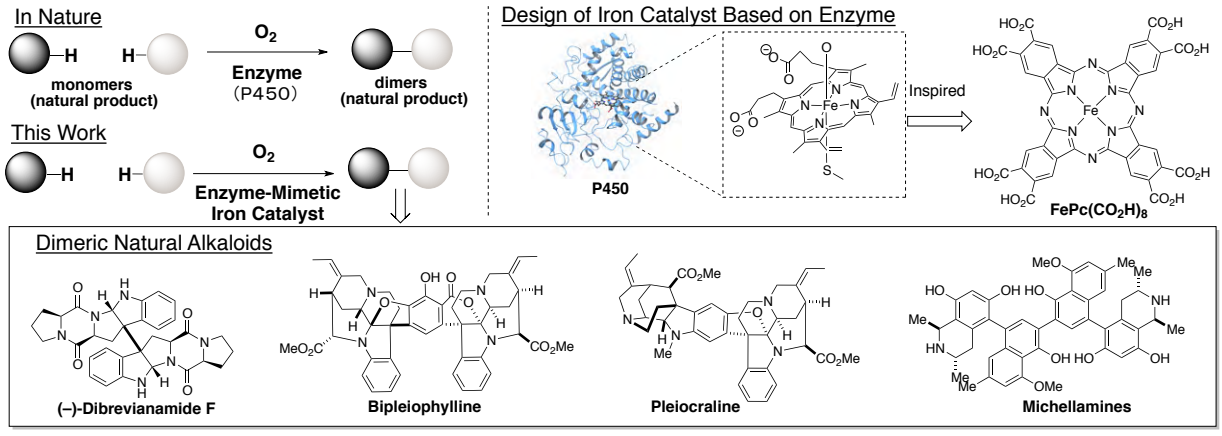

Figure. Outline of This Research

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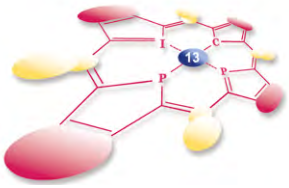

Metal-Organic Frameworks for Advanced Polymers

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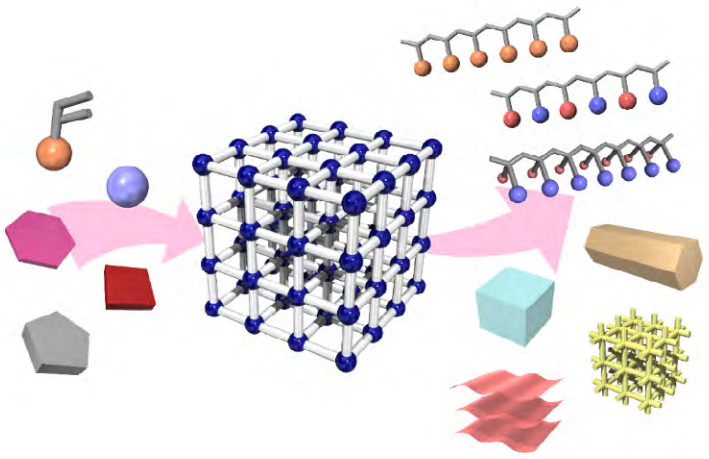
Metal-Organic Frameworks (MOFs) composed of metal ions and organic ligands have been extensively studied. The characteristic features of MOFs are highly regular channel structures with controllable pore sizes approximating molecular dimensions and designable surface functionality.Thus, MOFs have been successfully applied in numerous domains, including storage and separation, catalysis, energy, and sensing. However, the majority of relative studies in the early stages of MOF research focused on gas and solvent molecules as guests, despite the potential of infinite nanochannel structures for the encapsulation of macromolecules.

Since 2005, we have utilized the regular and tunable channels of MOFs for a field of polymerization, which can allow multi-level controls of polymers, nanoparticles, and nanographenes [1]. In addition, construction of nanocomposites between MOFs and polymers provides unprecedented material platforms to accomplish many nanoscale function [2]. We have also developed direct insertion of polymers into nanochannels of MOFs, which enables powerful macromolecular recognition and separation technologies with exceptionally high selectivity [3]. Designing nano-sized pores of MOFs with a regular arrangement of reactive/interactive/responsive entities offers the possibility of universal polymer production and purification that cannot be accomplished by conventional methods.



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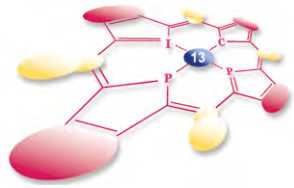

Using Spin Polarization and Transient EPR to Study Charge Separation in Aluminum(III) Porphyrin Homodimer – Fullerene Supramolecular Assemblies

Art van der Est[a] Stefan Charon[b], Niloofar Zarrabi[b], Jatan K. Sharma[c] Paul A. Karr[d], Francis D'Souza[c] and Prashanth Poddutoori[b]

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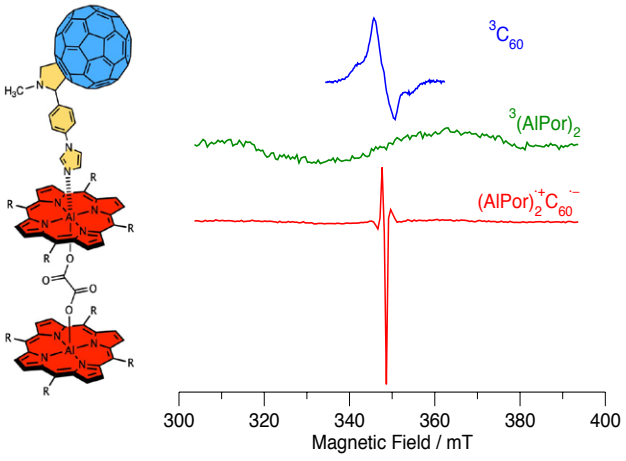
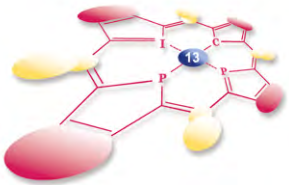
Aluminum(III) porphyrins exhibit properties that make them ideal candidates for mimics of the primary donors in photosynthetic reaction centers. Their ability to form axial covalent and coordination bonds makes it possible to construct co-facial dimeric structures that mirror the geometry of the special pair dimers found in reaction centers. Moreover, the axial bonding ability can also be used to functionalize these dimers with electron acceptors and donors to create complexes that mimic the photosynthetic electron transfer chain. We have been investigating using the electron spin polarization patterns observed using time-resolved EPR methods. These patterns are unique among the spectroscopic signatures of donor-acceptor complexes because they reflect not only the properties of the states being detected but also the pathway by which they were generated. An additional feature that makes this method very useful is the strong differences in the EPR spectral properties of triplet states and radical pair states so that demonstrating the presence of charge separation becomes trivial.



Here, we report on an Al(III)-porphyrins homodimer in which the two porphyrins are covalently bound face-to-face by an oxalate di-ester bridge. Using coordination of an appended imidazole to the Al center, C_{60} can be bound to the dimer to create a self-assembled donor-acceptor complex. The spin-polarized transient EPR spectra of the C_{60} and porphyrin dimer are strikingly different from one another and from the much narrower spectrum of the dimer-fullerene complex. The latter clearly shows that a high yield of charge separation between the porphyrin dimer and C_{60} occurs. Both the yield and lifetime of the charge separation in soft toluene glass are longer than in similar complexes in which the donor is a porphyrin monomer, illustrating the stabilization achieved with a dimeric donor.



Development of Topical Formulations for Porphyrinic Photosensitizers

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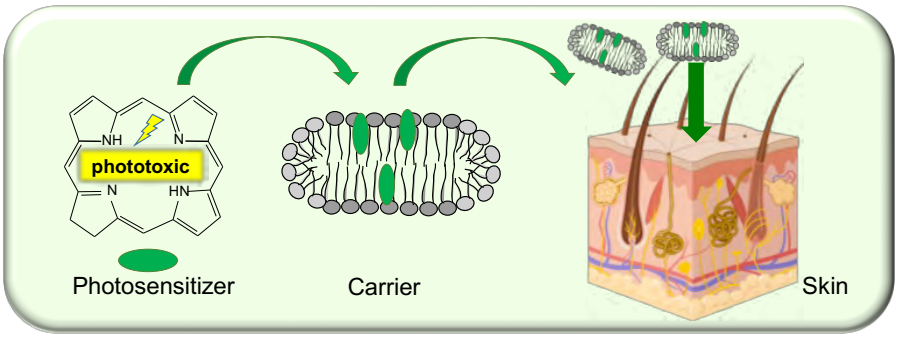
Topical Photodynamic Therapy (tPDT) of non-melanoma skin cancer (NMSC) is currently widely applied in dermatology using 5-aminolevulinic acid (5-ALA) or esters thereof as a precursor, from which the active component, protoporphyrin IX, is formed in the body's cells [1]. Extending tPDT to the direct application of porphyrinic compounds could offer new possibilities, i.e., opening up the field to a wide range of porphyrinic structures designed for the treatment of NMSC and precancerous skin lesions.
In the current contribution, the development of suitable formulations aimed at shuttling porphyrinic photosensitizers into the outer epidermal skin layer will be presented. Our recent work was focused on phospholipid bicelles as promising new skin delivery vehicles of porphyrinic compounds for their potential use in tPDT. Bicelles encompass the advantages of being inherently small, disc-shaped, and biocompatible [2]. The various steps involved in the formulation development will be discussed. These include the preparation of different bicelles and alternative systems, monitoring photosensitizer encapsulation by different methods like NMR spectroscopy [3], testing the performance of skin penetration enhancers, and finally evaluating drug uptake by the skin using different skin models.



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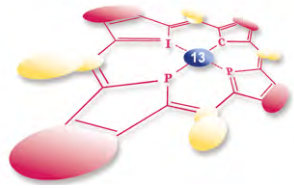

Synthesis and chemistry of tetrafluorobenzo[α]-fused BODIPY derivatives

Maria da Graça H. Vicente[a], Sebastian Oloo,[a] Guanyu Zhang,[a] Andrea Savoldelli,[a] Petia Bobadova-Parvanova[b], Frank Fronczek[a] and Kevin M. Smith[a]

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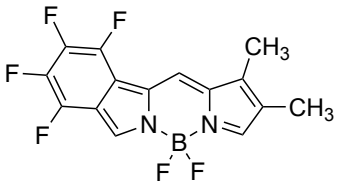
Fluorinated organic fluorophores have important roles in medicinal chemistry. We will discuss the synthesis and chemical reactivity of a series of tetrafluorobenzo[a]-fused BODIPY derivatives, including compounds **1** [1] and **2** [2]. The common precursor in the syntheses of these derivatives is 4,5,6,7-tetrafluoroisoindole [3]. The spectroscopic properties of these BODIPY derivatives and their potential applications in ^{19}F NMR and fluorescence imaging will be presented. The multiple fluorine atoms in these compounds not only enhance their solubility in multiple solvents but also provide reactive sites toward nucleophilic substitution reactions with high regioselectivity.



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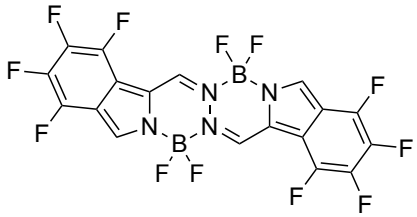

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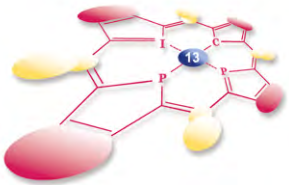
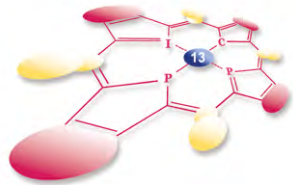


Porphyrin-Based Phosphorescent Probes: New Approaches to Imaging pH and Temperature Simultaneously with Oxygen

Srinivasa Rao Allu, Qi Sun, Mirna El Khatib, Thomas Troxler and Sergei A. Vinogradov

Department of Biochemistry and Biophysics, Perelman School of Medicine, and Department of Chemistry, School of Arts and Sciences, University of Pennsylvania, Philadelphia, USA

Phosphorescent probes comprising dendritically-encapsulated π-extended porphyrins, known as Oxyphors, have become a widely used tool for imaging of molecular oxygen with applications spanning across many areas of biology and medicine. Imaging phosphorescence decay times offers a number of significant advantages, including insensitivity to endogenous absorption, scattering and autofluorescence, which makes it superior to more commonly used fluorescence lifetime imaging, let alone intensity-based or ratiometric imaging schemes. Therefore, it would be desirable to extend the scope of the phosphorescence lifetime-based methods onto sensing environmental analytes other than oxygen. Here we present our efforts to exploit unique photophysical properties of tetraarylphalimidoporphyrins (TAPIP) and diarylphalimidoporphyrins (DAPIP) to create new schemes for unbiased imaging of pH and temperature in biological systems in parallel with oxygen. Using a combination of phosphorescent complexes of TAPIP and DAPIP, we are designing a sensor for pH and oxygen, termed pHOx, whose operation is based on a new principle: measuring ratios of phosphorescence lifetimes. Unlike all existing optical pH sensors, measurements by pHOx are not affected by optical heterogeneities of the medium and provide unbiased pH readings *in vivo* simultaneously with O_2. On another front, Pd complexes arylphalimidoporphyrins have been shown to emit both phosphorescence (PHOS) and thermally activated delayed fluorescence (TADF), suggesting an approach to optical sensing of temperature. However, to make temperature readings insensitive to optical heterogeneities of biological tissue, a Pd porphyrin probe would need to be supplemented by another probe system, which would emit signals insensitive to oxygen and temperature (such as prompt fluorescence) at the same wavelengths as those of PHOS and TADF, so that the signals of that probe could be used for optical correction. The progress and pitfalls in the two aforementioned projects will be discussed.



Biomimetic Pyrroles and Red-Wine Inspired Structures for Advancing Charge-Transfer Science

Valentine I. Vullev[a]

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Charge transfer (CT) sustains life on earth and ensures our modern ways of leaving possible [1]. CT is at the centre of photosynthesis, and understanding how to control it and improve the efficiency of the desired processes is crucial for energy sustainability. Biomimetics and biological inspiration offer key paradigms for advancing artificial photosynthesis [2]. Dipoles are ubiquitous, and their multifaceted effects on CT still remain unexplored. We design and devlop bioinspired molecular electrets to explore emerging dipole effects on CT [2]. Even a single electret residue can rectify CT and exert enormous effects on CT kinetics [3,4].As analogues of porphyrins, pyrrolopyrroles and diketopyrrolopyrroles (DPPs) are versatile electron-rich and electron-deficient structures, respectively, that can initiate photoinduced CT. As photosensitizers, DDPs can inject holes in electron-rich molecular electrets and initiate dipole-mediated CT [4,5]. Concurrently, the electrochromic response of DPP allows us to monitor the dipole-generated localized fields. In parallel, we develop pyranoflavyliums (PFs) based on structures of pigments formed during the maturation of red wines. The PFs are potent photooxidants and remarkably photostable. (How easy is to clean red-wine stains?). PFs have strong absorption in the visible spectral region and their reduction potentials can be as high as -0.2 V vs. SCE, placing them among the very best (if not the best) metal-free organic photooxidants. The pyrrole derivatives, the pyranoflavyliums and the anthranilamide molecular electrets present a valuable toolbox for exploring the emergence of new CT phenomena essential for advancing artificial photosynthesis.

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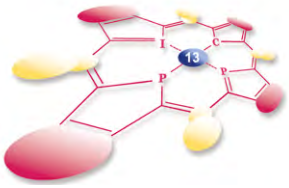

Chiral Molecules and their Chiral Induced Spin Selectivity Response

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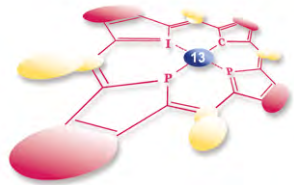
Chemistry Department, University of Pittsburgh, Pittsburgh PA 15260

The discovery of the chiral-induced spin selectivity, CISS, effect opens new possibilities for the control of the electron spin in materials, both organic and inorganic. Recent work has shown that the CISS properties of a material correlate with its chiro-optical properties. We describe recent work on the connection between chiro-optical properties and the CISS responses, including enantiospecificity in intermolecular binding and the use of chiral inorganic structures for spin-selective redox chemistry.



Complicated Photophysics of (some) Porphycenes

Anastasiia Svidzerska,[a] Idaresit Mbakara,[a] Katsiaryna Duk,[a] Michał Kijak,[a] Agnieszka Gajewska,[a] Arkadiusz Listkowski,[b] and Jacek Waluk[a,b]

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Contrary to porphyrins, free base porphycenes are usually good emitters, with fluorescence quantum yields reaching 50% in room temperature solutions.[1] However, some derivatives, e.g., *meso*-tetraalkyl-substituted porphycenes, exhibit extremely weak emission.[2] Interestingly, fluorescence intensity drastically increases when the chromophore is placed in a rigid environment.

In order to explain this rather unusual photophysical behaviour, various models have been proposed. All of them suggest distortion from planarity after electronic excitation. One of the models postulated S_1-S_0 conical intersection along the path of hydrogen transfer between the lowest energy *trans* and the highest energy *cis* tautomeric forms.[3] For many porphycenes, experiments demonstrated that efficient radiationless deactivation of the lowest excited singlet state correlates with the strength of two intramolecular hydrogen bonds.[4] This suggested a quantum nuclear effect, delocalization of the inner protons, as the factor responsible for rapid S_1 deactivation.[4-5]

Our recent studies of numerous novel porphycene derivatives bearing one or more such substituents as alkyl, aryl, halogen, nitro, and amino groups at different positions revealed that substituted porphycene isomers can exhibit very different photophysical properties. For instance, singly substituted chlorine or doubly substituted fluoro derivatives exhibit strong or weak emission depending on the position of the substituents. These findings will be analyzed in combination with quantum chemical calculations in order to find a common trait responsible for the loss of emissive properties in porphycenes.

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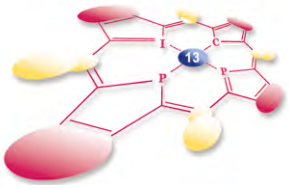

Hyperporphyrins: Charge-transfer Interactions with *meso*-Aryl Substituents

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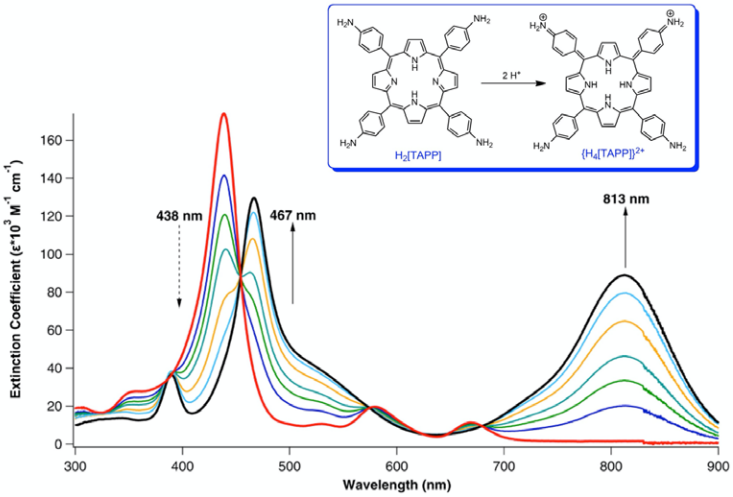
Martin Gouterman introduced the term hyperporphyrins for porphyrins that exhibit unusual redshifted spectra. The underlying changes that cause the spectra to deviate from the classic 4-orbital model are most commonly additional orbitals involving a central metal, leading to metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT).[1] Other causes have also been noted, especially charge-transfer interactions involving substituents.[2] In this presentation we will focus on *meso*-tetraarylporphyrins with significant charge transfer interactions between the aryl groups and the porphyrin macrocycle.

A definitive example of this dramatic redshift occurs on diprotonation of *meso*-tetrakis(4-aminophenyl)porphyrin [**TAPP**].[3] Two protons add to the porphyrin nitrogens but there is substantial delocalization of charge to the peripheral amino groups, as illustrated by relevant resonance forms. We have recently presented TDDFT (CAMY-B3LYP) calculations that elucidate the orbital changes that lead to this shift.[4]



We will also describe analogous charge-transfer spectra with hydroxyphenyl and pyridyl substituents as well as cases with mixed substituents. Both acid-base and redox reactions can lead to these effects.

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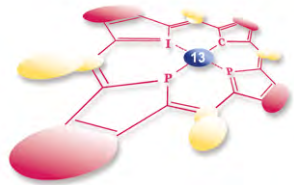

Fusion of *Pi*-Extended Porphyrins with Antiaromatic Components

Saad Shaikh, Courtney Cooper, Ajyal Alsaleh, Ram Kaswan, Francis D'Souza, Hong Wang

Department of Chemistry, University of North Texas, Denton, TX 76201, USA

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Photofunctional materials are on the center stage of modern science and technology for diverse application ranging from solar energy conversion to bioimaging. Understanding and learning to manipulate the excitation dynamics of photofunctional materials are critical to promoting advances in this important field.[1, 2] Porphyrins are known to possess exceptionally rich electronic and photophysical properties. The excited kinetics and dynamics of porphyrins play a key role in determining the functions of porphyrins in their applications. Incorporating antiaromatic moiety into porphyrins is expected to change the aromaticity both in the ground and the excited states and can become a driving force for photoreactivity and initiate new excited state properties. Several new synthetic methods to fuse different types of antiaromatic rings to the porphyrin periphery at the β, β-positions have been developed in our laboratory in the past two years. Using these methods, several novel π-extended porphyrin systems with fused 5-, 7- and 8-membered rings have been designed and prepared. Porphyrins fused with 12H-benzo[f]benzo[4,5]imidazo[2,1-a]isoindole demonstrated an unusually long-lived charge-separation state (37.2 μs).[3, 4] An unusual trend was observed in the fluorescence quantum yield upon converting thiophene-attached benzoporphyrin to naphthodithiophene-fused porphyrin.[5] A remarkable light effect was obtained with an acenaphtho[1,2-*b*]pentacene-fused porphyrin-phthalocyanine heterojunction device, which exhibited high ammonia sensitivity.[6] Unusual ring dynamics and reversal trend charge transfer were observed with 1,3,5,7-cyclooctatetraene (COT)-fused porphyrins.[7] The characterizations of these π-extended porphyrins including time-resolved emission and transient absorption spectroscopy, cyclic voltammetry, and DFT calculations will also be presented.

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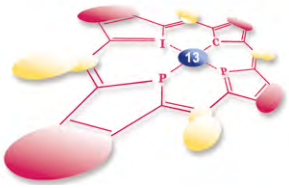

Ligand Binding Cooperativity and Conformational Changes in Globin Coupled Sensor Signaling

Emily E Weinert[a]

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Bacteria sense changes in their gaseous environment, such as oxygen and nitric oxide levels, and respond by changing intracellular pathways to allow for survival. Multiple families of heme proteins serve as bacterial gas sensors, controlling metabolism, growth, and biofilm formation. Globin coupled sensors (GCSs) are bacterial heme proteins that consist of a globin domain linked by a central domain to an output domain, such as diguanylate cyclase domains that synthesize c-di-GMP, a major regulator of biofilm formation. While O_2-binding typically activates enzymatic activity of GCS proteins, such as the GCS from *Pectobacterium carotovorum* (*Pcc*GCS), we have recently characterized a GCS from *Paenibacillus dendritiformis* (DcpG) that exhibits differential modulation of two enzymatic domains by O_2 and NO [1]. Comparison of DcpG with *Pcc*GCS has identified heme pocket residues involved in modulating O_2 affinity and ligand-dependent activation of GCS proteins. Using equilibrium oxygen binding studies, we have demonstrated that a subset of GCS proteins bind oxygen cooperatively and have identified residues required for cooperative binding. Using a variety of of structural techniques, we have linked key interactions at the heme edge [2]. and ligand binding with changes in protein conformation. Building on these results, we are investigating the roles of protein dynamics and conformational changes in modulating cooperative O_2 binding and ligand-dependent regulation of cyclase domain activity. Taken together, these studies provide new insights into the mechanism by which ligand binding modulates heme-protein interactions to control activity and downstream signaling of GCSs, as well as the broader physiological effects of O_2 sensing, including bacterial growth and virulence [3].

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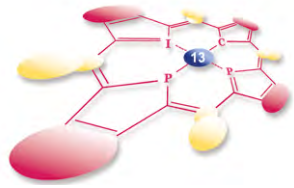

Strapped porphyrins: From bio-inorganic models to self-assembly and back

Jean Weiss

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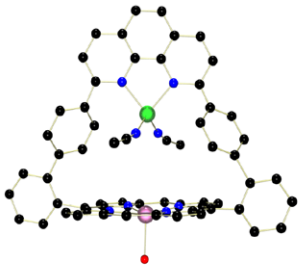
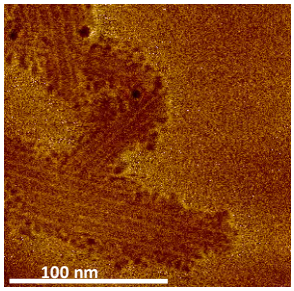
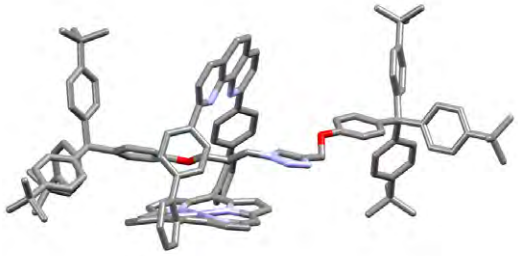
Since the early 90's our group has made extensive use of a phenanthroline-strapped porphyrin initially designed as a hemoprotein model. Our ability to control the introduction of functional groups on strapped porphyrins and the peculiar properties of this structure led to the very efficient formation of catalysts for the reduction of molecular oxygen,[1] self-assembled wires[2] and mechanically bound species such as rotaxanes.[3]







Following the various inspirations of students and erratic successes in grant applications, our interests are now back to bio-inorganic models with the design of structures incorporating bipyridines[4] in covalent and self-assembled strapped structures. The presentation will highlight the importance of copper coordination during a short journey in the land of phenanthroline and bipyridine-strapped porphyrins.

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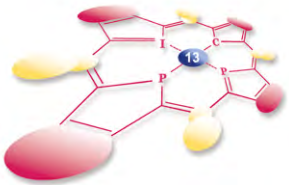

Modeling Bioinspired Reactivities of Heme Peroxo Intermediates: Nitric Oxide Synthase and Beyond

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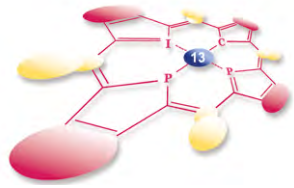
Dioxygen-activating heme enzymes mediate a medley of pivotal reaction pathways in humans, during which, they shuttle through a distinct panel of heme-oxygen intermediates. Mid-valent (i.e., Fe(III) containing) heme-oxygen intermediates, such as heme superoxo, peroxo, hydroperoxo, etc. are some of the first among this series and can facilitate extremely versatile reaction landscapes, making their detailed studies extremely challenging. To this end, meticulously designed synthetic heme mimics can be powerful mechanistic probes. This work specifically focuses on bio-relevant reaction landscapes driven by heme peroxo intermediates, mechanistic details which, as a whole, are only faintly understood. The precise mechanism of the therapeutically crucial, arginine degrading nitric oxide synthase (NOS) is one such example, which has been proposed to operate via an oxygen-dependent, two-step mechanism, wherein details of the second step have remained elusive. We have utilized synthetic heme peroxo analogues against oxime organic substrates to model this second mechanistic step of NOS, and have discovered that, as proposed in the enzymatic pathway, heme peroxo adducts mediate the conversion of oximes to the corresponding ketones with the concomitant generation of nitroxyl (NO^-). Detailed thermodynamic and kinetic analyses infer a rate-limiting step, during which, the heme peroxo adduct acts as a nucleophile, which then passes through a highly organized transition state in concert with the oxime substrate to produce the oxidized organic product. These findings, along with isotope labeling studies and relevant structure-activity findings led us to a detailed mechanistic proposal for these model compounds with striking similarities to that proposed for the NOS enzyme. We have also evaluated the role of axial ligation on this mechanism, illustrating how the electronic effects exerted by the axial ligand directly modulate the nucleophilic reactivity of heme peroxo adducts with oximes. Furthermore, these heme peroxo adducts can rapidly react with nitrosonium (NO^+), to generate heme peroxynitrite adducts with unprecedented stabilities. This isoelectronic pathway produces clean heme peroxynitrite intermediates compared to previous methods and will open new avenues for rigorous reactivity studies into heme peroxynitrite-mediated bio-relevant landscapes. Indeed, heme peroxynitrite intermediates are implicated in numerous biological pathways that are detrimental to human health (e.g., presumably resulting in carcinogenesis). Finally, these heme peroxo intermediates are also reactive against a series of other substrates that could have direct biological implications and will be discussed here in detail.



A heme-dependent conformational switch in the *P. aeruginosa* PhuS drives its function from transcriptional regulator to heme chaperone

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ORALS

Pseudomonas aeruginosa an opportunistic pathogen requires iron for survival and virulence. Within the host heme is the preferred source of iron, particularly in chronic infection where *P. aeruginosa* switches to utilize heme at the expense of iron-siderophores. Heme enters the cell through two non-redundant heme uptake systems, the heme assimilation system (Has) and the *Pseudomonas* heme uptake (Phu) system. Once in the cytoplasm, heme is bound by PhuS, which selectively transfers heme to heme oxygenase (HemO) for metabolism and release of iron and the biliverdin (BVIX)β and BVIXδ metabolites (1). The transfer of heme from holo-PhuS to HemO proceeds through a conformational rearrangement on protein-protein interaction that facilitates heme release (2). We have recently shown that in its apo-form PhuS binds to the promoter upstream of the *prrF1,F2* operon encoding the iron-regulated sRNAs PrrF1 and PrrF2, and regulating the expression of the read-through transcript PrrH in a heme dependent manner (3). Previous hydrogen-deuterium exchange mass spectrometry (HDX-MS) studies showed significant differences in dynamics and flexibility between apo- and holo-PhuS, as well as long-range conformational rearrangement and allostery, providing significant insight into the mutual exclusivity of the apo- and holo- forms and their respective functions. Herein utilizing a combination of bacterial genetics, biochemical and biophysical analyses we show the PhuS H209A variant which is compromised its ability to bind to and transfer heme to HemO, also binds to the *prrF1* promoter in both the apo- and holo-form. HDX-MS analysis suggests the holo-PhuS H209A variant is trapped in an intermediate conformer that lies along the conformational landscape between the apo- and holo-PhuS structures. The *in vitro* biochemical and biophysical analysis is consistent with *in vivo* studies showing decreased heme utilization and loss of heme-dependent regulation of PrrH in the *phuSH209A* strain, linking the conformational flexibility and cooperativity of PhuS to its distinct physiological functions.

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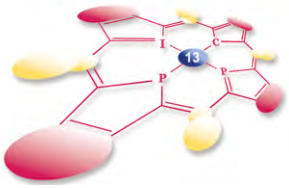

PhotoDynamic Therapy and PhotoChemical Immune Stimulation in Melanoma

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Melanoma is a highly aggressive malignancy. Although arising primarily in the skin, it occurs also in the eye and other sites. Until recently, photodynamic therapy using a variety of photosensitizers, including porphyrins, had not been successful in treating melanoma, either preclinically or clinically. In part, this is due to the high attenuation of the treatment light by melanin. Here we have developed two different approaches to enable effective treatment even in highly pigmented tumors.

In a mouse model of conjunctival melanoma, we have investigated 2-photon activation using fs pulsed laser excitation of either Visudyne, a liposomal formulation of benzoporphyrin derivative-MA (verteporfin), and Oxdime, a porphyrin dimer designed to have a very high 2-photon cross-section [1]. *In vitro* studies in melanotic and amelanotic melanoma cells have revealed a novel mechanism of action involving primary light absorption by melanin with subsequent energy transfer to the photosensitizer. *In vivo*, complete eradication of conjunctival melanoma has been achieved [2].

For cutaneous melanoma we have shown in an intradermal-tumor model in immunodeficient mice that primary melanotic tumors up to 1 mm thickness can be eradicated by first using an optical clearing agent to increase light penetration followed by conventional single-photon activation of a combination of tumor cell- and vascular-localized photosensitizers [3]. Moreover, in immunocompetent mice, tumors at least 4 mm thick are eradicated and survival is markedly increased. When these mice are subsequently re-challenged by *i.v.* injection of melanoma cells, there is no evidence of tumor at 30d later, whereas untreated mice without primary tumor have massive tumor burden through the body. Melanoma-specific immune activation by the primary tumor treatment has been confirmed using a panel of cytokine and immune-cell biomarker assays. Studies are in progress to use this approach as a surgical adjuvant and in combination with immune checkpoint inhibitors, with the goal of eventual clinical translation.

Photochemical immune stimulation in melanoma has also been demonstrated using multifunctional porphyrin-lipid nanoparticles (Porphysomes [4]) that are being investigated also in a range of immunologically "cold" and "hot" tumors, using both light and high-energy X-ray activation.

Acknowledgements. This work was supported by the Canadian Institutes for Health Research, the Cancer Research Society, the Princess Margaret Foundation and the Terry Fox Research Institute.

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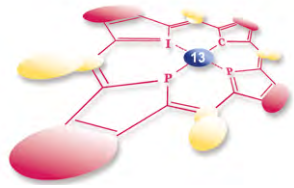

Advanced Strategies For Assembling Chromophores Into Molecular Designer Solids Using The MOF Approach

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The field of organic electronics, which includes photovoltaics, photodetectors, and light-emitting devices, has experienced significant advancements with the integration of organic chromophores into metal-organic frameworks (MOFs). This innovative method [1] utilizes organic chromophores, such as anthracene, Hexa-peri-hexabenzocoronene (HBC), and planar aromatics, coupled with metal-oxo nodes to create ditopic linkers. The development of layer-by-layer (LbL) deposition techniques have facilitated the production of high-quality, monolithic MOF thin films, known as SURMOFs [2]. These films exhibit exceptional optical properties and low defect densities. The periodic structure of MOFs enables the precise design of chromophore assemblies, which enhances optical absorption and allows for the creation of structures such as J-aggregates, as well as the realization of band-structure phenomena, including indirect band gaps [3, 4] and chiroptical effects [5, 6]. Furthermore, SURMOFs have been instrumental in developing heterostructures for photon up-conversion applications and in integrating functional additives like C60 for improved photoconductivity and diode functionality [7, 8]. There have also been significant strides in assembling non-centrosymmetric SURMOFs, leading to notable advancements in nonlinear optical properties, particularly second harmonic generation (SHG) [9]. This presentation will focus specifically on the strategic fabrication of 'Designer Solids' using porphyrins and phthalocyanines. Through the MOF approach, we assemble these photoactive compounds into crystalline materials suitable for various technologies, including electrochemical, photoelectrochemical, photovoltaic, and sensing applications. The talk will elaborate on the principles of SURMOF construction and their electrical and photophysical properties, including their impact on band structure in crystalline porphyrin arrays. We will also discuss the incorporation of nanoparticles or quantum dots into MOFs and the creation of molecular solids without inversion symmetry for SHG [9]. In tackling the challenges of forming stable electrical contacts with MOF materials and producing MOF thin films of high optical quality, our research has harnessed robotic systems controlled by machine learning (ML) algorithms. This innovative approach allows for the precision tuning of thin film attributes, such as orientation, crystallinity, conductivity, and surface smoothness, through advanced, unsupervised experimentation. Overall, our presentation will highlight key examples of successfully incorporating organic chromophores into SURMOFs for device manufacturing, underlining the harmonious integration with theoretical models and the extensive potential of MOFs in the realm of organic electronics.

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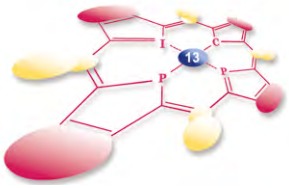

Porphyrin-Graphene Hybrid Systems

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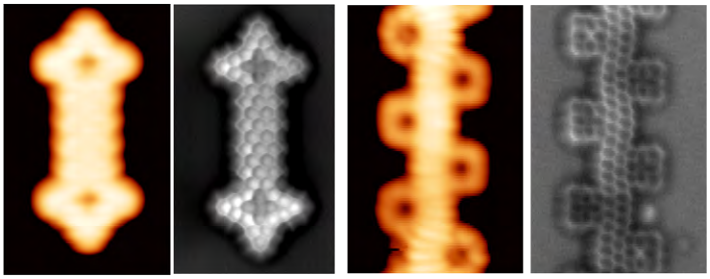
Graphene provides a versatile carbon-based platform for finely controlling physical properties across a broad spectrum. By precisely adjusting the size and edge topologies of graphene nanostructures, such as graphene nanoribbons (GNRs) or nanographenes (NGs), it becomes possible to engineer their band gap, induce topological energy modes, or even create exotic magnetic ground states [1-3]. Expanding the potential applications of graphene to include light harvesting and gas sensing involves designing hybrid molecular systems, e.g. by integrating porphyrins into graphene nanostructures. However, the performance of such hybrid materials in devices is significantly hindered by concerns regarding yield and defect density. Addressing these challenges necessitates the creation of well-defined nanostructures with atomic precision. Bottom-up on-surface synthesis, coupled with rational precursor design, provides a viable approach to achieving this level of structural engineering.



Here, we present our recent progress in the synthesis and characterization of porphyrin-graphene hybrid systems, including porphyrin-graphene nanoribbons (Por-GNRs) [4-6] and porphyrin-nanographene (Por-NG) hybrids [7,8]. Por-GNRs exhibit lower band gaps compared to their pristine GNR counterparts and possess robust, tunable backbones that enable modification of their electronic structures simply by varying the metal centers in the porphyrin units. On the other hand, Por-NGs typically exhibit diradical characteristics, wherein spins are ferromagnetically coupled. Introducing magnetic metal atoms can further enhance *d*-π interactions between the metal center and porphyrin ligand, which has important implications for the creation of spin chains based on Por-GNRs.

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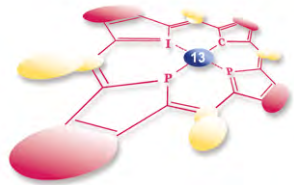

Facile Synthesis and Reactivity of Subporphyrin Borenium Cations

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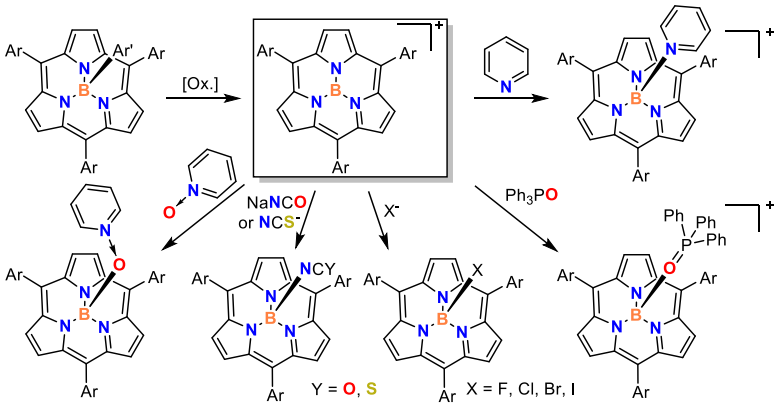
ORALS

Subporphyrins, a group of ring-contracted porphyrins containing three pyrrole units and three methine carbon atoms, have received considerable attention since their first synthesis in 2006.[1-3] While subporphyrins usually appear as bowl-shaped molecules, subporphyrin borenium cations have been proved planar.[4] The positive charge carried by the central B atom renders the motif more electrophilic than the neutral analogues. Therefore subporphyrin borenium cations exhibit extensive reactivity towards nucleophilic reagents and can work as the key intermediates towards axial-modified neutral subporphyrins. However, highly sensitive silylium cation was required in the achieved route to remove the axial OMe group of the precursor to afford the subporphyrin borenium cations.

Here we show a facile route for the synthesis of subporphyrin borenium cations via the oxidation of *B*-aryl subporphyrins. The key intermediate subporphyrins cation radical was isolated and fully characterized by modulating the substituents on the *meso* positions. The mechanism for this oxidation-induced B-C bond cleavage process was investigated by kinetic methods as well as DFT calculations. We found that subporphyrin borenium cationic species could coordinate with various Lewis bases such as pyridine, pyridine oxide and triphenylphosphine oxide. These cationic compounds could associate with halides, isocyanate, or isothiocyanate, forming neutral subporphyrin species.



Scheme 1. Synthesis and reactivity of subporphyrin borenium cations

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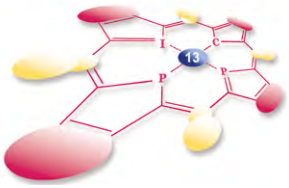

Unsymmetrical 5,15-Disubstituted Tetrabenzoporphyrins: Effect of Molecular Symmetry on the Packing Structure and Charge Transporting Property

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One of the key issues in the development of organic field-effect transistor (OFET) materials is the improvement of charge mobility. Since charge mobility depends on intermolecular interactions in solid state, it is important to control the crystal structure. In the current mainstream OFET materials, such as acenes and heteroacenes, which have one-dimensionally (1D) extended polycyclic aromatic frameworks, the effect of substitution on the crystal structure has been intensively studied. On the other hand, some bulky (trialkylsilyl)ethynyl-substituted derivatives such as 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) have been known to afford brickwork packing. In comparison, two-dimensionally (2D) extended π-conjugated molecules tend to form a sandwich herringbone, a co-facial herringbone, and a 1D columnar structure, due to their enhanced π–π interaction. The molecular design strategy to control the crystal structure of two-dimensional (2D) π-extended organic semiconductors has not been intensively explored [1].

We synthesized an unsymmetric tetrabenzoporphyrin derivative (TIPS-Ph-BP) and its metal complexes to demonstrate the effect of molecular symmetry on crystal packing (Figure 1) [2]. An unsymmetric structure would make 2D π-stacking more stable than a one-dimensional (1D) columnar structure to counteract steric and electronic imbalance in the crystal. TIPS-Ph-BP formed an antiparallel slipped π-stacking and 2D herringbone-like structure as expected, but, it formed a dimeric herringbone packing consisting of slipped π-stacking in an antiparallel manner in the crystal. OFETs using TIPS-Ph-BP achieved the maximum hole mobility of 0.71 $cm^2 V^{-1} s^{-1}$ due to the partially 2D packing structure. Although TIPS-Ph-BP gave dimeric herringbone packing, this strategy could be used to control the crystal structures of various 2D extended π-conjugated systems. Further modification of the porphyrin substituents is ongoing.

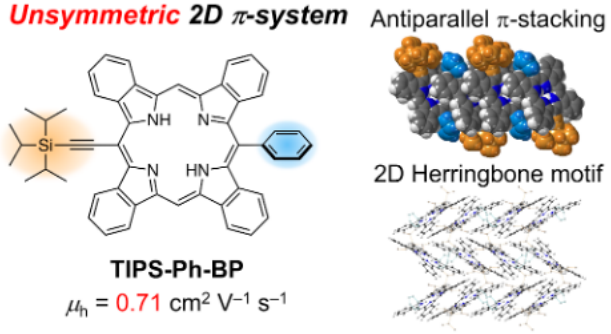

Figure 1. X-ray single crystal structures and hole carrier mobilities of TIPS-Ph-BP.

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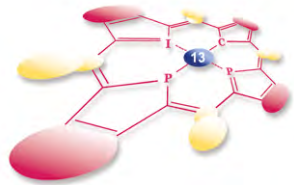

Resonance Raman study of Cytochrome *c* oxidase with a positive regulator, MNRR1

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Cytochrome *c* oxidase (CcO) is the terminal oxidase in the mitochondrial respiratory chain. Oxygen reduction is the enzymatic reaction of CcO, which is coupled with a proton-pumping reaction by CcO across the mitochondrial inner membrane. Mitochondria Nuclear Retrograde Regulator 1 (MNRR1) is a soluble protein present in mitochondrial intermembrane space (IMS) and the nucleus. In mitochondria, it binds directly to CcO and allosterically enhances its enzymatic activity, which has been obtained as an increase in oxygen consumption and ATP level *in vivo* [1, 2] and cytochrome *c* oxidation rate *in vitro*. Under 4 % oxygen concentration, MNRR1 is also found in the nucleus and it regulates the transcription of *MNRR1* itself, *COX4I2* (CcO subunit 4 isoform2) [1] and some others. Based on the amino acid sequence of MNRR1, it is predicted that the C-terminus forms a CHCH domain which is characteristic of IMS proteins, whereas the structure of the N-terminus is unknown, and likely to be frexible. The presence of the N-terminus flexible region precludes crystallization of this protein, therefore the overall structure remains unknown. Its binding site to CcO is not clear either. We are interested in the activity enhancement mechanism of CcO in mitochondria by MNRR1 binding. Since MNRR1 allosterically enhances the activity, we would like to elucidate the mechanism of activity enhancement by investigating the structural changes in the CcO active center heme upon MNRR1 binding.

In this study, visible resonance Raman spectra of reduced CcO and CO-bound CcO, as a mimic of oxygenated CcO, were measured to understand the effect of MNRR1 binding to CcO on the initial state of the enzymatic reaction cycle. As a result, we detected slight but reproducible differences mainly in the resonance Raman spectra of reduced CcO. There were differences in the vinyl bending of the two hemes and the formyl C=O stretching of heme a_3, the Fe-His stretching, the propionic acid bending as well as some of the skeletal vibration modes of the heme including ν_8. According to the comparison of the CcO crystal structure and the position of atoms involved in the vibrational modes altered by MNRR1 binding, a possible site where MNRR1 binds to CcO has been suggested. On the other hand, in CO-bound CcO, although there was a slight difference in the Fe-Co stretching vibration, no difference was detected in the skeletal vibration or other Raman modes. Based on these results, structural alteration in hemes due to MNRR1 binding mainly occurs in the reduced state rather than in CO-bound form. Possible mechanism of CcO activity enhancement will be discussed in the presentation.

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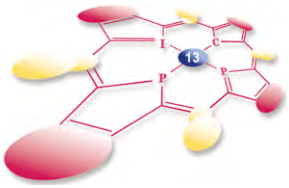

Interactions of N-methyl mesoporphyrin IX with G-quadruplex DNA

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N-methyl mesoporphyrin IX (NMM) is exceptionally selective for G-quadruplex (GQ) DNA vs other DNA structures, notably Watson-Crick-Franklin duplex. GQ DNA is a non-canonical DNA structure involved in a variety of biological processing, including cancer and aging. Ligands with high selectivity for GQ structures may serve as promising novel anticancer therapies. My lab has been investigating how NMM binds GQ DNA for over 10 years. We utilize biophysical methods (e.g. UIV-vis spectroscopy, fluorescence spectroscopy, circular dichroism) and structural studies using X-ray crystallography to probe the interactions between NMM and a variety of important G-rich structures. Here I will present our recent findings on two projects. One concerns telomeric DNA from Tetrahymena thermophila with the general sequence (GGGGTT)n that forms rare four-tetrad GQs [1]. We show that NMM establishes conformational homogeneity of TET favoring parallel structures; improves its thermal stability, and exhibits moderate binding strengths and a 1:1 stoichiometry. Additionally, we report high-resolution crystal structures of NMM in complex with TET. In the structure, DNA adopts parallel topology and interacts with NMM at the 3' G-tetrads. NMM forms dimers observed only in one other GQ-NMM structure. In the second project, we investigate the interaction of NMM with the short DNA sequence from the SLC2A1 gene, which encodes for the major glucose transporter protein, GLUT-1, which is over-expressed in many human cancers [2]. SLC2A1 folds into a four-tetrad two-subunit GQ where the first subunit is right-handed and the second subunit is left-handed. NMM interacts with the right-handed subunit only and stacks at its 3' terminal G-tetrad. Its binding to SLC2A1 is characterized by a relatively high binding constant of 2.9 ± 0.7 μM-1, and stoichiometry of 1:1. In addition, NMM increases the stability and homogeneity of SLC2A1 by 10 ℃ at 1 eq. Just like in the earlier example, NMM forms dimers in the crystal structure. NMM dimers were recently confirmed in a solution of NMM alone via temperature dependence of UV-vis and fluorescence signals.

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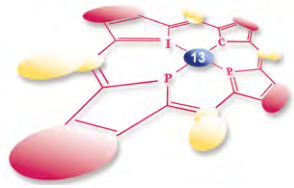

Feedback Regulation Mechanism of Human Tryptophan Dioxygenase

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L-Tryptophan (Trp) is the least abundant essential amino acid. Approximately 1% of dietary Trp is utilized through the serotonin pathway for the synthesis of serotonin and melatonin, while the majority of it (~95%) is metabolized through the kynurenine (KYN) pathway, which ultimately leads to the production of nicotinamide adenine dinucleotide (NAD^+) (Fig. 1). The first and rate-limiting step of the KYN pathway is catalyzed by a tetrameric hemepeotein, tryptophan dioxygenase (TDO), in the liver. The hepatic TDO hence plays an important role in regulating the systemic Trp flux in the body. Owing to its physiological importance, TDO activity is intricately regulated by a variety of cellular factors, including NADH, the reduced form of the end-product of the KYN pathway, *via* an unknown feedback inhibition mechanism. Here we show that NADH binding to TDO triggers heme degradation, thereby leading to the formation of an inactive apo-protein. Kinetic studies showed that the heme degradation reaction is anti-cooperative, with a protein-bound oxy-heme and verdoheme as the major intermediates, similar to that found in the canonical heme oxygenase (HO) reaction. However, unlike the HO reaction, the hTDO reaction cannot be supported by exogeneous ascorbate or H2O2, suggesting that NADH binding to hTDO introduces structural changes to the active site, thereby repurposing the active site from Trp dioxygenation to heme degradation. This previously unidentified suicidal heme degradation activity of hTDO is significant as it defines a novel redox-sensitive feedback regulation mechanism of hTDO by the end-product of the kynurenine pathway. In addition, it offers a potential molecular mechanism that at least partially accounts for the under-saturation of the TDO protein by heme in the liver.

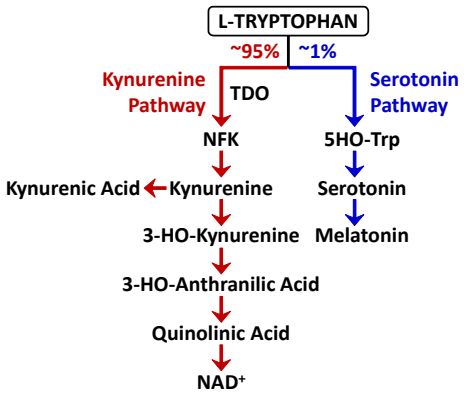

Fig. 1. Two major Trp metabolic pathways. The first and rate-limiting step of the kynurenine pathway is catalyzed by TDO.

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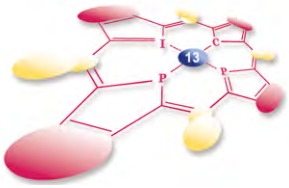

Singlet Oxgyen-activatable Prodrugs for Improving Therapeutic Effects of PpIX-Photodynamic Therapy

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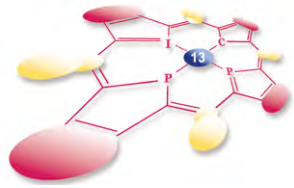
We have explored an enhanced approach for treating non-muscle invasive bladder cancer (NMIBC) using Photodynamic Therapy (PDT). Traditional PDT methods, including the use of Photofrin and hexaminolevulinate (HAL, forming protoporphyrin IX (PpIX)), have been limited by issues such as permanent bladder contraction and low efficacy. Our novel method combines singlet oxygen (SO)-cleavable prodrugs with PpIX-PDT, aiming to improve antitumor effectiveness while minimizing systemic side effects. We employed a Fisher rat model with orthotopic NMIBC to compare three treatment modalities: prodrugs alone, PpIX-PDT alone, and a combination of prodrugs and PpIX-PDT. Treatments were administered using a green laser (532 nm) at a total power of 50 mW for 20 minutes (delivering 60 J per treatment) in conjunction with 8 mM HAL and prodrug concentrations ranging from 0.25 to 1 mM. The study assessed tumor staging, PpIX formation, prodrug diffusion, antitumor efficacy, and local toxicity through histological and microscopic analysis. Our findings indicated a higher concentration of PpIX in tumor tissues compared to normal bladder areas. Significantly, the combined prodrug and PpIX-PDT treatment demonstrated superior antitumor efficacy compared to PpIX-PDT alone. Both the standalone and combined PDT treatments resulted in only mild damage to the bladder epithelium without affecting the muscle layer. In conclusion, the integration of SO-cleavable prodrugs with PpIX-PDT presents a promising advancement in NMIBC treatment, offering increased antitumor effectiveness while safeguarding against severe bladder muscle damage.



Interaction of Zn-protoporhyrin IX with RSAD1 protein

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A recently discovered mitochondrial protein, **R**adical **S**-**A**denosyl methionine **D**omain-containing **1** (RSAD1), plays an important, but not fully defined role in cell function. In particular, it was shown to have increased expression in Alzheimer's disease neuritic plaques [1]. RSAD1 contains a single S-adenosyl methionine coordinating [4Fe-4S] cluster. Using chromatography and UV-vis spectroscopy we showed that RSAD1 can bind heme. Our molecular docking simulations showed that the specific binding takes place at the heme-binding domain that contains His304 residue near the porphyrin center.

To elucidate the heme - RSAD1 interaction we first reconstituted the purified human RSAD1 with the fluorescent analogue of heme, Zn-protoporphyrin IX (Zn-PPIX), but without [4Fe-4S] cluster, and measured its absorption and fluorescence spectra, fluorescence quantum yields, and lifetimes. Absorption spectral shapes, peak positions, of the Q- and Soret bands, and radiative and nonradiative rates of fluorescence decay (k_r and k_{nr}, respectively) were used to elucidate two structural features of the Zn-PPIX molecule embedded in RSAD1, namely (1) extra-coordination number, *n*, and (2) degree of non-planarity. This structural information can provide some insights into the RSAD1 biochemical functions. To this end, we first studied the photophysical properties of Zn-PPIX in several model systems where these structural properties were known from the literature. These included Zn-PPIX either in pure DMSO or with addition of 1-methyl-imidazole (1-meim), Zn-PPIX dimethyl ester either in pure toluene or with addition of 1-meim [2], Zn-PPIX in human serum albumin (pdb 1N5U), Zn-PPIX in myoglobin (pdb 1WLA), and Zn-PPIX in IsdG protein [3]. The IsdG is a heme-degrading bacterial protein that strongly distorts from planarity the heme group after binding [3]. Our analysis shows that for planar Zn-PPIX, extra-coordination results in systematic redshifts of the Soret (from 415 – 427 - 428 nm) and Q-bands (from 579 – 590 – 598 nm) when *n* increases from 0 to 1 and 2. Also, the radiative rate decreases from $1.7\text{x}10^7$ ($n = 0$) to $(1.3 - 1.4)\text{x}10^7$ s^{-1} ($n = 1,2$). The non-planarity of Zn-PPIX results in a significant broadening of the Soret and Q-bands and an increase of nonradiative decay rate (from $\sim 5\text{x}10^8$ to $\sim 6\text{x}10^8$ s^{-1}). For the Zn-PPIX embedded in RSAD1, we observed a broadening of absorption peaks at $\lambda_{Soret} = 421$ nm, $\lambda_Q = 588$ nm and measured fluorescence lifetime $\tau = 1.7$ ns, and quantum yield $\varphi = 0.02$, resulting in $k_r = 1.2\text{x}10^7$ s^{-1}, $k_{nr} = 5.8\text{x}10^8$ s^{-1}. Comparison of these properties with the reference systems suggests that the porphyrin macrocycle is weakly coordinated (possibly with His304, $n = 1$) and has a structure of macrocycle moderately distorted from planarity.

We also studied the effect of the [4Fe-4S] cluster on fluorescence lifetime and found that upon reconstitution of the Zn-PPIX-containing RSAD1 with [4Fe-4S], fluorescence lifetime slightly shortens from 1.7 to 1.5 ns. This observation is consistent with either a heavy atom effect of the cluster, accelerating the singlet-triplet relaxation or FRET from Zn-PPIX to [4Fe-4S], or both.

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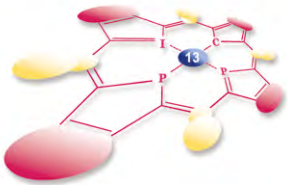

Reactivity Descriptors and Guidelines based on Ligand Parametrization for Electroreduction of O_2 Catalyzed by Metallophthalocyanines and Metalloporphyrins

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Since the discovery of the phthalocyanines one important quest has been the tailoring of their properties to obtain molecular materials for multiple applications. Electrocatalysts based on bioinspired MN4 macrocyclic complexes (M = transition metal, N4 = phthalocyanines, porphyrins, corroles, etc..) have been studied for decades as alternatives to the use of expensive noble metals like Pt for promoting the O_2 reduction (ORR). The search and design of catalysts with high electrocatalytic activity for ORR can be assisted by computational chemistry and different methods based on quantum mechanics. The rational design of MN4 molecules for ORR requires the knowledge of reactivity descriptors. A classical reactivity descriptor in electrocatalysis is the binding energy (coordination of O_2 to the central metal) of key intermediates to the catalyst active sites [1,2]. This has been developed mostly for metal electrodes [1]. We have developed theoretical models to predict which MN4 complexes will present a higher activity for the ORR according to the binding energies, which according to the Sabatier Principle need to be not too strong not too weak. We have also found that the M(III)/(II) redox potential of the metal complex correlates linearly with the binding energies [2,3]. So this experimental parameter is a powerful reactivity descriptor. The binding energies and redox potentials in the interaction between oxygen and the metal center of the MN4 systems are strongly affected by changes in the electronic structure caused both by the presence of substituents in the aromatic rings (in the same plane of the molecule) and also by axial ligands in the metal center (perpendicular to the plane of the molecule) that are used in self-assembled systems. These findings agree with the reports of Lever and Alexiu [4] that there is a linear correlation between the M(III)/(II) redox potentials and the total contributions of the planar ligand and extra planar axial ligands. The behavior of the electrocatalytic activity of porphyrins and phthalocyanines has been analyzed in the context of volcano correlations [1-3]. The systematic study of the effect of the different substitution patterns in these MN4 molecular systems on the behavior of volcano correlations allows us to understand the nature of the electronic effects that govern Sabatier's principle (which determines the limit of catalytic efficiency in a rather narrow range of binding energies), an issue that is key to optimizing the design of new catalysts for oxygen reduction and any electrochemical reaction that requires the presence of electrocatalysts in order to proceed at rates compatible with fuel cell or electrolyzer performance. These reactivity descriptors are valid for many other electrochemical reactions catalyzed by metallophthalocyanines and metalloporphyrins.

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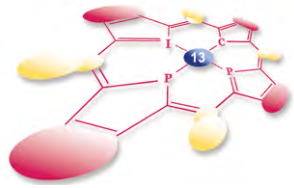

Blue phthalocyanines and green chemistry: A sustainable combination?

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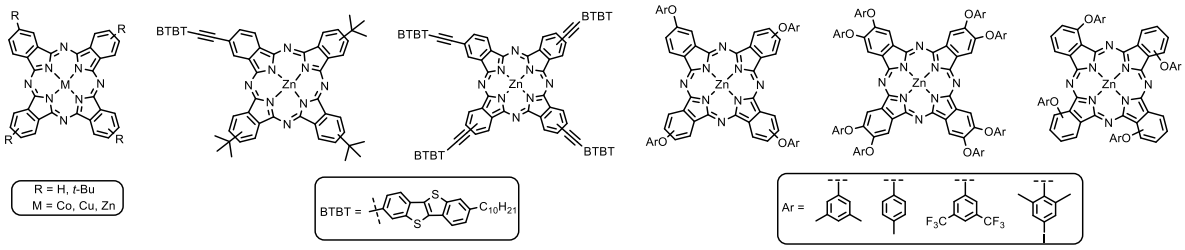
The interest in reducing the ecological and economic impact of chemical processes, with an important focus on developing more environmentally friendly procedures and methodologies in organic synthesis, is constantly increasing. Given the extreme versatility and technological importance of phthalocyanines (Pcs), the design and study of alternative and less-impacting synthetic approaches for their production have gained importance in the last few years. Their lab-scale synthesis in solution frequently requires reaction media such as high boiling point alkyl alcohols, dimethylaminoethanol, chlorobenzene, and quinoline, most of which are toxic and non-environmentally friendly. Some green synthetic approaches based on solvothermal methods, mechanochemistry, or alternative sources of energy such as microwaves and ultraviolet radiation, have been developed. At the same time, the choice of a more sustainable reaction medium has so far relied mostly on ionic liquids and deep-eutectic solvents.

In this contribution, we present our recent results on developing more environmentally sustainable approaches for obtaining state-of-the-art and novel phthalocyanines in solution. The chosen synthetic strategies have been focused on (1) the replacement of harmful solvents (dimethylaminoethanol, quinoline, chloronaphthalene) with more sustainable and cheap alternatives like anisole, glycerol, 1,2 propanediol and PEG-400, for the metal-templated cyclotetramerization of unsubstituted and 4-substituted phthalonitriles[1-3] and (2) the use of "one-pot" approaches to obtain variously substituted phthalocyanines by exploiting the compatibility of the reaction environment of the two sequential steps necessary to obtain the final products[4]. This approach allowed to minimize the required amounts of potentially toxic solvents, reduced the number of purification steps concerning conventional procedures and consequently decreased the amount of waste, eventually positively impacting also on the economic cost of the entire synthesis.

The environmental accessibility of our novel protocols will also be discussed in terms of the E-factor, an important green chemistry metric useful for evaluating the effectiveness of a synthetic process based on the ratio between the mass of waste produced per mass of desired product.



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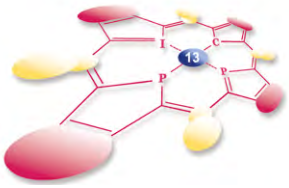

Ni-Corrin Derivatives For Biomimetic Cofactor F430 Chemistry

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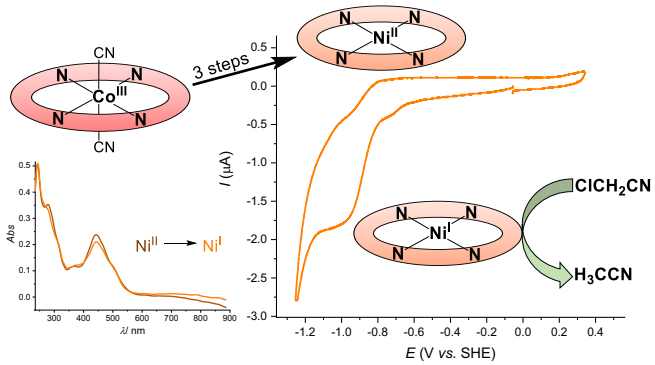
The nickel hydrocorphinate cofactor F430 plays a key role in the anaerobic, enzymatic formation and oxidation of methane [1]. Inspired by this versatile chemistry, my group synthesizes modified corrins for biomimetic catalysis. In this lecture, I will highlight the preparation and study of a new catalytically active Ni(I) corrin derivative and discuss its applications in electrocatalysis [2, 3].



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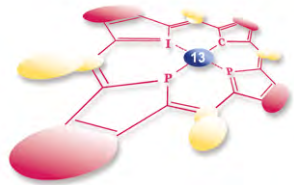

Design of Nickel(II) Phototheranostics

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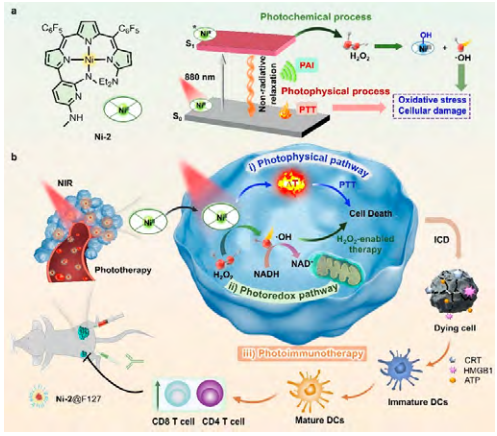
Abstract Phototheranostics have emerged as a promising subset of cancer theranostics owing to their potential to provide precise photoinduced diagnoses and therapeutic outcomes.[1] Recent work from our laboratory revealed that appropriately designed Ni(II) complexes can function as phototheranostics agents whose excited state energies can be dissipated via thermally accessible radiationless relaxation mechanisms.[2] In this work, we prepared a set of Ni(II) linear tripyrrins, featuring intense NIR absorption bands in the near-infrared (NIR-I and NIR-II) biowindow.[3] Upon 880 nm NIR photoirradiation, the nickel complex catalyzes a Fenton-like reaction to generate •OH *via* a photochemical pathway and impacts the overall ROS levels by attenuating endogenous antioxidants (i.e., NADH). An *in vivo* study of photoacoustic imaging-guided tumor ablation under NIR photoirradiation revealed that the use of nickel complex as a PS inhibited cancer metastasis while triggering a long-term immunological memory effect.



Scheme 1. Photoactivated H2O2-Enhanced Immunotherapy Mediated by nickel tripyrrole.

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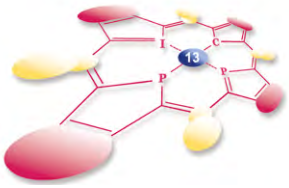

Open-Shell Metalloporphyrins as Metalloradical Catalysts for Homolytic Radical Reactions

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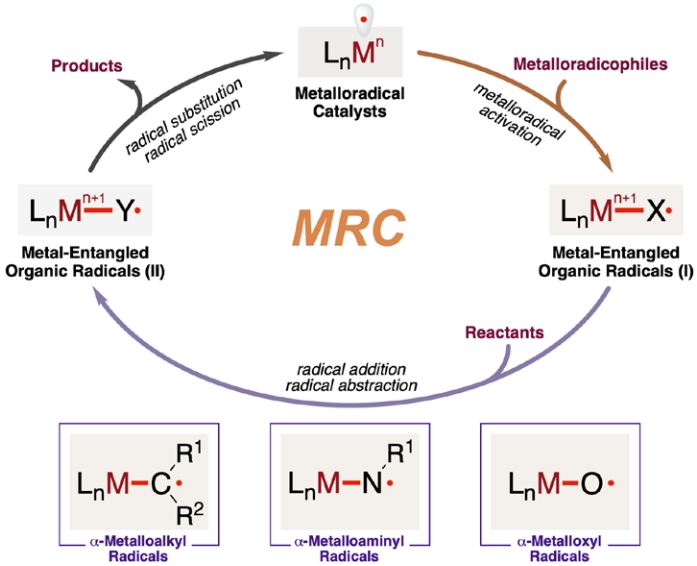
Organic synthesis has predominantly relied on the development of chemical reactions based on two-electron heterolytic ionic processes. While one-electron homolytic radical chemistry is equally rich and exhibits unique features, its application for achieving a stereoselective synthesis of organic molecules has been impeded by persistent challenges. In the past two decades, my laboratory has been dedicated to formulating metalloradical catalysis (MRC) as a general concept to guide the development of innovative approaches for controlling both reactivity and stereoselectivity in radical reactions. MRC harnesses the potential of metal-centered radicals within metalloradical complexes as one-electron catalysts for homolytic activation of substrates to generate metal-entangled organic radicals as key intermediates to direct the reaction pathway and influence the stereochemical outcomes of subsequent catalytic radical processes. To achieve enantioselective radical reactions via MRC, we have introduced a unique family of chiral metalloradical catalysts based on structurally well-defined open-shell metal complexes of D_2-symmetric chiral porphyrins, such as Co(II) and Fe(III) complexes. These chiral metalloradical catalysts offer tunable electronic, steric, and chiral environments. They have demonstrated exceptional efficacy in a wide range of stereoselective organic reactions, including olefin cyclopropanation, olefin aziridination, C–H alkylation, and C–H amination. The Co(II)- and Fe(III)-based MRC exhibits distinctive stepwise radical mechanisms involving α-metalloalkyl and α-metalloaminyl radicals as key intermediates. These metalloradical systems not only address long-standing challenges in these important organic transformations but also provide ample opportunity for the development of new synthetic tools.



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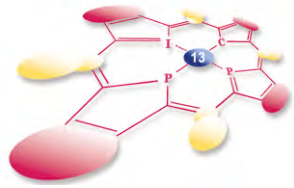

Aromatic Carbon-rich Molecular and Polymeric Architectures Constructed via Dynamic Covalent Chemistry

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Dynamic covalent chemistry (DCvC) has proven to be highly effective in the construction of well-defined molecular and polymeric architectures.[1-2] The error-correction mechanism enabled by the reversible formation of dynamic covalent bonds leads to the formation of structurally ordered, thermodynamically favored species. One such example is the solvothermal synthesis of covalent organic frameworks (COFs) with periodic structural order and low defect density.[3-6] The chemical compositions of such frameworks are usually well-defined and inter-monomer connectivity (covalent bonding) is robust. Bottom-up synthesis of covalently linked molecular or polymeric architectures through DCvC has many critical advantages, such as easy tunability of functional and structural properties in a controlled fashion through rational design of the precursors, formation of highly stable linkages, minimized structural defect, and possible access to sophisticated architectures that are hard to obtain otherwise. This talk will focus on our recent progress in the development of DCvC, specifically alkyne metathesis [7] and spiroborate bond exchange [8]. These powerful transformations enabled the bottom-up design and synthesis of novel functional materials, such as ethynylene-linked crystalline organic frameworks [9] and shape-persistent organic molecular cages consisting of porphyrin or phthalocyanine building blocks with high performance in molecular separation, light harvesting, and electrocatalysis [10-12].

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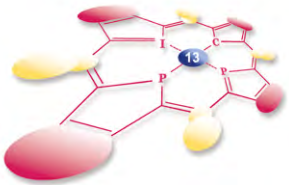

Origin of Reactivity Differences of Porphyrin Catalyst Components and Substrates in Carbene Transfer Reactions

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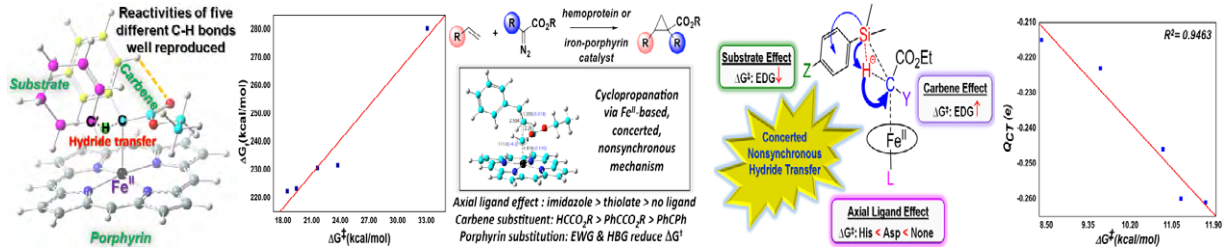
Various porphyrins and engineered heme proteins exhibit excellent catalytic properties for numerous carbene transfer reactions, such as C-H functionalization, cyclopropanation, and Si-H insertion. Based on our systematic DFT studies of these three heme carbene transfer reactions with different substrates, carbenes, porphyrins, and axial ligands,[1-5] these non-native reactions were found to possess an Fe^{II}-based concerted carbene transfer mechanism, which is different from the native heme enzymatic reactions which typically employ ferryl intermediates and radical mechanisms. The computed concerted reaction features are supported by experimental radical trapping and isotope labelling. The calculated kinetic isotope effects are also in excellent quantitative agreements with available experiments: expt (~1.97) vs calc (~1.99) for C-H insertion; expt (0.96) vs calc (0.99) for cyclopropanation; expt (1.19-1.30) vs calc (1.19-1.31) for Si-H insertion.



The dominant electronic driving force is the charge transfer from substrate to carbene, which is well correlated with reaction barriers in all three reaction types. As a result, carbenes and porphyrins with strong electron-withdrawing substituents and substrates with better electron-donating substituents have enhanced reactivities. In addition, the porphyrin substituent with a hydrogen-bonding capability also increases the reactivity due to the additional stabilization effect from the hydrogen bond. The *trans* effect of axial ligands overall weakens the Fe-carbene bond and promotes carbenes' attack toward substrates and thus improves reactivities compared to catalysts without axial ligands. The studied C-H and Si-H insertions catalyzed by porphyrin or heme carbenes were found to involve hydride transfer. Consequently, substrates with smaller hydride formation energies have low barriers. These computational mechanistic origins help understand experimental reactivities and guide the future development of heme-based catalysts for these synthetically important carbene transfer reactions.

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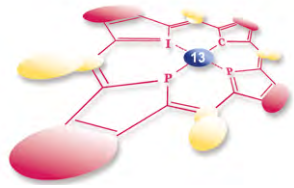

Design and application of porphyrinic covalent organic frameworks

Yushu Zhang[a], Yao Chen[a] and Zhenjie Zhang[a]

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Covalent organic frameworks (COFs) constructed by organic building blocks linked by covalent bonds, as an emerging crystalline porous material, have achieved increasing attention from diverse research fields in the past decade. Porphyrin has been widely studied due to its great application potential in many fields such as catalysis, biomedicine, and dyes. The introduction of porphyrin groups in COFs can generate a new class of functional materials. However, up to now, the construction of porphyrinic COFs is mostly limited to two-dimensional (2D) COFs, and three-dimensional (3D) COFs are still in their infancy, hampered by the limited building blocks and topologies and the challenge of precisely determining their structures. Addressing these challenges, we develop high-connection (e.g., 8-c) building blocks and successfully construct a series of 3D COFs.[1] After employing various characterization such as 3D electron diffraction (ED) and modeling studies, the structures of these COFs can be determined precisely. [2]

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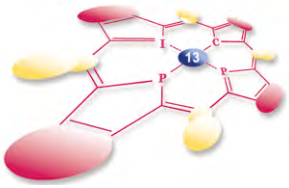

Report on the results of an initial clinical trial of sonodynamic therapy for refractory brain gliomas

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Purpose: Brainstem gliomas and recurrent glioblastomas (rGBM) are a class of clinically refractory malignancies and guidelines from NCCN, CSCO recommend clinical trials as an option for appropriate patients [1]. Ultrasound and radiation can activate haematoporphyrins, producing sonodynamic and radiodynamic effects to kill cancer cells. Therefore, we are conducting this phase I clinical trial of sonodynamic therapy (SDT) combined with chemoradiotherapy for the treatment of patients with brainstem gliomas and rGBM to validate its safety and efficacy [2].

Methods: We conducted a study of SDT combined with chemoradiotherapy in 20 patients (patients with brainstem gliomas and rGBM). Following the administration of haematoporphyrin, the patients underwent SDT. MRI was performed to assess the tumour and adverse events (AEs) were recorded.

Results: There were no treatment-related deaths during the course of treatment. All patients experienced grade 1-2 AEs, no grade 3 or higher AEs were observed, and most AEs were not related to SDT. By the date of follow-up, two patients with brainstem gliomas had achieved partial remission; three patients with brainstem gliomas and one patient with rGBM remained in stable disease. Patients with brainstem gliomas had a median progression-free survival of 9.2 months and a median overall survival of 10.5 months. The median overall survival after relapse in rGBM patients was 6.7 months.

Conclusion: SDT combined with chemoradiotherapy has a good safety and feasibility profile and deserves further exploration.

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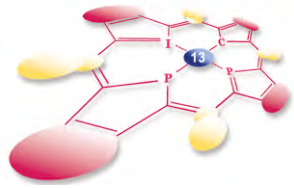

Zr-Porphyrin Metal-Organic Frameworks

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Porphyrins are ubiquitous in nature and play an essential role in many key biological functions, such as light harvesting, oxygen transport, and catalytic transformations. The rigid, robust, and multifunctional nature of porphyrins enables them to be a unique building unit of metal-organic frameworks (MOFs) for many important applications. The Zhou group has designed and synthesized a series of popular Zr-porphyrin MOFs [1-5]. In 2020, we summarized the studies on catalytic porphyrin frameworks, aiming at facilitating the research on ligand design, framework synthesis, and the future development of efficient catalysis [6]. Recently our group mainly focused on the optical and catalytic properties of Zr-porphyrin MOFs. In 2020, we developed a facile one-pot synthesis to incorporate multi-functionalities via secondary ligand pillaring to form stable Zr-MOFs, to serve as a heterogeneous catalyst for the selective oxidation of anthracene [7]. We also reported a versatile and effective strategy to generate hierarchically porous MOFs through laser photolysis towards porphyrin-modified UiO-66, which exhibited merits in spatial resolution, fabrication speed, power consumption and cost [8]. In 2021, we reported a new Zr-MOF (PCN-625) with two types of 1D channels, which was utilized as an efficient heterogeneous catalyst for the size-selective [4+2] hetero-Diels–Alder cycloaddition reaction [9]. Energy-transfer process was also utilized to increase charge separation, thus enhancing the catalytic performance of a series of Zr-MOFs, while the acceptor-on-donor catalysts show more enhanced catalytic performances than donor-on-acceptor catalysts due to site-isolation [10]. In 2023, we summarized bioinspired framework catalysts, highlighting the porphyrin-based MOF domain in bioinspired heterogeneous catalysts with superior stability and customizable structures [11]. In 2024, we demonstrated a bottom-up synthetic method for embedding photoactive cores into a series of 2D MOF nanosheets, while the efficiency of photoinduced energy transfer in these nanosheets was demonstrated through photoborylation reactions and the generation of reactive oxygen species [12]. In summary, a series of Zr-porphyrin MOFs and MOF derivatives have been designed and synthesized in our lab, which exhibited not only excellent structure stability mainly thanks to the Zr-cluster, but also exciting optical and catalytic properties due to the porphyrin ligands.

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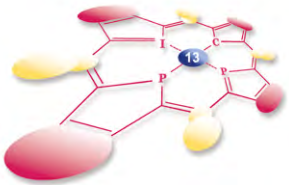

New Developments in Chelating Isoindoline Chemistry

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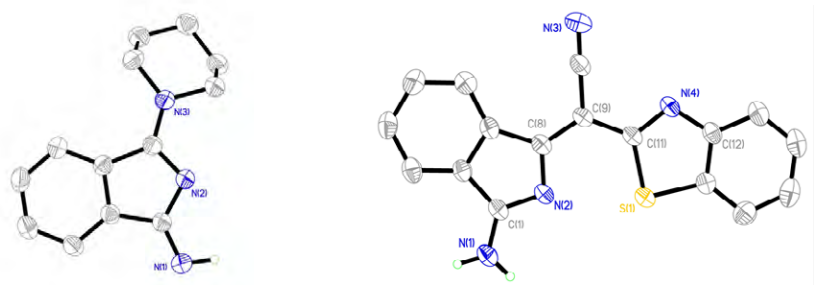
As the chemistry of isoindoline as a precursor for phthalocyanine chemistry enters its 8th decade, this reagent remains a highly useful starting point for the synthesis of novel phthalocyanine analogs as well as BODIPY and aza-BODIPY variants. In this talk, new chemistry from the Ziegler lab on developing isoindoline chelates and macrocycle precursors will be discussed. This includes diiminoisoindolines with secondary amine functional groups, which exhibit temperature dependent dynamic behavior. Imineylidene isoindolines will also be presented; these compounds can be used as precursors for open ring phthalocyanine analogues as well as asymmetric chelates for forming BODIPY-type compounds. This chemistry builds upon our previous work on the biliazines as well as the BOSPHY fluorophores.



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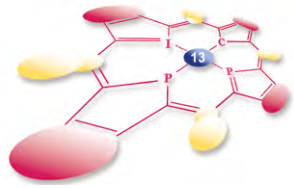

J-dimers of Phthalocyanines

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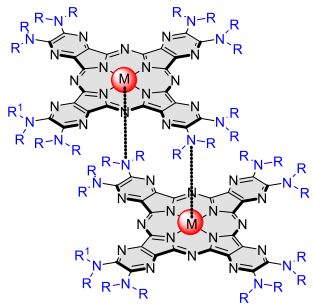
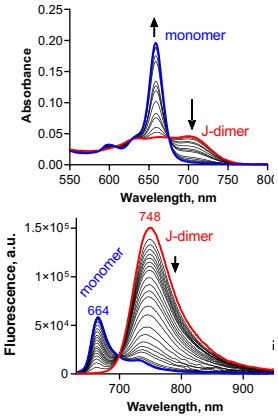
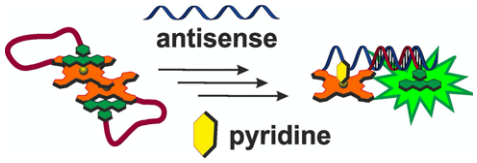
Phthalocyanines (Pcs) are macrocyclic dyes that tend to form aggregates based on the π-π stacking of the planar core. Such aggregates are called H-aggregates and typically are characterized by blue-shifted Q-band and non-fluorescent nature. On the other hand, several papers have reported the formation of slipped J-dimers with retained fluorescence and red-shifted absorption Q-band, however, the examples are extremely rare [1-4]. Our work has been focused on various aza-analogues of Pc (AzaPcs) that formed the slipped J-dimers based on the coordination of peripheral substitutes (various dialkylamino substituents or heteroaryls) with central cation (Zn(II) or Mg(II)). In one of the series, we focused on the stability of the J-dimers in dependence on the size of the peripheral substituents. Unequivocal dependence between dimerization constant and bulkiness of peripheral binding sites was observed. The J-dimers can be disassembled into monomers with changes to shape and intensity of fluorescence and also in the production of singlet oxygen using various external stimuli – increased temperature, presence of external coordinating ligand (see figure below) or protonization of the binding site by acids. Selected compounds forming strong J-dimers were also attached to the oligodeoxynucleotide probes where they served as dark quenchers of the fluorescence of the reporter (fluorescein, FAM). The J-dimers of such conjugates were formed also in the buffers and exerted strong stability. Additionally, they formed stable heterotetramer in probes labeled by AzaPc and FAM that were disassembled only after the addition of coordinating solvent [5]. The spectral changes were subsequently converted to a simple biomolecular logic gate. The work was supported by the Czech Science Foundation, grant Nr. 23-06177S.







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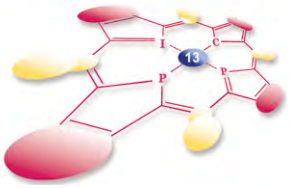

Synthetic Approach to Unsymmetrical ABAC-type Phthalocyanines via [3+1] Intermolecular Cyclization

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Phthalocyanines (Pc) are a class of π-conjugated heteroaromatic macrocycles, consisting of four isoindole rings linked by nitrogen bridges. Upon introducing asymmetry, the molecular structure gets perturbated electronically allowing a fine-tuning of the physical properties. However, the chemistry of structurally modified low-symmetric phthalocyanine has received mediocre attention than that of Pc^{2-} or Pc metal complexes with D_{4h} symmetry. The mixed condensation reactions using multiple precursors limit the feasibility of the formation of low-symmetric Pcs owing to the identical molecular weight and properties of the product formed.[1]

Controlled formation of target Pc with a minimal amount of side products could be achieved by a [3 + 1] approach *i.e,* a base-promoted condensation of pre-linked trisphthalonitrile (ABA-trimer) and a free phthalonitrile (C) in the presence of a metal template (M).[2] Developing this approach to synthesize ABAC-type Pc also allows the advantageous orientation of specific functionalities on subunits B and C (Figure 1).

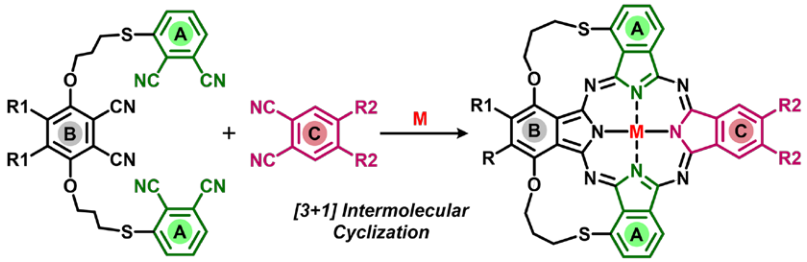

Figure 1. Cyclization of preconnected trisphthalonitrile (ABA-trimer) and a free phthalonitrile (C) in the presence of a metal template (M).

We have successfully synthesised the subunit B of ABA-trimer with *tert*-butylthio linkers at the β-position and propoxy linkers at the α-position. Correspondingly, the propoxy linkers at the α-position of subunit B are connected to the α-position of phthalonitrile A, *via* a sulphur atom constituting the targetted trimer. Eventually, the ABAC-Pc is obtained via the cyclization reaction of ABA trimer with 4,5-bis(2,6-bis((1H-imidazol-1-yl)methyl)-4-methylphenoxy)phthalonitrile (C). Similarly, with improved selectivity and yield, this approach could be pursued for the preparation of low-symmetrical phthalocyanines having hydrophilic and/or lipophilic moieties attached covalently. Also, the thio-linker attached to the α-position could induce pronounced effects on their structural properties. Moreover, the pre-connected ABAtrimer and free phthaonitrile C can be appropriately chosen to generate exotic phthalocyanine derivatives for varied applications.

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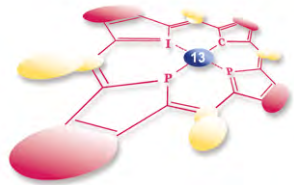

Photophysical properties and photodynamic antimicrobial study of 2,6 – dibromo – BODIPY substituted by 3-bromo 4-hydroxy styryl at 3,5 positions

Crispin Ndundu Akwesi

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Boron dipyromethene known as BODIPY dyes has attracted many researchers because of their different applications in bioimaging, photodynamic therapy, solar cell sensitization and photodynamic antimicrobial chemotherapy. In this work, 3-bromo 4-hydroxy styryl bodipy, and 2,6 – dibromo – BODIPY were synthesized and used Photodynamic antimirobial chemotherapy activity against *Staphylococcus aureus* and *E. Coli*. In the best of my knowledge, 2,6-Dibromo-3,5-distyryl BODIPY dye used in this work is novel. The results found in this study are promising for both negative and positive gram bacteria used.

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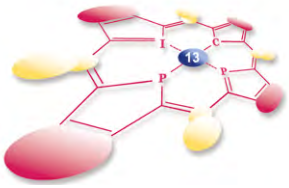

In-cell Activatable Phthalocyanines for Photodynamic Therapy of Cancer

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The conventional chemotherapeutic treatment of cancer poses a threat to healthy cells, presenting the need for selective cell death. Although photodynamic therapy [1] for cancer is an efficient non-invasive therapy, an ideal photosensitizer (PS) is still on the lookout. Silicon Phthalocyanines are macrocycles with interesting photophysical properties and highly applicative singlet oxygen production capabilities that can be fine-tuned. The presence of axial ligands can be exploited to reduce aggregation and in turn, introduce moieties for solubility and targeted therapy. Cathepsin B is a lysosomal cysteine protease that plays a pivotal role in tumour development and its overexpression is associated with tumour environments. Its dicarboxypeptidase activity makes it cleave a combination of dipeptidic linkers [2] at the C-terminus, of which the valine-citrulline labile bridge is a highlight.
In this work we develop an optimized photosensitizer for precision medicine, possessing desired water solubility, absorption in the biological window of tissues and high singlet oxygen production potential to maximize cell death The element of selectivity is brought about by the Cathepsin B sensitive, Valine-Citrulline cleavable dipeptidic, axial ligand. It is modified further with ferrocene to make the PS a PET-controlled switch for in-cell activation.

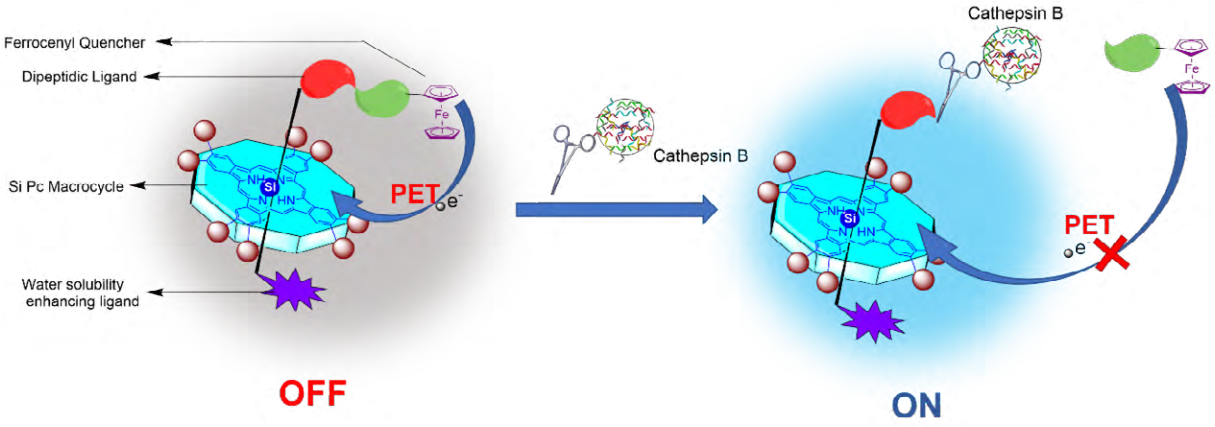

Figure 1: Schematic functioning of the antibody-drug conjugate with the cleavable Valine-Citrulline ligand.

Acknowledgments: The work was supported by the Ministry of Education, Youth and Sports (ERC-CZ, Grant No. LL2318).

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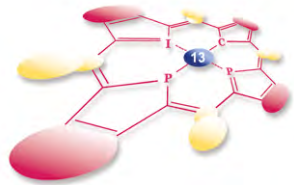

Antimicrobial Photodynamic Therapy (aPDT) for the treatment of bacterial urinary infections

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Urinary tract infections (UTI) are prevalent bacterial infections often associated with urinary catheter use due to biofilm formation [1]. Conventional antibiotic treatments face challenges from increasing antimicrobial resistance, necessitating the exploration of alternative strategies [1]. Antimicrobial photodynamic therapy (aPDT) presents a promising solution, utilizing a photosensitizer (PS) and visible light to inactivate bacteria without promoting resistance [2]. Methylene Blue (MB), a well-studied PS, has shown potential, especially when combined with potassium iodide (KI), which enhances aPDT efficacy [3-4]. Our study aims to evaluate MB-mediated aPDT, with and without KI, as an alternative to antibiotics for UTI control.

We conducted aPDT assays in urine samples to assess the efficacy of photodynamic treatments against the most prevalent UTI-causing bacteria: *Klebsiella pneumoniae*, *Escherichia coli*, *Enterococcus faecalis*, *Proteus mirabilis*, and *Pseudomonas aeruginosa* [5]. Initially, we evaluated bacterial inactivation individually and then with the five bacteria simultaneously to mimic real UTI scenarios. Additionally, we investigated the effectiveness of these treatments against *E. coli* biofilms, the most prevalent bacteria in UTI, formed in urinary catheters.

Our findings indicate that MB alone effectively inactivated *E. coli, P. mirabilis and E. faecalis* in planktonic form, with limited activity against *K. pneumoniae* and *P. aeruginosa*. However, the addition of KI significantly improved the photodynamic effect, resulting in a more pronounced inactivation and reduced treatment duration Moreover, the treatment also proved effective against mixed bacterial populations. Additionally, MB+KI treatment successfully eradicated *E. coli* biofilms on urinary catheters, achieving reductions of 3.9 and 6.0 Log_{10} CFU mL^{-1} after one and two treatment cycles, respectively.

Overall, these findings suggest MB and KI-mediated aPDT as a promising therapeutic approach for UTI control, particularly in biofilm destruction on urinary catheters.

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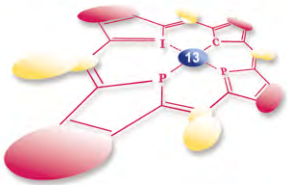

A nanotube binding *molecular cleft*: Role of carbon nanotubes in slowing charge recombination in supramolecular C_{60}-bisstyrylBODIPY-(zinc porphyrin)$_2$ donor-acceptor hybrids

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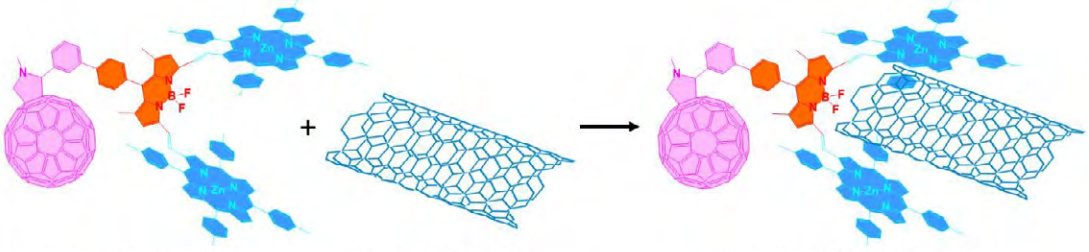
In the realm of building light energy harvesting nanomaterials, all-carbon structures such as fullerene, endohedral fullerene, nanotubes, and graphene have played a pivotal role. This study focuses on the design and synthesis of a multi-modular molecular cleft capable of binding diameter-sorted single-wall carbon nanotubes (SWCNTs) and stabilizing charge-separated states for enhanced light energy conversion. The designed C_{60}-bisstyrylBODIPY-(zinc porphyrin)$_2$, *molecular cleft* **1**, employs a strategic arrangement of electron donor and acceptor entities to facilitate efficient charge transfer processes. The synthesis of **1** involved a series of well-defined steps resulting in a high-yield product. Spectroscopic studies revealed the optical properties and electrochemical behavior of **1**, indicating its suitability for light energy harvesting applications. Binding studies with diameter-sorted SWCNTs demonstrated effective interaction and formation of donor-acceptor nanohybrids. Computational simulations provided insights into the geometry and electronic structure of the hybrids, confirming their compatibility with SWCNTs of different diameters. Energy profile diagrams elucidated the thermodynamic feasibility of various photochemical events, akin to natural photosynthesis processes. Femtosecond transient absorption studies further corroborated the occurrence of charge separation and stabilization in **1**:SWCNT hybrids, with efficient electron transfer kinetics. GloTarAn-Target analysis revealed prolonged lifetimes of charge-separated states in the presence of SWCNTs, underscoring their role in enhancing energy harvesting efficiency. Overall, this work highlights the potential of SWCNT-based donor-acceptor hybrids in advancing light energy conversion technologies.



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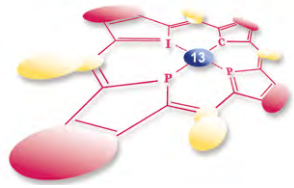

A Biomimetic Ni-*seco*-corrin Complex

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Methyl-coenzyme M reductase (MCR) catalyzes both the synthesis and the anaerobic oxidation of methane.[1] The catalytic site of this enzyme contains a Ni-hydrocorphinate complex called cofactor F430. Understanding the mechanism of these cofactor-catalyzed reactions has large implications for developing new technologies to catalytically generate and activate methane.[2] Unfortunately, the mechanism of methane formation and oxidation is not fully resolved on a molecular level, mainly because intermediates in the catalytic cycle have not been identified. Therefore, structural and functional mimics of F430 play important roles in elucidating the mechanism and developing new catalysts for green chemistry applications.[3]
In this work, we synthesized and characterized a novel Ni-corrinoid target compound as a model of F430. Afterwards, electrochemical studies for its reduction chemistry and catalytic activity were performed to compare the reduction chemistry of the model compound with its natural counterpart F430. The experiments included: cyclic voltammetry, spectro-electro-chemistry, and electronic paramagnetic resonance spectroscopy. Similarities in the reduction chemistry of the model and F430 were observed demonstrating that the new Ni-seco-corrinoid is a structural model of the natural cofactor.

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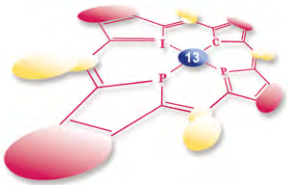

Structure-activity relationship of functionalized porphyrins for ZIKV inactivation

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The global impact of microorganisms in the past years provided an unprecedented impetus to antiviral drug research. In parallel, climate changes expanded the ecosystem of mosquitoes carrying Zika. Diverse molecules have been studied for their potential antiviral activity against Zika virus.[1] Among these, tetrapyrrolic macrocycles, including porphyrins and chlorins, are a promising class of molecules with intriguing antiviral properties. They can function as photosensitizers when exposed to light,[2] but may also show antiviral activity in the absence of light.[3] Research on structure-activity relationships of porphyrin-derived antivirals is necessary. This study addresses the synthesis and application of selectively designed porphyrin derivatives aiming at the inactivation of ZIKV in the dark.

In this communication, we will present and discuss novel approaches for the synthesis of meso-substituted porphyrins using flow chemical processes. Additionally, porphyrin structure determinants for ZIKV inactivation were explored by modulating porphyrin size, charge distribution and the presence of functional groups including sulphonic, hydroxy and carboxy groups.
Porphyrins with sub-micromolar activity against ZIKV in the dark were obtained, namely when polar substituents were added. Porphyrin cytotoxicity was also evaluated in Caco-2 cells and JEG-3 and did not present cytotoxicity to Caco-2 cells in the tested concentrations (CC50>50mM).

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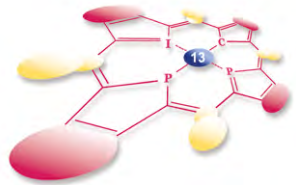

Synthesis of meso-aryl porphyrins using flow chemical processes

Zoe A. Arnaut[a], Alexandre P. Felgueiras[a], Fábio M.S. Rodrigues[a], Rafael T. Aroso[a], Alberto A.C.C. Pais[a], Mariette M. Pereira[a]

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Flow chemical synthesis, when compared to traditional batch processing, offers higher mass and heat transfer rates, enhances safety, increases reaction efficiency, reduces waste production, and improves scalability, and reproducibility of the chemical processes.[1] Being among the most versatile classes of organic compounds, meso-aryl porphyrins hold significant potential for diverse applications. Thus, it is imperative to surpass the existing batch synthesis methods, described by Lindsey [2] and Pereira-Gonsalves [3] towards streamlined flow processes [4]. To identify the optimal reaction temperature and residence time, we started our studies by conducting a factorial design of experiments. Using these results, we were able to fine-tune reaction parameters, resulting in enhanced meso-aryl porphyrin yields. Moreover, we successfully scaled up the reaction, maintaining a consistent yield of 25% of the targeted porphyrin over an uninterrupted 8-hour period. All these results will be presented and discussed in this communication.

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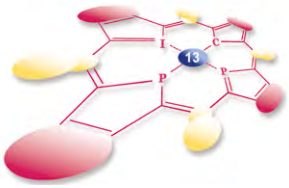

Unraveling the Impact of Photosensitizer Structure on the Antibacterial Prowess of Photodecontaminant Biopolymers

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Infections by multi-drug resistant (MDR) microrganisms are one of the biggest concerns of modern medicine and constitute an enormous burden to healthcare systems worldwide. They are currently responsible for 1.3 million direct deaths annually, a number which is expected to grow considerably over the coming decades.[1] One of the most established causes for the rise of MDR bacteria is contact with contaminated hospital surfaces and devices, which can swiftly result in deadly infections, especially in immunocompromised patients.[2] It is, therefore, crucial to tackle this issue through the development of surfaces with broad-spectrum antibacterial properties, capable of inactivating bacteria deposited onto their surface, reducing their pathogenicity and preventing the formation of biofilms. This can be achieved through the use of photosensitive materials,[3,4] which combine polymeric matrix, ideally biopolymers with improved biodegradability, and photosensitizers. Porphyrins constitute one of the most attractive classes of photosensitizers for the preparation of photosensitive materials, due to their stability combined with robust photophysical and photochemical properties.[4] Herein, we present our recent results on the preparation of new photosensitive materials containing either synthetic cationic porphyrins or a naturally derived photosensitizer. The photosensitive materials were characterized by standard techniques such as Differential Scanning Calorimetry, X-ray Powder Diffraction, Thermogravimetry, Scanning Electron Microscopy and Fourier-Transform Infrared Spectroscopy. Additionally, the photoinactivation efficiency of both Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) bacteria was conducted under blue light irradiation, with light doses ranging from 16 to 33 J/cm^2. Under these conditions, full inactivation of the bacterial inocula (7 log reduction) was achieved with the bipolymer containing a monocationic porphyrin, showcasing the effect of the photosensitizer structure on both the material's stability and antibacterial activity.

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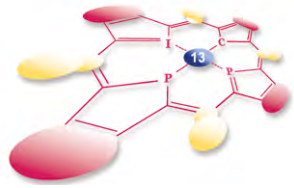

Ratiometric nanothermometry *via* porphyrin inner filter effect applied to colloidal ZnS quantum dots

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Thermal sensing at the nanoscale is an attractive research field with potential in different areas like micro/nanoelectronics and nanomedicine. One of the driving forces of these studies is related to the design and construction of ratiometric thermometers based on the combination of materials with distinct thermometric properties [1]. Although nanoassemblies obtained from porphyrins and quantum dots (QDs) are reported to present promising features as sensors, photocatalysts and photosensitizers, only a few studies describe the temperature-sensing properties of such systems [2].
Herein, we provide the first example of luminescence ratiometric thermal sensors that act within the biological temperature range using non-covalent nanoassemblies prepared in situ from 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (TPFPP) and colloidal ZnS/AOT QDs.[3] Taking advantage of the excellent overlap of the absorption band of the porphyrin with the emission band of ZnS/AOT QDs, the thermal sensing assays were carried out via steady-state fluorescence measurements and were based on the so-called inner filter effect (IFE). The preparation of the nanoassemblies composed of porphyrin TPFPP and colloidal ZnS/AOT QDs, their characterization and also the results from the nanothermometry studies will be presented and discussed,

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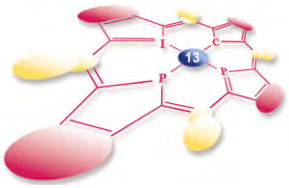

Studies of antimicrobial efficiency of corroles against *Staphylococcus aureus*

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Corroles are aromatic contracted tetrapyrrolic macrocycles with unique physicochemical features to be used in different fields, namely in therapeutic applications such as Antimicrobial Photodynamic Therapy (aPDT) [1,2]. Although aPDT is a promising approach with recognized efficiency to eradicate bacteria, viruses and fungi, the use of corroles as photosensitizers in aPDT is more limited compared with other porphyrinoids [2].
In this study, we focus on evaluating the photodynamic effects of these contracted macrocycles on bacterial strains. We will discuss the antimicrobial effectiveness of *trans*-A_2B *meso*-arylcorroles derived from 5,10,15-tris(pentafluoro)corrole with different substituents (B = -C_6H_4CN, -C_6H_4COOMe and –C_5H_4N) against the Gram (+) bacterium *Staphylococcus aureus*. The choice of this strain was influenced by the increasing prevalence of multidrug-resistant strains leading to a higher mortality rate [3].
Additionally, we evaluated the cytotoxicity of the most promising compounds on Vero cells to explore their potential as antibacterial agents in future clinical applications

Funding: This work received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e a Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) for the financial support for the LAQV-REQUIMTE (LA/P/0008/2020 DOI 10.54499/LA/P/0008/2020, UIDP/50006/2020 DOI 10.54499/UIDP/50006/2020 and UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020), CESAM (UIDP/50017/2020+UIDB/50017/2020+LA/P/0094/2020) and the FCT project Corlutna (POCI-01-0145-FEDER-031523) funded by FEDER funds through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI). MB and PSSL thank FCT for funding through project Corlutna for research grant BI/UI88/7701/2021 and research contract, respectively. This research was also funded by FCT and UCP through the CEEC institutional financing of A.T.P.C.G. (CEECINST/00137/2018/CP1520/CT0022) and A.S.D. (CEEC-INST/00137/2018/CP1520/CT0013).

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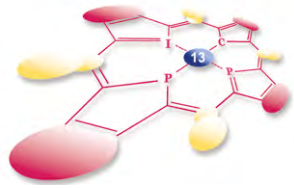

Assembly of phthalocyanine analogues into J-dimers

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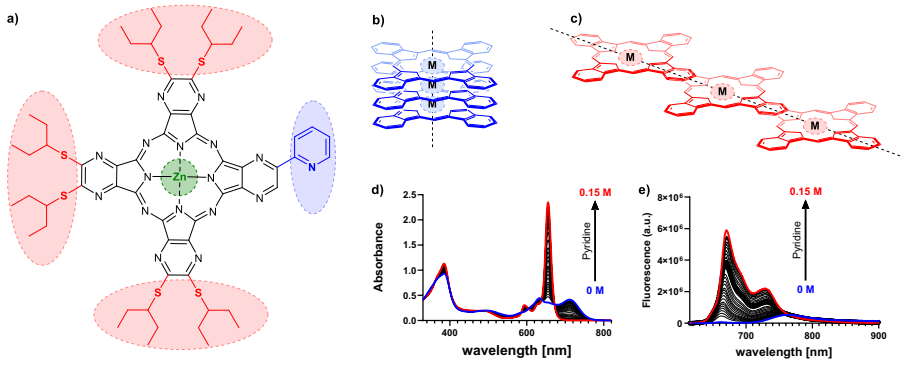
Phthalocyanines (Pcs) are synthetic macrocyclic dyes formed by four isoindoline units connected by azomethine bridges, structurally close to porphyrins. Due to their extended 18 π-conjugated system, they show unique photophysical properties and they have been largely investigated in various fields such as fluorescence sensors or photosensitizers in photodynamic therapy (PDT) [1]. However, these properties are related mostly to the monomeric form of the Pcs only. Aggregation of the Pcs is usually an unfavorable phenomenon that plays a major role in final photophysical properties. The planar Pc core tends to aggregate due to π-π stacking interactions leading to the formation of supramolecular structures. The most common, H-type aggregates (Figure b) align molecules into sandwich-like arrangement that results in increased absorption at blue-shifted wavelengths and strongly decreased fluorescence emission and singlet oxygen production. On the other hand, J-aggregates (Figure c) are extremely rare and only several papers reported their formation. They give rise to red-shifted absorption bands, and they retain fluorescent properties as well as singlet oxygen production [2-3]. In this work, we synthesized unsymmetrical Pc derivatives (Figure a) containing one ligand (coordinating moiety, e.g., pyridyl) that formed slipped J-dimers upon coordination to the central cation of the second Pc molecule in non-coordinating solvents. The stability of the J-dimers is evaluated by observations of changes in absorption and emission spectra (Figures d and e) with the tested coordinating ligands, which compete with central cation and dissociate the dimer while the acid will protonate the basic nitrogen in ligand substituent leading to dissociation as well. J-dimer can also be monomerized by increasing the temperature of the solvent. Absorption and emission spectra unequivocally confirmed the formation of J-dimers. The work was supported by Charles University (GAUK 230723) and the Czech Science Foundation (grant No. 23-06177S).



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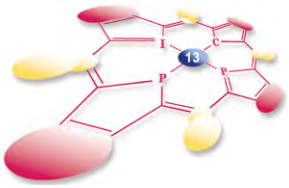

A new water-soluble supramolecular complex for O_2 reduction

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Cytochrome c oxidase (C*c*O) catalyses the reduction of dioxygen (O_2) to water via a four-electron pathway by using a heme/copper hetero-binuclear active site. [1-2] This finely tuned reactivity is only possible because of the high degree of sophistication of the peptide structure that surrounds the "active" metallo-porphyrin unit. In these molecular scaffolds, the polypeptide envelope controls the solubility, the access of exogenous ligands, and the reactivity of the central heme. Due to the extreme sophistication of these natural systems, the design of functional and structural hemoprotein models has always been a synthetic challenge.

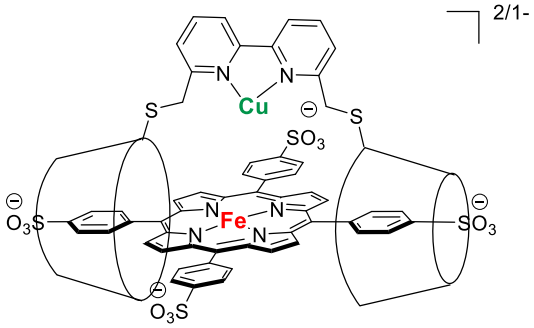

Figure 1. Molecular structure of [**FeTPPS/CuBipy-CD$_2$**]$^{2/1-}$ supramolecular complex

In collaboration with the group of Prof. Kitagishi, who specialized in the synthesis and studies of water-soluble hemoproteins models, [3-4] a new functional model of C*c*O [**FeTPPS/CuBipy-CD$_2$**]$^{2/1-}$ was prepared for O_2 reduction (Figure 1). This model combines an iron tetraphenylporphyrin sulfonate [**FeTPPS**]$^{3-}$, and a cyclodextrin dimer with a copper-binding bipyridine linker [**CuBipy-CD$_2$**]$^{2/1+}$ The latter provides water solubility and mimics a globular environment. This work aims to study the O_2 binding and reactivity of this new model in an aqueous medium.

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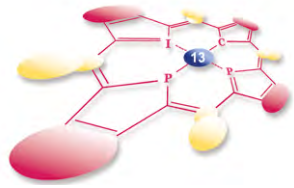

π-Extended Nonplanar Cobalt Porphyrins Immobilized MWCNTs as Efficient Electrocatalysts for Selective ORR

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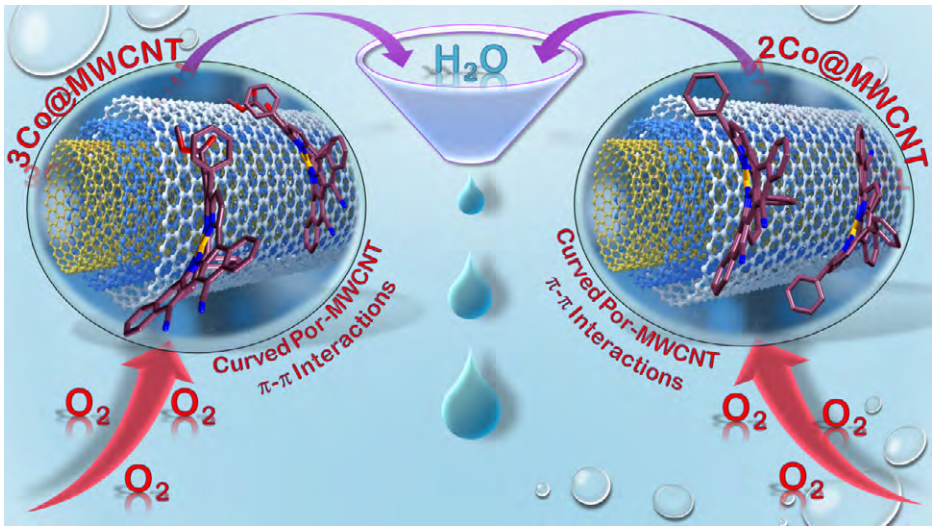
The rapid industrialization and consumption of non-renewable fuel sources have led the world to an alarming edge. This increasing energy crisis forces researchers to switch to renewable sources of energy, including solar cells and fuel cells.[1] The catalytic reduction of O_2 is crucial for energy transduction. Platinum supported on graphitic carbon is currently considered the state-of-the-art catalyst for the ORR. However, it is expensive and has certain stability and selectivity issues.[2] Therefore, developing electrocatalysts for the efficient and selective $4e^-$ ORR under minimal overpotential is highly desirable. Considering this, we have designed nonplanar saddle-shaped cobalt porphyrins as building blocks to fabricate novel nanocomposites through effective π–π interactions.[3] Herewith, we are presenting the synthesis and characterization of two π-extended nonplanar (*curved*) cobalt porphyrins and their nanocomposites and utilizing them as efficient electrocatalysts for selective ORR. Both the nanocomposites displayed ~ 200 mV positive shift in the O_2 reduction peak potential in aqueous media and ~ 100 mV shift in the onset potential of the O_2 reduction relative to the control CoTPP nanocomposite. The nanocomposites efficiently catalyzed selective $4e^-/4H^+$ O_2 reduction under ambient conditions with excellent methanol tolerance and high stability and could be an alternative for expensive Pt-based cathode materials in fuel cells.



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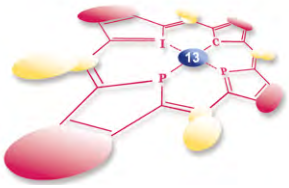

π-Extended NIR Absorbing Porphyrin−Tetracyanobutadiene (TCBD) Chromophores for Optoelectronic Applications

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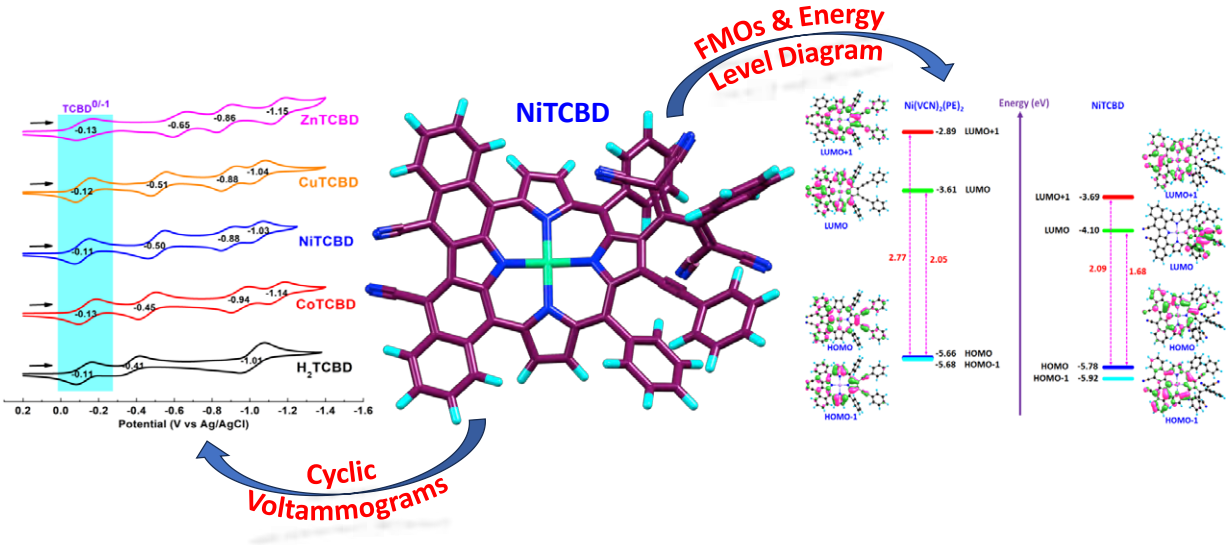
Excited state charge transfer in donor–acceptor conjugates has been a widely investigated topic in recent years due to its usage in building energy-harvesting photonic devices.[1] 'Push–pull' chromophores, derived from closely linked, highly interacting near-IR absorbing molecular systems, have been studied for various technological applications, including multi-photon absorption, organic photovoltaics, and optoelectronics.[2] Therefore, developing novel 'push–pull' chromophores for demanding photonics and energy storage and transduction applications is highly desirable in modern technology. Considering this, we have designed and synthesized π-extended nonplanar NIR absorbing porphyrins as a donor (D) and a high-energy charge transfer species tetracyanobutadiene (TCBD) as an acceptor (A) conjugate for the optoelectronic applications particularly, multi-photon absorption and optical limiting properties. These D−A chromophores revealed panchromatic absorption covering the whole visible and extending to the NIR region owing to their extended π-conjugation and intramolecular charge transfer. The present study demonstrates the synthetic route to the new D−A chromophores, spectroscopic and crystallographic characterization, intriguing electrochemical redox properties and computational analyses to correlate the energy levels of the donor and acceptor entities. Finally, the utilization of these 'push−pull' chromophores in optoelectronic applications will be discussed.



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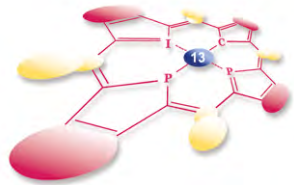

Study of peptide-mediated photo-induced electron transfer in a porphyrin-titania system for dye-sensitized solar cells

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Inspired by the activity of proteins and peptides as mediators of Electron Transfer (ET) in biological systems [1], we present the design of a biomimetic system in which a peptide spacer acts as a linker between a free-base tetraphenyl porphyrin (the electron donor), attached to its N-terminal, and titanium oxide (TiO_2) nanoparticles (the electron acceptor), used as photoanode in Dye-Sensitized Solar Cells (DSSCs), to which the peptide is bound through the C-terminal [2]. The use of a peptide spacer made up of residues favouring an alpha-helix structure is aimed at maintaining an efficient photo-initiated ET between the porphyrin dye and the TiO_2 nanoparticles while at the same time increasing the distance between TiO_2 and the porphyrin in a rigid and well-defined structure, thus reducing the detrimental fast charge recombination [3].

In this work, the photo-induced ET process, occurring upon excitation with a Xe lamp, has been studied using continuous-wave Electron Paramagnetic Resonance (EPR) spectroscopy at 80 K [4, 5], both in dried powder samples and solution, in an environment closer to a working DSSC.

Furthermore, the effect of irradiation on the system is compared to the case in which the chromophore is directly connected to the surface of the nanoparticle. A comparison between the EPR results with and without the peptide linker shows enhanced photo-stability of the system for a long time. Therefore, this approach can be fruitful for the development of more efficient and stable DSSCs.

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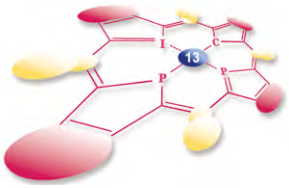

Characterization of the photoexcited triplet state of an Al(III) porphyrin with enhanced electron acceptor properties

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Al(III) porphyrins have been proposed as a novel building block for donor-porphyrin-acceptor systems in which the hexa-coordination of Al(III) is exploited to develop triads with axial orientation for the porphyrin plane [1, 2].
In this work, we characterize the photoexcited triplet state of a fluorinated Al(III) porphyrin and its non-fluorinated counterpart [3] *via* optical spectroscopy techniques, Time-Resolved Electron Paramagnetic Resonance (TR-EPR) spectroscopy and Electron Nuclear Double Resonance (ENDOR) spectroscopy [4].
In particular, we study the effect of different Jahn-Teller distortions on the photoexcited triplet state [5] and characterize the charge transfer interaction within the electron-rich periphery of the porphyrin macrocycle and the electropositive metal in the center.

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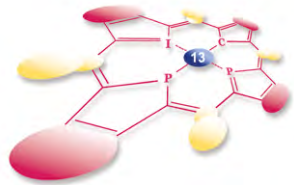

Corrination mitigates peptide aggregation as exemplified for glucagon

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Pharmaceutical development of glucagon for use in acute hypoglycemia has proved challenging, due in large part to poor solubility, poor stability and aggregate formation [1]. Herein, we describe highly soluble, low aggregating, glucagon conjugates generated through the use of the commercially available vitamin B12 precursor dicyanocobinamide ('corrination'), which retain full stimulatory action at the human glucagon receptor [2, 3, 4]. The modified glucagon analogs were tested in a chemical stability assay in 50 mM phosphate buffer and the percentage of original concentration retained was determined after two weeks of incubation at 37 °C. Aggregate formation assays were also performed after 48 h of agitation at 37 °C using a thioflavin (ThT) fluorescence-based assay. All corrinated compounds retained their original concentration to a higher degree than glucagon controls and showed markedly decreased aggregation compared to their respective noncorrinated analogues. Based on the statistically significant increase in chemical stability coupled with the notably decreased tendency to form aggregates, analogues 2 and its corrinated conjugate 5 were used for a functional assay study performed after agitation at 37 °C for 24-hr after which agonism was measured at the human glucagon receptor using a cAMP FRET assay. Corrinated 5 exhibited a 6.6-fold increased potency relative to glucagon, which was shown to have a 165-fold reduction in potency. The relative potency of 5 was also improved compared to that of 2 with EC50 values of 5.5 nM and 9.6 nM for 5 and 2, respectively. In conclusion, the corrination of peptides mitigates aggregation, presenting a compound with prolonged stability and agonism as demonstrated for glucagon.

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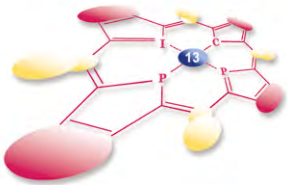

Diazaporphyrins Based Novel Photosensitizers for PDT

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Cancer is one of the leading causes of death worldwide after cardiovascular disorders. As per the World Health Organization (WHO) cancer facts; in the world there are five most dangerous types of cancer viz. Breast, Lung, Colon, Prostate, Skin, and Stomach. Among all these cancers, breast cancer is considered most dangerous type. In 2020, there were 68.5 billion deaths globally due to breast cancer. Treatment of breast cancer depends on the subtypes of cancer [1,2]. Currently, cancer treatment includes surgery, radiation, and chemotherapy to minimize recurrence of cancer. But such combination approach may not be effective due to drug resistance. So, to overcome this problem Photodynamic Therapy (PDT) is an excellent therapeutic approach for the treatment of different subtypes of breast cancers, especially Triple-Negative Breast Cancer (TNBC)[3].

Our group at IIT Gandhinagar is involved in the synthesis of porphyrins, BODIPYs and metal dipyrrinato derivatives for biological applications [4-6]. In this poster, the synthesis of novel diazaporhyrins (**DAP-1** to **DAP-5**) and their photocytotoxicity studies on breast cancer cells (MDA-MB-321) will be discussed. In this work, diazaporphryin (**DAP-1)** showed potential to be developed as theranostic agent for anti-cancer applications.

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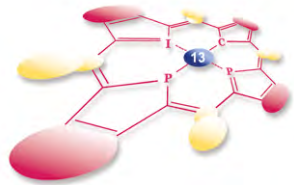

Zinc phthalocyanine/biopolymer complex as a bifunctional agent for wound dressing

Dorota Chelminiak-Dudkiewicz[a], **Aleksander Smolarkiewicz-Wyczachowski**[a], **Kinga Mylkie**[a], **Marta Ziegler-Borowska**[a]

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As the human body's largest organ, the skin is a barrier to the environment. Skin damage interferes with proper functioning, increasing the probability of wound infection [1]. Therefore, it is essential to quickly protect the wound with an appropriate dressing to prevent infection, speed up wound healing, and reduce the number of complications. A good wound dressing should meet many conditions, such as adequate moisture content (which will protect the wound from dehydration), biocompatibility, degradability, and non-toxicity [2]. Moreover, the wound dressing should have sufficient mechanical properties: it should be strong enough to withstand physical stress and, at the same time, soft enough to support the patient's regular activity. However, synthetic polymers could cause side effects that are highly unfavorable to patients' health and safety. Therefore, more and more attention is focused on the use of biopolymers.

Chitosan (CS) is an ideal choice for wound dressings for all biopolymers due to its exceptional biocompatibility, antioxidant activity, and biodegradability. In addition, CS has been shown to promote tissue growth and differentiation during wound healing [3]. The fabrication of a new antibacterial system is an essential medical requirement to treat wounds caused by multidrug-resistant *Gram-negative* bacteria. In this context, zinc phthalocyanine was incorporated into the chitosan sponge.

The material was characterized in terms of its physicochemical and biological properties. Moreover, the interaction of the obtained sponge with human serum albumin (HSA) was also studied. The results study showed this material could be potentially used as wound dressing.

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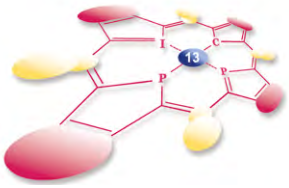

Tailoring Heme Peroxidase Models: Engineering Saddle-Shaped High-Valent Iron-Oxo Porphyrin Structures with Imidazole Ligands

Ping-Yu Chen[a], Yan-Yu Kuo[a], Jun-Ting Hong[a]

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Saddle-shaped hemes have been identified in the structural compositions of numerous peroxidases.[1,2] The oxidation reactions of two five-coordinate, imidazole-ligated, saddle-shaped iron(III) porphyrins—[(OETPP)Fe^{III}(4-MeIm)]ClO_4 (**1**) and [(OETPP)Fe^{III}(Im)]ClO_4 (**2**)—were systematically examined using *tert*-butyl hydroperoxide (TBHP) at -40 °C. Unlike the crystal structure of **2**, the ligated imidazole aligns to minimize steric hindrance with the porphyrin shape while encountering maximum hindrance in the case of **1**. UV-Vis and EPR spectral data unveil a two-stage reaction for these species. Initially, TBHP coordinates to form the six-coordinate (4-MeIm)Fe^{III}(OOtBu) (**3**) and (Im)Fe^{III}(OOtBu) (**4**), respectively, revealing a significantly higher formation rate for **3** (2.19×10^{-3} s^{-1}) compared to **4** (9.32×10^{-4} s^{-1}). Subsequent reactions are spectroscopically characterized as O-O bond cleavages. Intriguingly, a comparable rate is noted for **3** (4.67×10^{-4} s^{-1}) in contrast to **4** (4.26×10^{-4} s^{-1}). The activation enthalpy ($\Delta H^{\ddagger}$) and activation entropy ($\Delta S^{\ddagger}$) for the O-O bond cleavage reactions were calculated were determined to be $\Delta H^{\ddagger}$ = 34.52(2) kJ mol^{-1}, $\Delta S^{\ddagger}$ = -151.34(2) J K^{-1} mol^{-1} for **3**, and $\Delta H^{\ddagger}$ = 26.97(4) kJ mol^{-1}, $\Delta S^{\ddagger}$ = -182.86(2) J K^{-1} mol^{-1} for **4**. A comparison with our previously reported O-O bond homolysis involving [(OETPP)Fe^{III}]ClO_4 and TBHP suggests that these O-O bond cleavage reactions entail heterolysis,[3] underscoring the electronic effects resulting from the combination of imidazole ligands with saddle-shaped porphyrins.

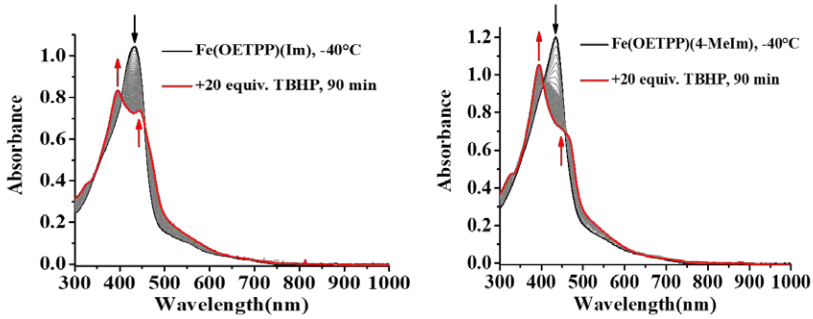

Figure 1. UV-Vis spectral transformations were observed for **1** (left) and **2** (right) upon oxidation with 20 equivalents of TBHP at -40℃.

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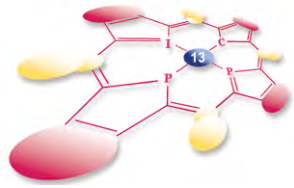

Design and Synthesis of Conjugated Polymers Based on π-Extended Porphyrin.

Jishnu Chevayil Vasudevan[a] and Hong Wang[a]

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Porphyrin-based conjugated polymers are interesting organic materials that combine the distinctive properties of both porphyrins and conjugated polymers. Porphyrins are aromatic macrocycles that can bind various metal ions at the center. This metal-binding ability and the unique structure give porphyrins unique electronic and optical properties, such as strong light absorption, efficient energy transfer, etc. Conjugated polymers are macromolecules with alternating single and double bonds along their backbone. The long conjugation length in conjugated polymers allows for efficient delocalization of electrons, leading to interesting electrical, optical, and mechanical properties. Most of the porphyrin functionalization is at the meso-position. In this study, we present the utilization of beta-functionalized porphyrins as the building block for polymer synthesis. A bottom-up approach is employed to construct the polymer and the properties of the polymers are compared with monomer, dimer, trimer, and pentamer. The optical and electronic properties of the porphyrin polymers will be investigated with UV-Vis absorption and fluorescence spectroscopies and will be presented in this poster.

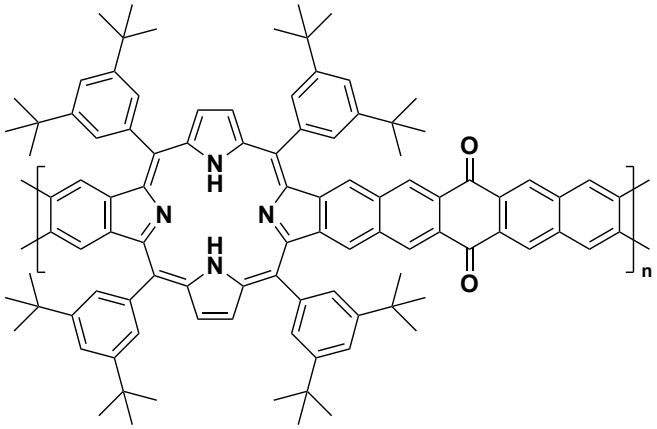

Figure 1. Proposed design for the polymer

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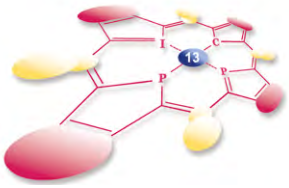

Retention of Intrinsic Photophysical Properties of Porphyrin Building Blocks in 3D Organic Frameworks through Magic Angle Alignment

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Construction of three-dimensional (3D) frameworks maintaining intrinsic photophysical properties of monomeric building blocks is difficult and challenging due to the existence of various molecular interactions, such as metal–organic and π–π interactions. A 3D hydrogen-bonded organic framework (**YSH-1$_{Zn}$**) with permanent porosity was constructed using a porphyrin having six carboxylic acid groups (**1$_{Zn}$**). Brunauer–Emmett–Teller surface area measurement indicated that **YSH-1$_{Zn}$** has a porous structure with a surface area of 392 m^2/g. Single-crystal X-ray diffraction analysis revealed that **1$_{Zn}$** creates a 5-fold interwoven 3D network structure adopting a monoclinic system with a space group of P_{21}/c. Each **1$_{Zn}$** within a single crystal exhibits parallel alignment with a slip-stack angle of 54.6°, in good agreement with the magic angle. Although the center-to-center distance of the nearest zinc atoms in **YSH-1$_{Zn}$** is only 5.181 Å, the UV/vis absorption and fluorescence emission of **YSH-1$_{Zn}$** are not different from those of **1$_{Zn}$**, indicating the absence of an interaction between excitons. Due to the magic angle alignment of **1$_{Zn}$**, the fluorescence lifetime, decay profiles, and quantum yield remained uniform even in the solid state,

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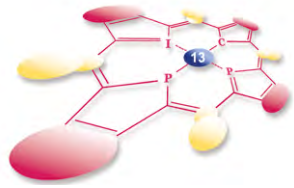

Porphyrin-based photosensitizers decorated with carbonic anhydrase inhibitors for targeted treatment of hypoxic tumours

Amina Merabti[a,b], Christophe Nguyen[b], Alessio Nocentini[c], Sébastien Richeter[a], Magali Gary-Bobo[b], Claudiu T. Supuran[c], Jean-Yves Winum[b] and Sébastien Clément[a]

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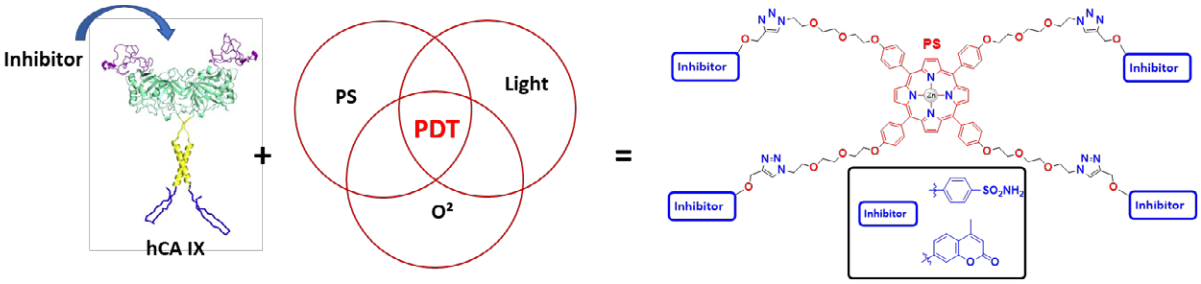
Photodynamic therapy (PDT) has garnered increasing attention as a promising avenue for cancer treatment, owing to its minimally invasive nature and low systemic toxicity.[1] However, the effectiveness of type II PDT is heavily influenced by oxygen levels within the tumor microenvironment.[2] This presents a significant challenge, as the hypoxic regions within solid tumors exhibit reduced oxygen pressure, thereby diminishing PDT efficiency.[2] Moreover, the existing hypoxia is exacerbated by oxygen consumption and vascular closure, triggering the activation of angiogenic factors and potentially fostering cancer recurrence and progression.[3]
To address this issue, we design porphyrin photosensitizers incorporating human carbonic anhydrase inhibitors (hCAi) of the sulfonamide and coumarin types to mitigate the effects of PDT-induced hypoxia by combining the benefits of hCA IX knockdown with PDT.[4] Specifically, porphyrin-containing coumarin moieties exhibit selective inhibition against tumor-associated hCA IX and hCA XII. The compound demonstrated the ability to accumulate on the cell membrane and inhibit the proliferation of pancreatic cancer cells (Capan-1) under normoxic conditions as well as effective photosensitizing capabilities, inducing cancer cell death upon light irradiation.



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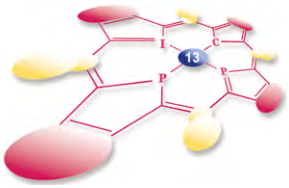

Solution Processable N-Type Silicon Phthalocyanines for OTFTs

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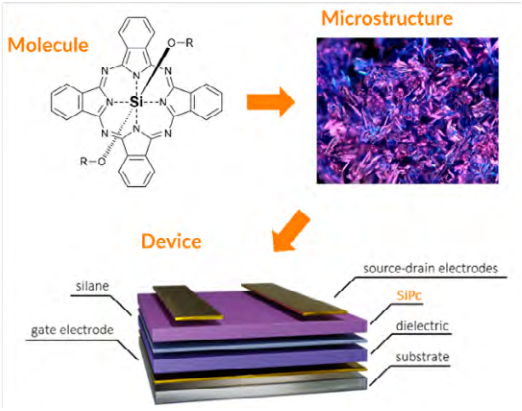
Despite significant advances in the field of organic electronic devices there remains a critical need for soluble, stable, and high performing n-type organic semiconductors that are compatible with the leading p-type materials. The favourable intermolecular stacking, crystallinity, chemical versatility, and compatibility with solution fabrication techniques, positions axially substituted metal phthalocyanines as promising materials for these applications. Silicon phthalocyanines ((OR)$_2$-SiPcs), are among the highest performing n-type materials in this family and remain relatively under explored. Understanding how molecular design and thin-film fabrication conditions impact the formation, microstructure, and morphology of (OR)$_2$-SiPc films, and the interplay with the electronic properties of organic thin-film transistors (OTFTs) is crucial to expanding their use as semiconductors.



(OR)$_2$-SiPc derivatives with alkyl chains of varying length, symmetry, and branching position were studied in OTFTs, establishing a relationship between molecule structure, film morphology and device performance.[1]The effect of surface energy and fluorination, using an asymmetric (OR)$_2$-SiPc consisting of one axially substituted fluorine and one trialkyl silane group, were investigated at the dielectric/semiconductor interface. Through low surface energy dielectric modifications, and the incorporation of fluorine interactions, films with large area crystalline domains were produced, yielding higher performing OTFTs with increased operating current and improved operating voltage.[2]

Fabrication method, parameters, and post-deposition processing play an important role in (OR)$_2$-SiPc thin-film formation and resultant OTFT performance. We found and explored the significant differences between solid state deposition, lab scale spin coating fabrication, and scalable solution deposition methods such as blade coating or printing. Additionally, key parameters such as deposition rate, time, solvent, temperature, and post fabrication processing were examined to control thin-film nucleation and obtain high performing devices.[1,3] These works demonstrate the effectiveness of axial substitution as a strategy to control crystal packing and the charge transport properties of (OR)$_2$-SiPcs, highlighting their potential as solution processable low-cost n-type semiconductors.

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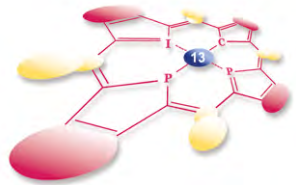

Exploring Molecular and Electronic Structure of Cofacial Porphyrin Prisms Formed by Coordination-Driven Self-Assembly

Matthew R. Crawley [a], **Daoyang Zhang** [a], **and Timothy R. Cook**[a]

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Over the last 50 years, cofacial porphyrin prisms have been the subject of numerous studies given their impressive and unique reactivities in the context of small molecule activation catalysis.[1-4] In more contemporary work from our group, we have used coordination-driven self-assembly as an enabling synthetic technique to rapidly populate a library of catalytically competent cofacial architectures.[5-9] This approach circumvents many of the drawbacks of traditional synthetic strategies used to form cofacial porphyrins structures, such as tedious multistep syntheses, and low overall yields. Our previous studies have focused on the synthesis and electrocatalytic oxygen reduction reactivity of these prisms. In this work, we develop a deeper understanding of prism molecular and electronic structure to rationalize their reactivity, guide future design, and address outstanding structural debates in the field.[10] Solution-state dynamics were investigated using variable temperature NMR (VT-NMR) and supported with density functional theory calculations. Electronic and structural metrics were informed on using EPR spectroscopy of Cu(II) and Co(II) metallated prisms. Finally, X-ray crystallography in tandem with 1D and 2D NMR techniques was used to address the cofacial prism versus monoporphyrin "bowtie" debate.

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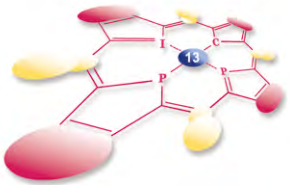

Exploring oxy phosphorus triazatetrabenzocorrole (POtbc) and its analogues as *p*-type semiconductors in organic thin film transistors

Mélanie Cyr[a], Halynne Lamontagne[b], Benoît Lessard[b], Jaclyn Brusso[a]

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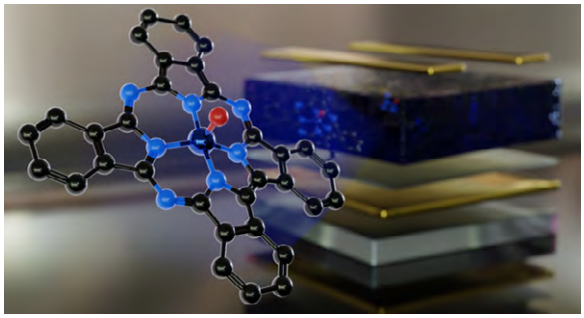
Metal and metalloid phthalocyanines (MPcs) have distinguished themselves substantially in organic thin film transistor (OTFT) applications due to their strong semiconducting abilities.[1] Among these MPcs, titanyl phthalocyanine (TiOPc) has been recorded as the best performing phthalocyanine semiconductor in *p*-type OTFTs to date.[2] This work looks upon the use of oxy phosphorus triazatetrabenzocorrole (POtbc), which holds a similar structural resemblance to TiOPc, and its performance as a *p*-type semiconductor in OTFTs. Triazatetrabenzocorrole (tbc) holds a similar framework as a phthalocyanine, minus one of the bridging nitrogen atoms within the conjugated macrocycle. Furthermore having a group 15 element at the centre of a Pc core helps reduce the molecule's lowest unoccupied molecular orbital (LUMO) level, thus narrowing the overall bandgap of the material to facilitate charge mobility.[3] POtbc can be readily synthesized in a 1-step synthesis using commercially available H_2Pc and PBr_3.[4] The synthesis of other POtbc derivatives was also explored by synthesizing its perfluorinated analogue (F_{16}POtbc) as well as adding *tert*-butyl units at the periphery (^{t}Bu$_4$POtbc), both of which can be obtained in 2-step pathway starting from the commercially available phthalonitrile analogues. All 3 materials were incorporated in bottom-gate top contact OTFT devices via physical vapour deposition. Different dielectric/semiconductor interface surface treatments were also tested to better influence the surface energy of the thin films. Preliminary results have shown octyltrichlorosilane to be the best surface treatment for the device fabrication, from which OTFTs fabricated with POtbc were able to obtain an average field effect mobility of 6.4×10^{-3} cm^2 V^{-1} s^{-1} and a threshold voltage of -21.9 V. Although this work is still ongoing, these preliminary result show great promise in developing phosphorus tbcs as a new class of materials for their application in OTFTs.



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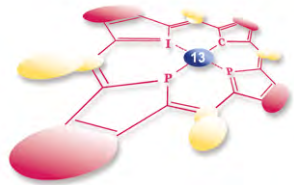
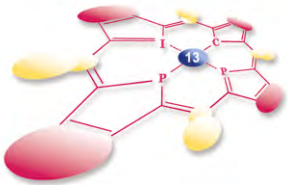


Charge-Transfer in Panchromatic Porphyrin-Tetracyanobuta-1,3-Diene-Donor Conjugates: Switching the Role of Porphyrin in the Charge Separation Process

Andrew Dawson, Bijesh Sekaran, Youngwoo Jang, Kusum MohanSingh, Rajneesh Misra, and Francis D'Souza

The University of North Texas, Denton, USA

Using a combination of cycloaddition-retroelectrocyclization reaction, free-base and zinc porphyrins (H_2P and ZnP) are decorated at their β-pyrrole positions with strong charge transfer complexes, viz., tetracyanobuta-1,3-diene (TCBD)-phenothiazine (**3** and **4**) or TCBD-aniline (**7** and **8**), novel class of push-pull systems. The physico-chemical properties of these compounds (MP-Donor and MP-TCBD-Donor) have been investigated using a range of electrochemical, spectroelectrochemical, DFT as well as steady-state and time-resolved spectroscopic techniques. Ground-state charge transfer interactions between the porphyrin and the electron-withdrawing TCBD directly attached to the porphyrin π-system extended the absorption features well into the near-infrared region. To visualize the photo-events, energy level diagrams with the help of free-energy calculations have been established. Switching the role of porphyrin from the initial electron acceptor to electron donor was possible to envision. Occurrence of photoinduced charge separation has been established by complementary transient absorption spectral studies followed by global and target data analyses. Better charge stabilization in H_2P derived over ZnP derived conjugates, and in phenothiazine derived over aniline derived conjugates has been possible to establish. These findings highlight the importance of the nature of porphyrins and second electron donor in governing the ground and excited state charge transfer events in closely positioned donor-acceptor conjugates.



Fundamental difference between simple arenes and PAHs found in *o*-PAH-connected porphyrins

Pradeep P. Desale, Min-Sung Ko and Dong-Gyu Cho*

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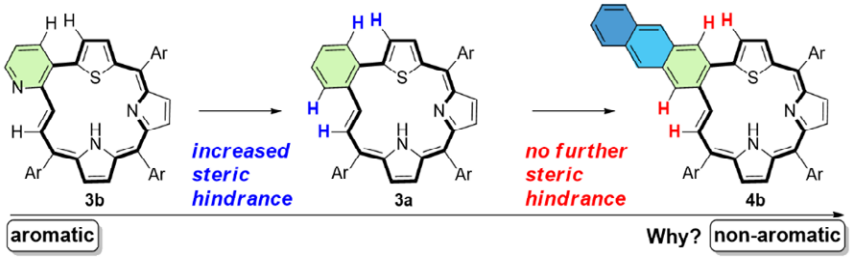
o-PAH-connected porphyrins (**4a** and **4b**) were synthesized as extended forms from aromatic *o*-benzene(pyridine)-connected porphyrin (**3a** (**3b**))[1], wherein naphthalene and anthracene motifs were employed for extension. Notably, the naphthalene and anthracene versions (**4a** and **4b**) were nearly non-aromatic. The ring current property of **4a** and **4b** should match aromatic **3a** due to minimal (or no) additional steric hindrance. Hence, the reduced aromaticity might stem from the distinct natures of simple arenes and PAHs. The significantly diminished aromaticity of **4a** and **4b** was confirmed by their ^{1}H NMR spectra and supported by the X-ray structure of **4a**, along with the weighted average NICS (0) values from conformers and tautomers at equilibrium. Differences arise from diverse FMOs of simple arenes and PAHs. As the size of PAHs increases, their FMOs become denser in the middle and less prominent at the edges. Consequently, the character of the ring current is dictated by the newly formed bonds at the edges of arenes. These effects were observed for the first time in this study. Furthermore, our findings applied to *meso*-arenoporphycene (**9**)[2] and predicted reduced aromaticity with PAHs replacing benzene.



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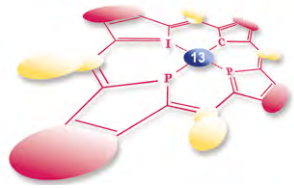

New corrole-based molecularly imprinted polymers for the degradation of chemical warfare agents

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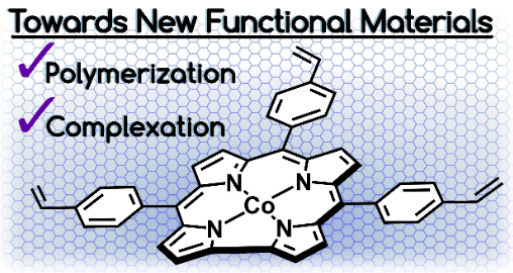
Chemical warfare agents (CWA) and pesticides are a major concern related to defense and public health issues. Among them, vesicants and nerve agents are considered the most harmful and dangerous compounds [1]. Poisoning is possible because large stocks of military-grade nerve agents and sulfur mustard still exist in many countries. Additionally, neurotoxic organophosphate (NOP) compounds are still used in agriculture and constitute one of the most widespread pesticides worldwide. Today, for the safety and health of the soldiers and the civil population, there is a crucial need to develop new effective, environmentally friendly, and cost-effective technologies for the decontamination of NOP and vesicants. Thus, the goals and objectives of the work are to develop innovative decontamination tools allowing the neutralization and detoxification of sulfur derivatives and NOPs, under mild conditions. For that purpose, we have developed a unique innovative biomimetic approach consisting of the design of enzymatic mimics, such as functional molecularly imprinted polymers (MIPs) equipped with a specific catalytic site [2]. Thus, an effective decontamination process of CWA could be achieved by aerobic oxidation. We have developed a synthetic route to introduce polymerizable arms on a corrole scaffold via a Suzuki-Miyaura cross-coupling reaction. Insertion of cobalt into the resulting tris(4-vinylphenyl) corrole yielded a complex with suitable coordination and polymerization capabilities. The physicochemical properties of this corrole will be presented, together with its ability to form a highly stable six-coordinate complex and a cross-linked polymer [3].



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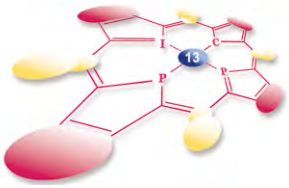

Azolium-Porphyrin Electrosynthesis

Fatima Akhssas, Rongning Lin, Michal Trojan, Ludivine Poyac, Thibault Ertel, Sophie Fournier, Emmanuel Lerayer, Hélène Cattey, Sébastien Richeter and Charles H. Devillers

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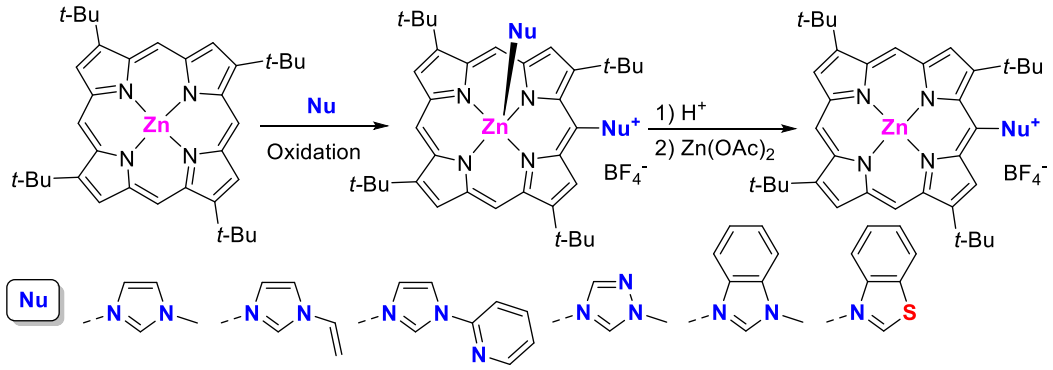
The functionalization of porphyrin is an important research field since this macrocycle is involved in numerous applications ranging from photovoltaic solar cells, and electro- and photocatalysis to photodynamic therapy. Despite the considerable efforts that have been devoted to this task for several decades, more efficient and (regio)selective functionalization of porphyrins is still in progress. Recently, the development and applications of imidazolium-porphyrins have motivated novel synthesis strategies that provide moderate to good yields of these cationic compounds [1]. Given the impressive resurgence of electrochemistry as a clean and sustainable way to transform and functionalize organic and organometallic derivatives [2], we wanted to explore the electrochemical synthesis route, as never done before for porphyrins. This alternative method will provide a new, selective, straightforward and metal-free pathway.

This work thus describes the electrochemical synthesis and characterization of original azolium-porphyrins starting with zinc(II) 2,7,12,17-tetra-*tert*-butylporphyrin (**Zn-1**) and the following nucleophiles: 1-methylbenzimidazole, 1-vinyl-1*H*-imidazole, 2-(1*H*-imidazol-1-yl)pyridine, 1-methyl-benzimidazole, 1-methyl-1*H*-1,2,4-triazole, and benzothiazole [3].



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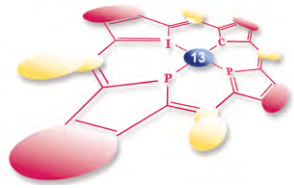

Pyridinyl-Based Modified Electrode as Nucleophile for the Oxidative Electrografting of Porphyrin

Fatima Akhssas[a], Anna Krystianiak[b], Olivier Heintz[b], Eric Lesniewska[b], Régis Parvaud[b], Rita Meunier-Prest[a], Charles H. Devillers[a]

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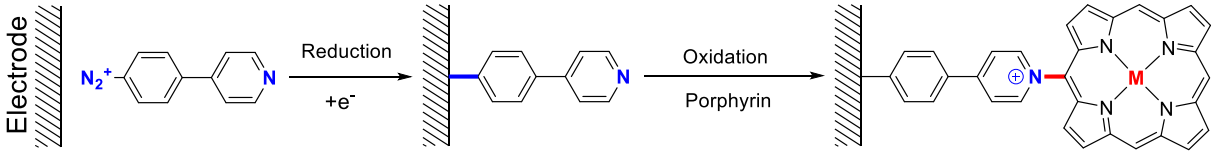
Immobilization of functional molecules on an electrode surface is a crucial step towards the development of applications. Among these molecules, porphyrins exhibit interesting physico-chemical properties. These molecules have been exploited for many applications in various research fields such as electrocatalysis [1], photoluminescent biosensors[2] nonlinear and optical limiting devices [3]. Several approaches have been developed to graft the porphyrin moiety by post-functionalization of the modified substrate. The coupling method can be performed *via* the formation of different chemical bonds: amide [4], ester [5], coordination [6], or using Huisgen cycloaddition reaction (click chemistry) [7].

We will show during this presentation that it is possible to immobilize a porphyrin *via* its oxidation on a pyridinyl-functionalized working electrode surface [8]. UV-vis. spectroscopy, cyclic voltammetry, XPS, SEM, AFM and TOF-sims analyses have been performed to confirm the chemical composition of the porphyrin material.



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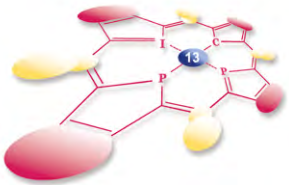

Synthesis and investigation of near-IR BODIPY-monoTKI and BODIPY-diTKI conjugates

Simran Dhingra[a], Prajesh Shrestha[b], Arpan Chowdhury[b], Zehua Zhou[b], Seetharam D. Jois[b], Maria da Graça H. Vicente[a]

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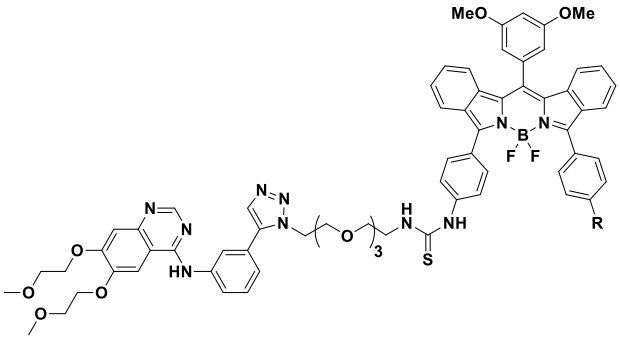
[b] *Department of Pathobiological Sciences, School of Veterinary Medicine, Louisiana State University, Baton Rouge, LA 70803, US*

BODIPYs display a highly tunable core structure and small modifications to the BODIPY core, using a variety of functionalization reactions or by total synthesis, enable the fine-tuning of their optical properties. Among their many applications, near-IR BODIPYs are promising fluorophores for labelling biomolecules, such as peptides and nucleic acids, as well as drug molecules that show specific binding to certain target receptors. Tyrosine kinase inhibitors (TKIs) are a class of small molecule inhibitors that specifically bind to the cytoplasmic intracellular domain of the human epidermal growth factor receptor (EGFR) [1, 2]. The synthesis of a near-IR BODIPY-di(NCS) and its conjugation to TKI erlotinib via a triethylene glycol linker is presented [3]. EGFR binding properties of the BODIPY-monoTKI and BODIPY-diTKI conjugates were investigated and compared. Our results show that these conjugates are promising imaging tools for the detection of EGFR-over-expression tumors.



BODIPY-monoTKI: R=NCS
BODIPY-diTKI: R= triethyleneglycol-Erlotinib

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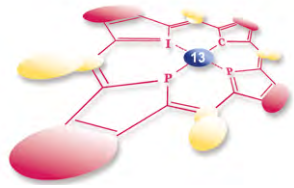

Hybrid materials based on silica nanohelices covered with porphyrins for volatile enantiomer detection

Ilaria Di Filippo[a], Zakaria Anfar[b], Reiko Oda[b], Manuela Stefanelli[a], Donato Monti[c], Gabriele Magna[a], Corrado Di Natale[d] and Roberto Paolesse[a]

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Chiral recognition [1] is an important task in many different fields, such as agrochemical, environmental, and health monitoring. Here, we applied the electronic nose (e-nose) concept to chiral recognition using hybrid chiral materials based on silica nanohelices [2] covalently functionalized with chiral porphyrins (D)/(L)-ZnP) and an achiral porphyrin (ZnpCTTP). FTIR, UV-Vis, and TEM characterization confirmed the grafting of porphyrins by amide linkage. Then, the Circular Dichroism (CD) technique revealed that the chiroptical features of these materials depend on helix handedness rather than on the molecular chirality of receptors. Subsequently, we deposited the suspensions of the materials on the Quartz Microbalance (QMB) surfaces to obtain an e-nose composed of 6 chiral sensors. The array was exposed to 5 pairs of pure enantiomers vapors at different concentrations (we measured 10 compounds at 6 different concentrations with 7 repetitions in a random order to obtain 420 samples). Linear Discriminant Analysis (LDA) was utilized to verify the classification performance of the array considering two different scenarios: an "achiral" task with 5 classes where the enantiomers belong to the same class and a chiral recognition task with 10 classes where each enantiomer is assigned to a separated group. Results show a generally good performance in recognizing both compounds and their enantiomers. The effortlessness of fabrication protocol and the ease of modifying the structure of porphyrin receptors open the way to quickly developing enantioselective e-noses with these materials.

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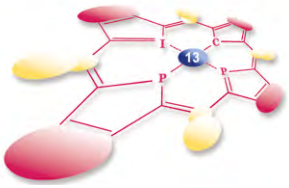

Chiral porphyrin aggregates for amino acid recognition

Ilaria Di Filippo [a], Manuela Stefanelli[a], Donato Monti[b], Gabriele Magna[a] and Roberto Paolesse[a]

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D-amino acids are essential metabolic biomarkers because their presence in the human body is related to neurological diseases, cancer, and kidney disorders [1]. In this context, the possibility to recognize and quantify different amino acids and their scalemic mixtures appears to be of fundamental importance. Porphyrins are very suitable building blocks to obtain chiral supramolecular aggregates. A protocol adopted by our group to assemble these macrocycles exploits the hydrophobic effect in a "good-bad solvent" environment. Chiral porphyrins (i.e., prolinated porphyrin enantiomers, (L)/(D)H_2P) are solubilized in ethanol (good solvent), and then a specific amount of a bad solvent (water) is added to induce the aggregation that occurs in a chiral fashion [2]. Here, we show our studies about the self-assembly process of (D)H_2P porphyrin in the presence of different amino acids (AAs) in water as co-solute (e.g., histidine, proline, phenylalanine, leucine, and tryptophan). The self-assembly process was studied from kinetic and thermodynamic points of view using spectroscopic techniques (e.g., UV-Vis and CD spectroscopies). Specifically, the data obtained have been processed using the well-known Pasternak's model, according to a "fractal type" exponential equation [3]. Remarkably, results show a different effect on the aggregation process related to both the type and the enantiomeric configuration of amino acids. (D)H_2P can recognize the different enantiomeric pairs, such as (L)/(D)-proline and (L)/(D)- tryptophan, as shown by the different kinetic constants found. The present contribution will illustrate the recent results obtained with these systems in depth as a proof of concept for preparing chiral sensing materials for recognizing different types of amino acids and their enantiomers.

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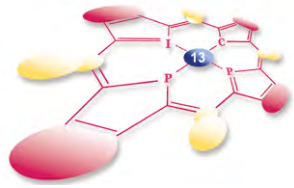

Template Assisted Formation of 32 and 34π Octaphyrins Embedded with Dithienopyrrole Cores: A New Scaffold to Unravel Proton Coupled Redox Switching and (Anti)Aromaticity

Aathira Edwin[a], Gayathri Krishnan[a], Ajay Jayaprakash[a], Sankeerthana Pathiyil Anilkumar[a] and Gokulnath Sabapathi*

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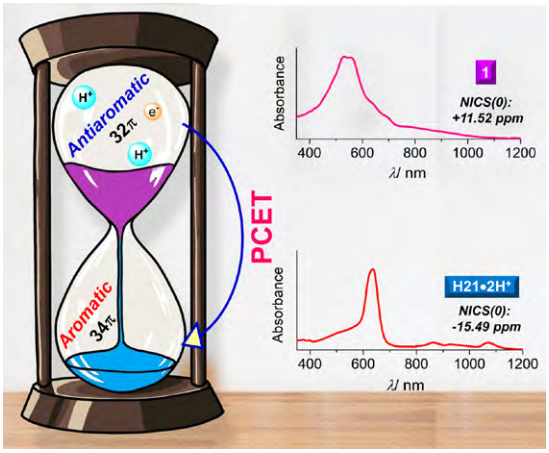

Octaphyrins are popular for their vast structural diversity and access to multiple electronic states, where the optoelectronic and redox properties are determined based on their tendency 'to twist or not to twist'.[1-2] Herein, we report two distinct octaphyrins obtained by the condensation of new dithieno[3,2-*b*:2',3'-*d*] pyrrole-based tetrapyrrane under two different acidic conditions. Fourfold *meso*-substituted octaphyrin was the major product when the reaction was performed in the presence of an aryl aldehyde using trifluoroacetic acid. On the other hand, sixfold *meso*-substituted octaphyrin was obtained when the precursor was condensed with pentafluorobenzaldehyde using *para*-toluenesulfonic acid. Such a template effect of aryl aldehydes in oxidative coupling reactions is realized for the first time in literature. Experimental and theoretical studies suggested that the oxidized form of fourfold *meso*-substituted octaphyrin is 32π antiaromatic and undergoes a facile proton-coupled electron transfer (PCET) to the protonated form of 34π aromatic congeners upon treatment with protic acids. Furthermore, small organic molecules such as alcohols and amines were also found to promote such chemical reduction. Single crystal X-ray structure revealed that the aromatic counterpart is highly planar and stabilized by several intermolecular H-bonding and F-F interactions, leading to a large 3D supramolecular arrangement and exhibiting colorimetric sensing for fluoride and hydroxide anions. However, the sixfold *meso*-substituted octaphyrin did not show (anti)aromatic features, PCET or anion sensing, but its intriguing absorption features associated with protonation could make it an ideal candidate for pH-dependent bioimaging.[3]

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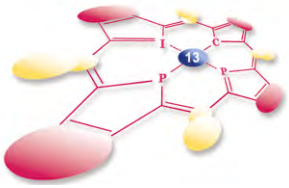

Non-biological ring openings of porphyrins

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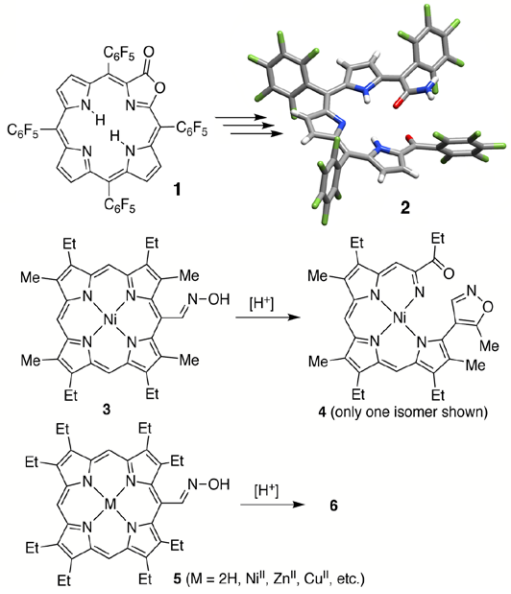
The biological pathway for the degradation of porphyrins and chlorins invariably involves ring cleavage reactions of the macrocycle that take place *between* the pyrrolic building blocks, forming bilins [1, 2]. Even subsequent degradation steps retain the pyrrolic building blocks. Likewise, the vast majority of synthetic porphyrin degradations take place between the pyrroles [3]. In the rare cases in which a pyrrole is ring-opened, macrocyclic products are isolated [4, 5].

In due course of our work on the oxidation of porphyrins to generate trilactones [6], we identified a unique tripyrrolic, open-chain tripyrrolic compound **2**, proposed to be derived from the degradation of porpholactone (**1**) [7]. The structure of this tripyrrin is unique among all previously reported biological and all but one non-biological biliverdin-like linear porphyrinoid degradation products. The lone exception is tripyrroyloxazole **4** derived from a pyrrole-opening reaction of etioporphyrin-5-formyloxime nickel **3** [8].



Having previously utilized porphyrin β-oximes in Beckmann-like ring expansion reactions [9, 10], we decided to reinvestigate and expand on the reactions of porphyrin *meso*-oximes. To simplify the approach, we are using octaethylporphyrin-5-formyloximes (free base and Ni(II), Zn(II), Cu(II), etc. complexes). We will report on the formation and stability of the oximes, and their Beckmann products.

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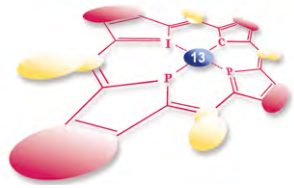

Crafting Functional Materials with Artificial Heme-Enzymes

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In the past few decades, there has been growing attention in the field of enzyme design and engineering. This interest is fueled by the capability of natural and artificial protein scaffolds to host a wide array of functions [1]. Indeed, the use of innovative tools and strategies enables customizing and enhancing enzyme activities for numerous applications. Within this context, Mimochromes (MCs) have risen to prominence as a notable class of artificial heme enzymes. MCs result from a process involving miniaturization and extensive redesign, drawing inspiration from the active sites of hemoglobin and horseradish peroxidase [2]. Due to their reduced but carefully designed peptide-based scaffold (~3 kDa), MCs effectively represent a bridge between metalloproteins and small-molecule complexes. This minimal design seamlessly integrates the remarkable catalytic prowess of natural enzymes with the versatile nature of synthetic catalysts. Among MC analogues, MC6*a stands out for its remarkable performance in modulating the reactivity of several metal ions in oxidative [3-5] and energy-related [6] catalytic processes. Our ongoing research is focused on immobilizing MCs on various surfaces to construct functional nanomaterials.

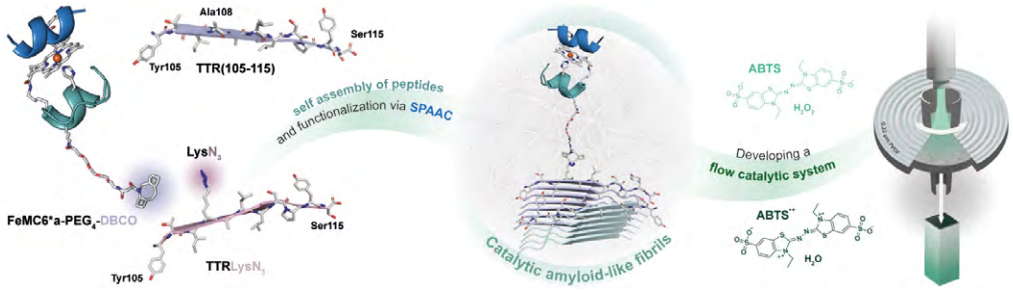

Figure 1: Schematic representation of the conjugation strategy and its application.

In particular, our research efforts have recently expanded toward the development of sustainable nanomaterials by integrating MCs into entirely peptide-based nanostructures. In this innovative approach, we have modified an amyloid-forming peptide sequence (TTR105-115) [7] to display an azide moiety (TTRLysN_3), suitable for the functionalization of the resulting fibrils. Specifically, FeMC6*a has been provided with a dibenzocyclooctyne tail and then covalently conjugated to fibrils, using strain-promoted azide–alkyne cycloaddition (SPAAC) as a click reaction **(Figure 1)**. Structural and catalytic investigations have demonstrated the significant potential of this strategy in producing catalytic amyloid materials, promising exciting advancements in the field of nanotechnology.

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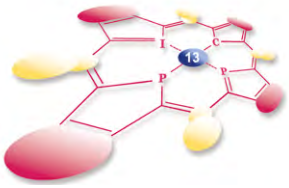

Free-base porphyrins containing nitrogen-donor moieties as photosensitizers against *Staphylococcus aureus*

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Antimicrobial therapy is increasingly utilized in modern medicine, contributing to extended lifespans within the population [1-2]. Nonetheless, the escalating and indiscriminate use of antibiotics, coupled with the rise in microbial resistance, presents a significant concern. Consequently, there is a pressing need to explore alternatives to mitigate the overreliance on these drugs [3].
Antimicrobial photodynamic therapy (aPDT) arises as an alternative to conventional antibiotics, with an emphasis on localized infections. This approach combines a photosensitizer (PS) with light of suitable wavelength and the presence of dioxygen ($^3O_2$), leading to the formation of reactive oxygen species (ROS), such as singlet oxygen ($^1O_2$), triggering mechanisms to promote cell death [4].
Tetrapyrrolic macrocycles, including porphyrins, have aroused significant interest in the scientific community owing to their distinct characteristics, rendering them one of the most extensively researched families of compounds. Their suitability for aPDT is underscored by several specific properties. These include absorption features within the visible region of the electromagnetic spectrum, capability to generate ROS, minimal cytotoxicity in the absence of light, stability, and compatibility with biological systems [3].
In this context, the main objective of this study was to synthesize and evaluate the photodynamic efficiency of porphyrins with C-N linked donor substituents at *meso* positions after being incorporated into polyvinylpyrrolidone (PVP). The synthetic approaches leading to the new formulations, their characterization and their photosensitizer efficacy against *Staphylococcus aureus* will be presented and discussed. Porphyrin incorporation into PVP allowed us to expand the study of porphyrins that are usually not considered in this kind of experiment due to their low solubility in polar solvents.

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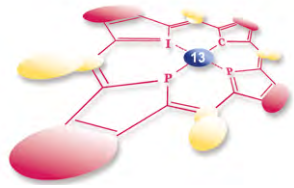

Perhalogenated TPyzPzs and Pcs as perspective compounds in various applications

Daniil N. Finogenov[a,c], Maxim A. Faraonov[b], Alina S. Kopylova[a], John Mack[c], Yurij A. Zhabanov[a], Pavel A. Stuzhin[a]

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Tetrapyrrolic macroheterocycles such as phthalocyanines (Pcs) and analogues are widely studied as perspective materials for organic electronics. Among modified Pcs their heterocyclic analogues containing electron-deficient heterocycle instead of benzene rings are especially interesting as acceptor materials with n-type conductivity. Tetrapyrazinoporphyrazines (TPyzPA) attract growing attention and their application potentialities in different fields (optical information recording, electrophotographic photoreceptors and photoconductors, organic transistors, etc) have been illustrated [1]. Peripheral halogenation can be used as a possible way to increase acceptor properties of the phthalocyanine-type macrocycle and in the case of TPyzPzs leads also to the reduction of the HOMO-LUMO gap. In this work, we used prepared complexes of perchlorinated TPyzPz with various transition metals and compared their spectral and redox properties with the corresponding complexes of peripherally halogenated and perfluorinated phthalocyanines to reveal their potential in different applications such as non-linear optics, molecular magnets, organic electronics, etc.

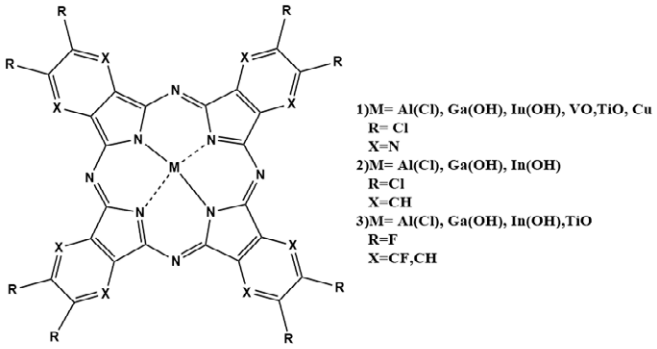

Figure 1. Macroheterocycles are studied in this work.

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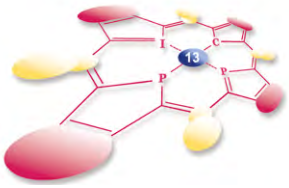

Octacarboxy TPyzPzM as perspective building blocks for organic frameworks

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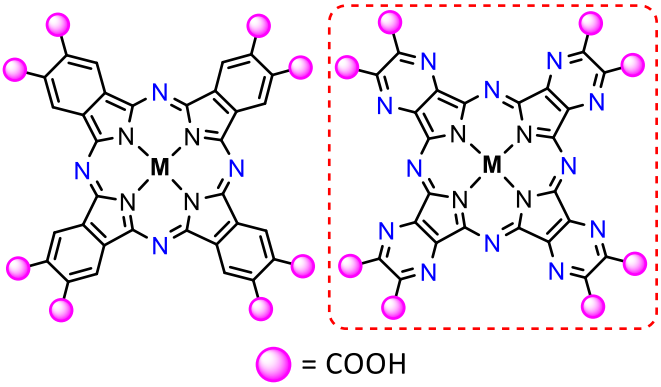
Phthalocyanines (Pcs) and their azaanalogues containing fused pyrazine rings instead of benzene fragments (tetrapyrazinoporphyrazines, TPyzPzs) are widely studied due to the unique spectral, photophysical and coordination properties determining their application in different fields – not only as dyes but also, as fluorophores and photosensitizers in medicine, semiconducting materials for organic electronics, redox catalysts etc. They are used as key building blocks for the design of functional materials and molecular devices [1]. The introduction of peripheral carboxyl groups endows Pc-type macrocycles with solubility in water and octacarboxy substituted phthalocyanines were explored as photosensitizers, (photo)catalysts, and electrode materials for lithium-ion batteries. Phthalocyanine with peripheral carboxy groups was also successfully used as building blocks for the design of nanomaterials and organic frameworks (COF, MOF) [2, 3]. Substitution of benzene rings in Pcs by electron-deficient pyrazine fragments in TPyzPzs increases the acceptor properties of the macrocycle and often enhances its photophysical and catalytic properties [1]. Carboxy-substituted TPyzPzs were briefly reported as potential photosensitizers [4, 5], however, organic frameworks based on TPyzPz are unknown. In this report we discuss the synthesis of octacarboxy TPyzPz(M or H_2), their identification of spectral-luminescence properties and application in the design of organic frameworks.



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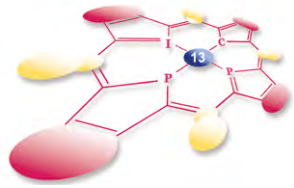

Metallo-porphyrin/amino acid conjugates for *Proton Coupled Electron Transfer*

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Proton Coupled Electron Transfer (PCET) is a crucial phenomenon in various biological processes, such as oxygen uptake and transport, water oxidation in Photosystem II (PSII) and DNA synthesis and/or repair.[1] Over the last decades, there has been a growing interest in developing artificial systems that try to mimic natural ones.[2] The distinctive electronic, optical and redox properties of Sn^{IV}-porphyrins make them intriguing as photoactive units.[3] On these premises, we developed a family of Sn^{IV}-$(aa)_2$porphyrins conjugates, with aa = *L*-tyrosine or *L*-tryptophan, that were easily assembled by axial ligation of the amino acid carboxylate moiety to the porphyrin metal centre: for two of such conjugates the formation of a radical pair state *via* PCET, by visible light excitation and in the presence of a base, was observed (Figure, left).[4] Encouraged by these promising results, we altered the relative position of the photoactive units, for instance by conjugating the amino acid residues at the porphyrin macrocycle periphery (Figure, right). Preparation, full characterization and preliminary photophysical studies of these new metallo-porphyrin/amino acid derivatives will be presented, also in comparison with the previously reported systems.

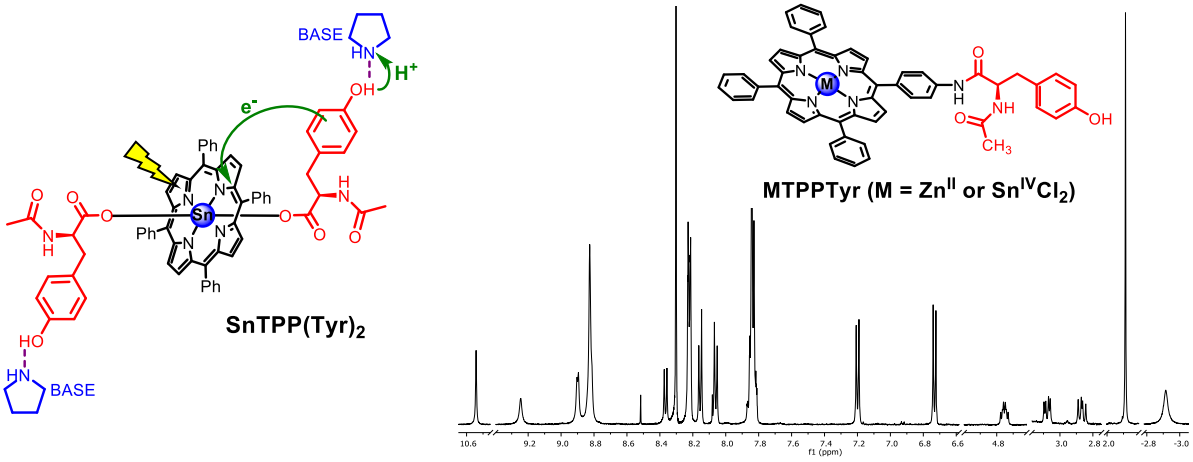

Figure. Left: Schematic representation of $SnTPP(Tyr)_2$ and photoinduced PCET. Right: Schematic representation of MTPPTyr.

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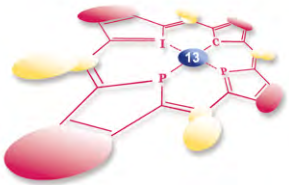

Synthesis of Cyclic Pyrrolopyrrole aza-BODIPY and its Circularly Polarized Luminescence

Shuhei Fukami and Soji Shimizu

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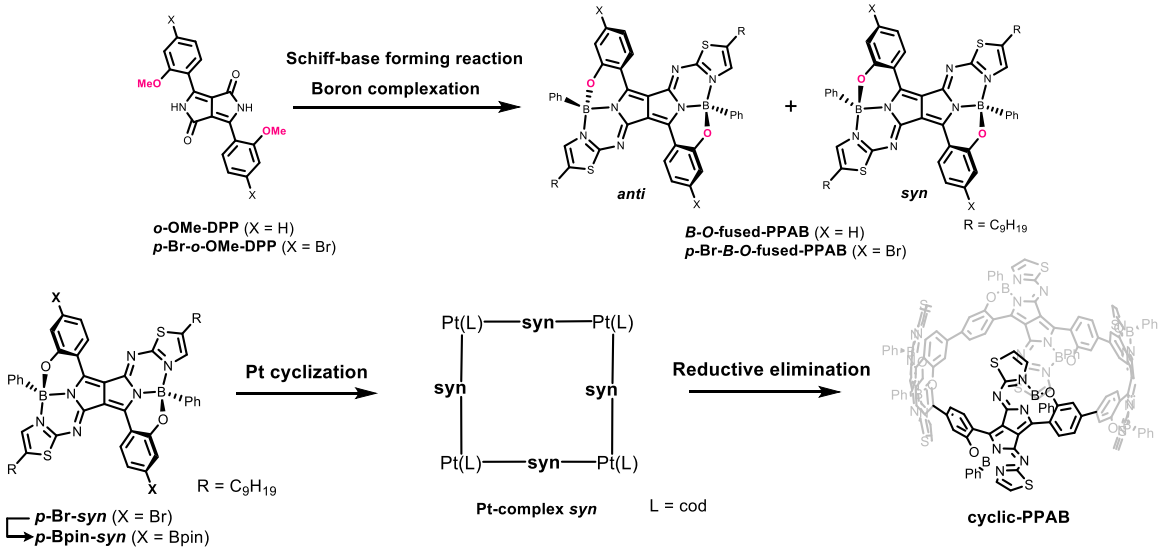
Circularly polarized luminescence (CPL) is a phenomenon, in which chiral molecules emit right-handed or left-handed circular polarized light. CPL materials can be broadly categorized into lanthanide complexes and organic luminescent molecules. Among them, lanthanide complexes are known to exhibit greater CPL properties. However, since lanthanide metals are rare-earth elements, there is a demand to create organic CPL materials with high CPL anisotropy toward practical application in various fields, such as organic electronics.

In this study, to create organic CPL materials and maximize CPL anisotropy, a cyclic tetramer structure (**cyclic-PPAB**) of pyrrolopyrrole aza-BODIPY (PPAB), which has a dimeric aza-BODIPY structure with a diketopyrrolopyrrole unit and exhibits intense absorption and emission in the visible and near-infrared regions, was designed and synthesized [1]. As a precursor of **cyclic-PPAB**, ***p*-bromo-*B*-*O*-fused-PPAB** was synthesized from diketopyrrolopyrrole with *o*-anisyl substituents (***p*-Br-*o*-OMe-DPP**), and its *anti* and *syn*-type isomers were separated. Due to the chiral structure, the chiroptical properties of the *syn*-type isomer were investigated. Cyclization reaction of ***B*-*O*-fused-PPAB** by platinum coordination and reductive elimination of the platinum ions to synthesize the target tetramer was attempted.

In this poster presentation, the synthesis of ***p*-Br-*o*-OMe-DPP**, ***p*-bromo-*B*-*O*-fused-PPAB**, and **cyclic-PPAB** will be reported.



o-OMe-DPP (X = H)
p-Br-*o*-OMe-DPP (X = Br)

B-O-fused-PPAB (X = H)
p-Br-*B-O*-fused-PPAB (X = Br)

p-Br-*syn* (X = Br)
p-Bpin-*syn* (X = Bpin)

Pt-complex *syn*

cyclic-PPAB

Scheme. Synthesis of the precursors and **cyclic-PPAB.**

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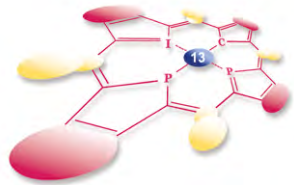

Search for photostable porphycenes

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When designing materials for applications that involve light-mediated processes, e.g., photodynamic therapy (PDT), a crucial factor is photostability. Porphyrinoids are a class of compounds that holds great promise for PDT Among them, porphycene is particularly attractive, due to strong absorption in the red region. This molecule, the first synthetized isomer of porphyrin (Vogel 1986), is a subject of growing biomedical interest in PDT of cancer,[1] bacteria photoinactivation, and fluorescence microscopy due to its spectral and photophysical. Our recent studies of porphycenes substituted with electron-donating or withdrawing moieties [2, 3] indicate that photostabilization can strongly vary depending on the substituent. For example, photodegradation quantum yield is about thousand fold larger in 9-aminoporphycene than in 9-nitroporphycene.
Here, we report the synthesis and comparison of photophysical properties of amino-, nitro- and newly obtained cyanoporphycenes. The goal is to find out whether cyanoporphycenes are better candidates for PDT and related areas than nitroporphycenes.

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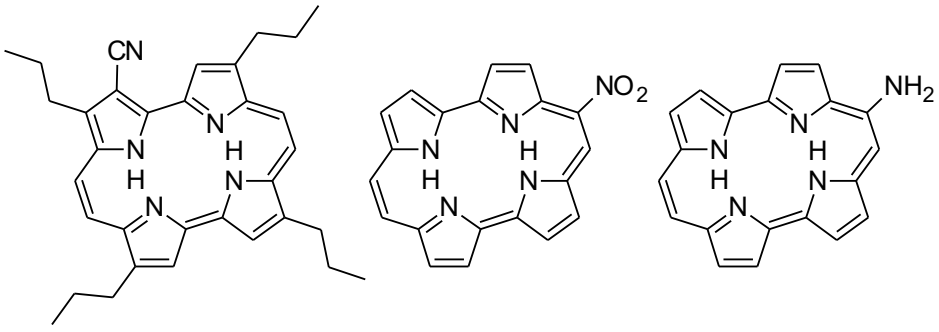

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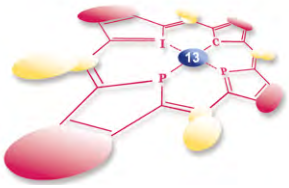

Trans-5,10,15,20-tetra(pentafluorophenyl)diazuliporphyrin – synthesis and characteristics

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The incorporation of azulene into the porphyrinoid framework is of interest due to the unusual electronic properties of this bicyclic system. Thus, azuliporphyrin [1-2] and its heteroanalogues [3-4], which exhibit borderline macrocyclic aromaticity and unconventional reactivity pathways, were synthesized. In addition, simple building blocks were used to construct cis- or trans-dicarbaporphyrins. A first example, β-substituted cis-diazuliporphyrin, was obtained in a one-pot synthesis, marking the first case of a mesoionic porphyrinoid [5]. In contrast, trans-diazuliporphyrinoids were prepared in a two-step procedure. Condensation led to the formation of diazuliporphyrinogen, which is non-aromatic and more flexible than the target porphyrin. Then, oxidation with controlled amounts of DDQ gave three species that form a peculiar multielectron redox system. Such reactivity was observed for dithia- [6], dioxa- [7], diselena- and ditelluraderivatives [8]. This study complements the trans-diazuliporphyrin family with the absent macrocycle composed of two azulene and two pyrrole rings. The precursors of both cis- and trans-diazuliporphyrin were synthesized through Lindsey-type condensation. Oxidation of the obtained carbaporphyrinogens produced the corresponding carbaporphyrins, most importantly, a neutral and dicationic form of trans-5,10,15,20-tetra(pentafluorophenyl)diazuliporphyrin, in which four hydrogen atoms are present in the core, making it a potential tetraanionic ligand. The resulting products were characterised by ^{1}H and ^{13}C NMR, UV-Vis, CV spectroscopic techniques and mass spectrometry.

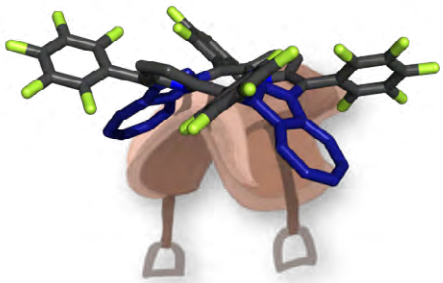

Figure 1. Saddle conformation of trans-5,10,15,20-tetra(pentafluorophenyl)diazuliporphyrin.

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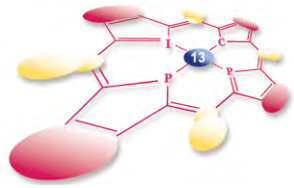

Structural Insights into Inhibitor-Protein Interactions in Tryptophan Dioxygenase

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Human tryptophan 2,3-dioxygenase (hTDO) and human indoleamine 2,3-dioxygenase 1 (hIDO1) are heme *b*-dependent enzymes that catalyze the oxidation of L-tryptophan (Trp) into N-formyl-L-kynurenine by dioxygen. This reaction is the first and rate-limiting step of the Kynurenine pathway, the dominant route of tryptophan catabolism.[1] Various cancer cells upregulate hTDO and/or hIDO1 expression which has been linked to immune evasion. Both the depletion of Trp and the accumulation of downstream catabolites promote an immunosuppressive environment in cancers allowing for tumor proliferation.[2] Therefore, both hTDO and hIDO1 are important cancer immunotherapeutic drug targets. A large group of hIDO1 inhibitors have been developed to date and more than 70 structures of hIDO1 complexed with a wide spectrum of inhibitors are available in the Protein Data Bank. In contrast, only a few classes of hTDO inhibitors have been reported and only three structures of hTDO in complex with two different inhibitors are available in the literature.[3] Consequently, there is a substantial knowledge gap of protein-inhibitor interactions for hTDO that has hampered the progress of drug development. Here we report several crystal structures of hTDO in complex with several types of inhibitors with diverse pharmacophores. Our structural data along with corroborating solution experiments provide a comprehensive assessment of inhibitor binding modes in hTDO, thereby offering new insights into the structure-based design of hTDO-selective inhibitors.

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POSTERS

Pyridine functionalized aza-BODIPYs for use in light-harvesting applications

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With the intent to further develop new light-harvesting systems; novel electron-deficient aza-BODIPYs were synthesized and functionalized with different nitrogen-containing heterocycles. These are being developed with the intent to be used as a non-fullerene acceptor in light-harvesting systems. These aza-BODIPYs were functionalized at the two and six positions of the aza-BODIPY core as well as the para positions along the four phenyl rings with molecules containing pyridine rings. These were synthesized using a variety of techniques including Suzuki coupling, nucleophilic substitution, and esterification. The molecules were then characterized by UV-Vis, fluorescence, and NMR spectroscopy methods, as well as mass spectrometry. Their redox and electronic properties were probed by chemical and electrochemical methods. New chromophores were coordinated to several donor zinc porphyrins and phthalocyanines. Density Functional (DFT) and time-dependent DFT (TDDFT) methods were used to elucidate their electronic structure and applicability towards non-fullerene acceptors for light-harvesting applications.

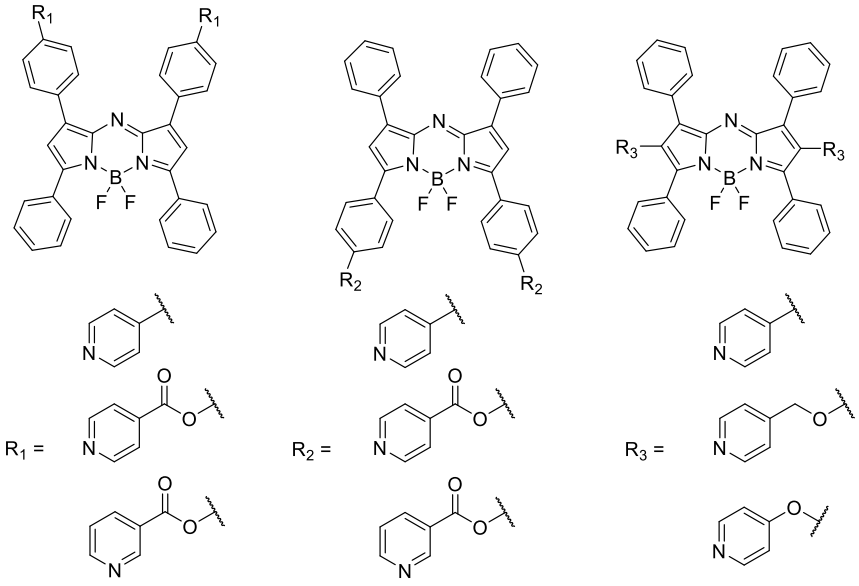

Fig. 1. Representative examples of functionalized aza-BODIPYs

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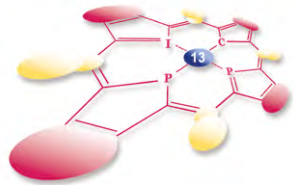

Grafting cobalt corroles to PCN-222 Metal-Organic Framework for the Detection of Carbon Monoxide

Claude P. Gros[a], Margerie Loze[a], Stéphane Brandès[a], Virginie Blondeau-Patissier[b], Nicolas Desbois[a], Laurie André[a]

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Carbon monoxide (CO) is well-known as a life-threatening gas both in households and in industrial environments. Indeed, CO detection is imperative before harmful levels of concentration are reached, leading to a wide range of symptoms (e.g. nausea, coma, …) and potentially causing death. Corroles are molecules derivatives of the porphyrin that present new properties when metalated.[1] In particular, cobalt corroles have demonstrated a highly selective behavior for the chemisorption of CO on the cobalt site. However, a stable and porous structure could improve the accessibility to the active sites and enhance the CO adsorption overall capacity.[2] Following this work, we have developed new materials based on the grafting of cobalt corroles on the cluster vacancies of PCN-222, a humidity-stable porphyrin-based Zr-MOF. The synthesis and grafting of four different cobalt corroles are presented, followed by their grafting inside PCN-222 and their resulting performances for CO detection. The materials were analyzed using XRD, SEM images, ^{1}H NMR, BET analysis, and CO sorption measurements.

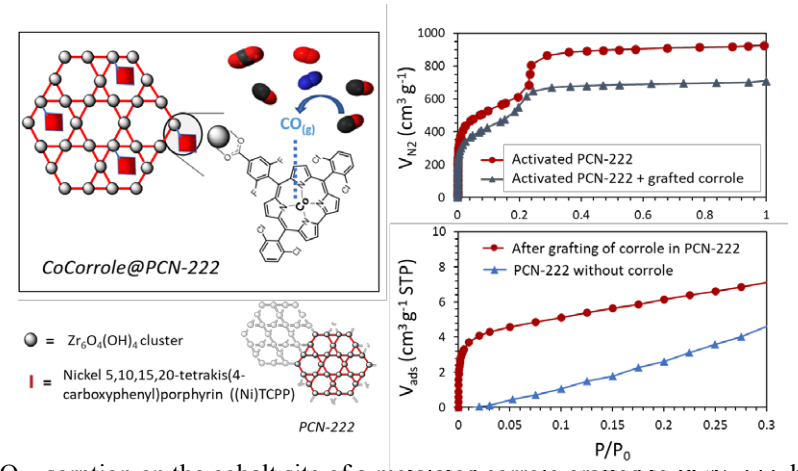

Figure 1. a) $CO_{(g)}$ sorption on the cobalt site of a metalated corrole grafted to PCN-222, b) BET adsorption isotherm of activated PCN-222 with and without CoCorrole grafted, c) CO(g) sorption measurement in activated PCN-222 before and after the grafting of CoCorrole.

Acknowledgments: This work was supported by the CNRS (UMR UB-CNRS 6302, the *Université Bourgogne Franche-Comté (UBFC)*, and the *Conseil Régional de Bourgogne* (ICE PhD thesis). The French Research Agency (ANR) is acknowledged for financial support (ANR-22-CE42-0016-02).

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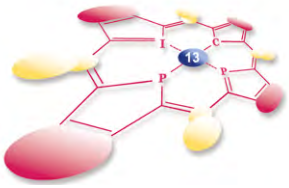

SubPcs as photoactive compounds for photoswitchable molecular wires

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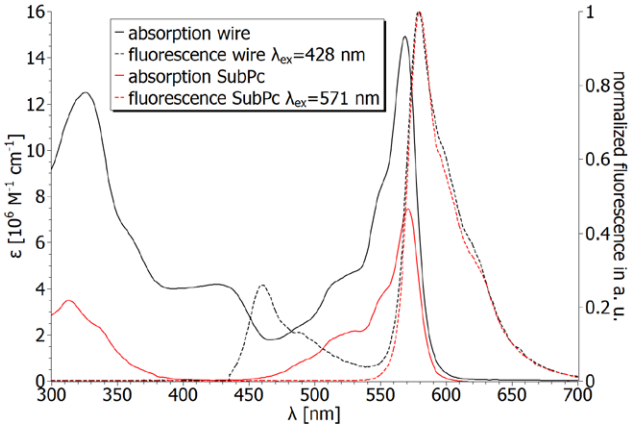
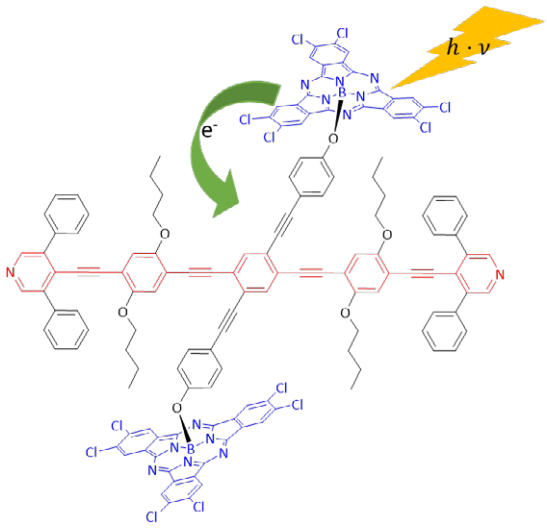
Molecular electronics is a diverse field of research aimed at replacing parts of the traditional electronics architecture with synthetic units.[1] Molecular wires are distinct organic molecules that have appreciable electric conductivity and can therefore serve as elementary building blocks for nanoscale devices.[2] In general, conductivity is achieved by applying a potential bias along a conjugated π-system. [3]





The aim of our current work is the synthesis and characterization of photoswitchable molecular wires of various lengths and with varying numbers of photoactive compounds. Pyridyl anchor groups are used for the connection to common electrode materials. The backbone of our wires consists of phenylene ethynyl building blocks which can be readily varied in length and to which the subphthalocyanines (SubPc) are connected to achieve a light-induced modulation of the electron density. We selected SubPc as the photoactive components because they are stable under irradiation with light and simultaneously serve as electron donors [4]. We will report here the synthesis and a preliminary photophysical characterization of several examples of these photoswitchable molecular wires.

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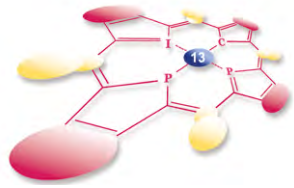

Synthesis and Characterization of a Novel Cationic Porphyrin *via* Click Chemistry

Jason Guzman and James Hanson

[a]*Seton Hall University. USA*

The preparation of cationic porphyrins is an area of interest for both biochemical studies as well as bio-sensing applications. These molecules are particularly suited to binding to G quadruplex DNA which are thought to play widespread biological roles. Using click chemistry, we have prepared a novel meso-substituted tetra cationic porphyrin *via* a copper-catalyzed azide-alkyne cycloaddition (AAC). Click chemistry has become a powerful tool for the design and synthesis of a wide range of compounds under mild conditions. This work will present the click chemistry preparation and spectroscopic characterization of a new meso-substituted tetra cationic porphyrin namely, meso-5,10,15,20-tetra-(4-(3-1H-1,2,3-triazol-1-yl)-N, N, N, trimethylpropan-1-aminium) phenyl porphine tetra-bromide.

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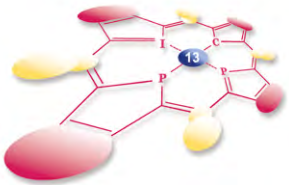

Synthesis of near-IR *meso(8)*-pyridyl-BODIPYs and their investigation as photosensitizers for PDT

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BODIPYs that absorb within the phototherapeutic window (650-800 nm) of the electromagnetic spectrum have promising applications as photosensitizers for photodynamic therapy (PDT) and as biological imaging agents since near-IR light penetrates deeper into human tissues [1]. We have recently developed synthetic routes to 1,3,5,7-tetramethyl-8-(2, 3 and 4-pyridyl)-BODIPYs and their pyridinium derivatives [2]. The synthesis of near-IR meso(8)-pyridyl-BODIPYs using Knoevenagel reactions will be presented. We will discuss the photophysical and *in vitro* biological properties of the new series of near-IR meso(8)-pyridyl-BODIPYs.

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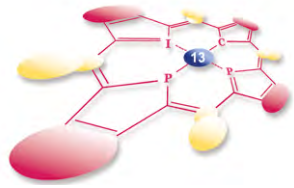

Synthesizing and The Antimicrobial Photodynamic Inactivation of Phthalocyanine-Chitosan Conjugates

Sercan Teke[a], Gizem Gümüşgöz Çelik[a], Duygu Aydın Tekdaş[b], Çiğdem Yılmaz Çolak[b], Devrim Atilla[a], Ayşe Gül Gürek[a]

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Antimicrobial photodynamic inactivation (aPDI) is recognized as a powerful therapeutic approach to reduce the incidence of clinical infections, inflammations, and even lethality caused by antibiotic-resistant bacteria [1]. Zn(II) phthalocyanine derivatives are effective photosensitizers (PSs) with low dark toxicity, strong absorption at far-red wavelength, long triplet lifetime, and high singlet oxygen quantum yield generation [2,3].

In this study, cationic water-soluble AB_3 type Zn(II) phthalocyanine derivatives having carboxylic acid functional groups that may be effective in aPDI have been synthesized. Then to increase their efficiency and to obtain a gel-like coating, they interacted with chitosan which is effective as an antimicrobial both by covalent bond and physical interactions. aPDT activities of these compounds have been determined by in vitro cell studies on the microorganisms.

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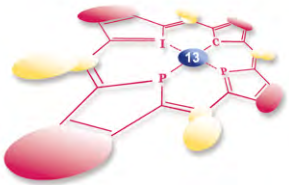

Intramolecular Charge Transfer Induced High Energy Triplet Emission in Hypervalent Phosphorus(V) and Antimony(V) Porphyrins Black Dyes.

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Triphenylamine (TPA), and TPA-based porphyrins have been synthesized to study the charge transfer character as a function of the oxidation state. The central atoms, elements from the 3rd period: Mg(II), Al(III), Si(IV), and P(V), were the source of varying oxidation states. For comparison purposes, Sb(V) was also chosen. The porphyrins have been characterized using UV-VIS & fluorescence spectroscopy and cyclic voltammetry. Among the series, P(V) and Sb(V) manifested strong intra-molecular charge transfer from the electron-rich TPA to the electron-poor porphyrin moiety. Such charge transfer character is ideal for designing artificial photosynthetic systems, dye-sensitized solar cells, and photo-electrochemical cells for the production of solar fuels as they provide directionality to the electron flow.

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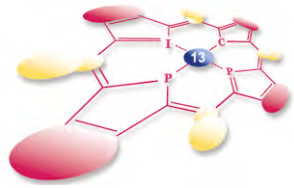

Design and Synthesis of Polyimide Covalent Organic Frameworks based on the β-Functionalized Porphyrin

Ting Han[a], **and Hong Wang**[a]

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Since the seminal work of Yaghi and co-workers made the first COFs in 2005, the rapid development in this research area has attracted intensive interest from researchers with diverse expertise.

There is a growing interest in tetrapyrrolic macrocycle-based COFs in which naturally occurring porphyrin and the synthetic analogues of porphyrin are employed as building blocks. Due to the intriguing properties of porphyrin units, the resulting COFs have found applications in different areas such as gas absorption, energy storage, optoelectronics, and catalysis. All the porphyrin-based COFs have utilized meso-functionalized porphyrins. In contrast, β-functionalized porphyrins of the type shown below have remained unknown.

In this project, the synthesis and characterization of the first examples of β-functionalized porphyrin polyimide covalent organic frameworks will be presented.

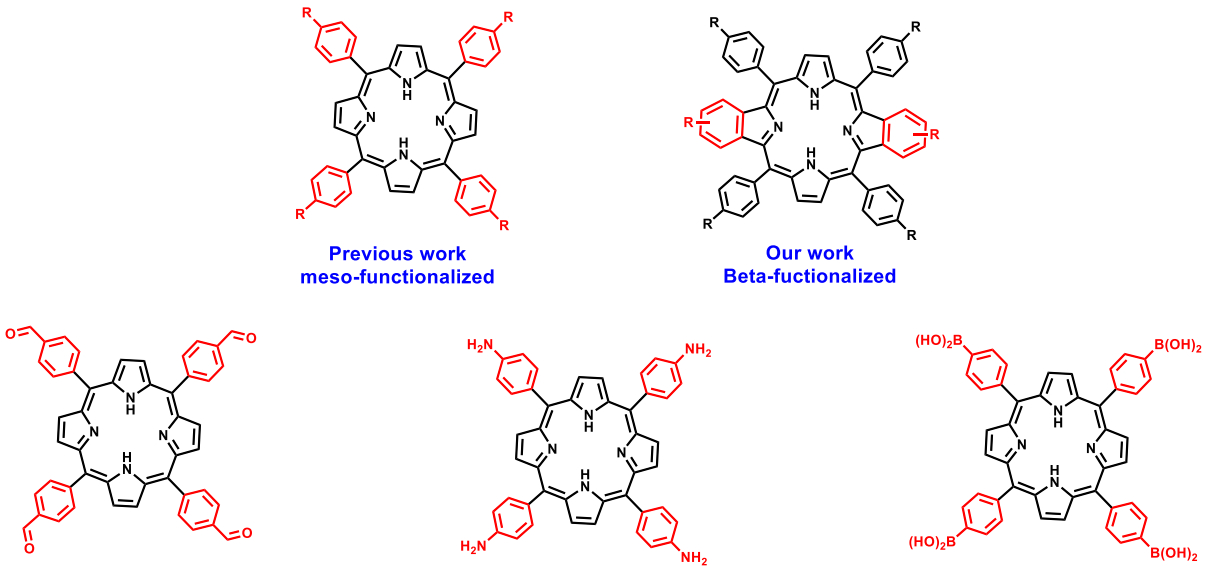

Figure 1. Selected examples of meso-functionalized porphyrins and β,β'-π-Extended porphyrins

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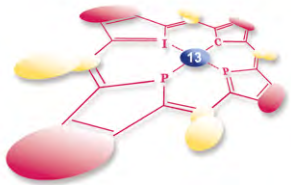

Porphyrin Stabilised G-Quadruplexes

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DNA-porphyrin Interactions have been extensively investigated over the last few decades, especially in the case of the stabilisation of G-quadruplex (G4) formation.[1] It is known that DNA sequences rich in guanine $(GGGX)_4$ can form both inter- and intramolecular structures composed of stacking G-quartets surrounding monovalent cations such as potassium.[2] G4 structures play a crucial role in the maintenance of genomic integrity by protecting the terminal DNA of chromosomes (telomeric regions) from repair enzymes, especially telomerase.[3]
Telomerase is a ribonucleoprotein enzyme that can add short telomeric DNA strands onto the 3' terminal overhang of chromosomes, which is normally shortened during mitosis. The reduction in overhang length is essential in determining how many times a cell can divide, eventually causing cell death.[4] Telomerase counteracts strand shortening and therefore stops cells from dying. Its expression is suppressed in most somatic cells, but telomerase presence is detected in 85% of cancers.[5]
Here, the synthesis of a novel G4-forming DNA sequence based on the human telomeric repeat (GGGTTA) where porphyrins are covalently attached to thymidine at the 7 and 13 positions is presented. It is shown by thermal denaturing experiments that the addition of porphyrins to the sequence greatly stabilises the G4 formation. We will present further results regarding stability with different cations, structure analysis *via* molecular dynamic simulations, and biological activity using telomerase assays.

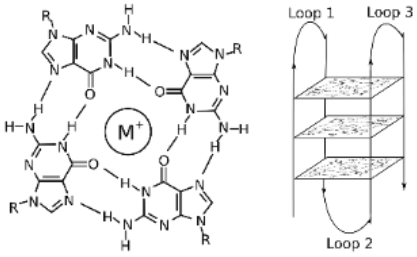

Fig. 1: The structure of a G-tetrad (left) and an intramolecular G4 complex (right) [6]

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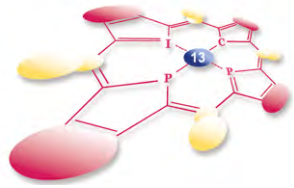

Green Light for Corrole and Porphyrin Dimers

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It has been reported that proper tuning of the photophysical properties of corrole complexes allows the design of photoredox catalysts that can convert bromide to bromine.[1] These molecular photocatalysts are non-toxic, active at low concentrations, and useful for the bromination of organic molecules by using HBr rather than Br_2.[2] The motivation of the current research was to uncover the advantages of using bi-molecular dimeric corroles and porphyrins (selected examples shown in Figure 1) rather than simple monomeric/monometallic derivatives [3]. The main outcome of this ongoing project is that the former class of complexes are good photocatalysts for reactions carried out by using green light.

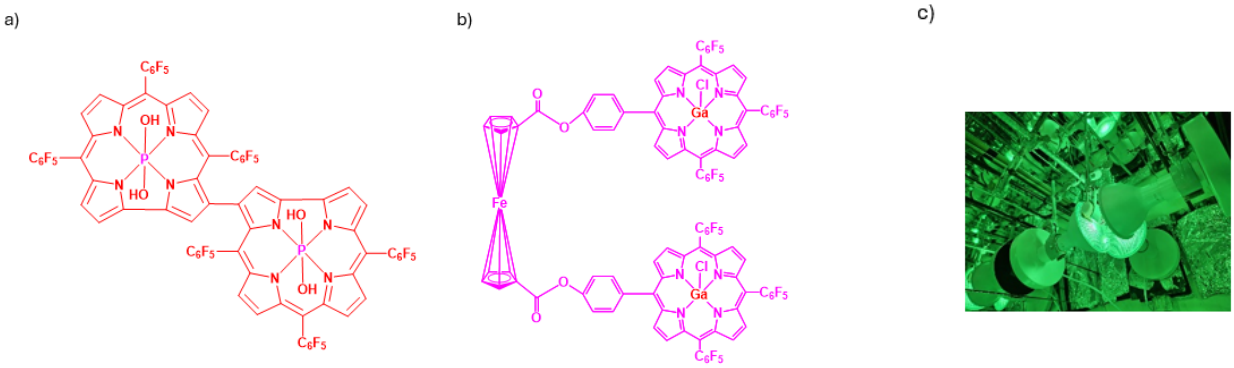

Figure 1. Chemical structures of a) β-β' linked phosphorous corrole dimer, b) Gallium porphyrin dimer, and c) photocatalytic setup for illumination by three green-light lamps.

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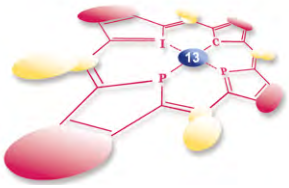

Panchromatic Light-Capturing Bis-styryl BODIPY-Perylenediimide Donor-acceptor Constructs: Occurrence of Sequential Energy Transfer Followed by Electron Transfer

Chamari V. Ileperuma,[a] José Garcés-Garcés,[b] Shui Shao,[a] Fernando Fernández-Lázaro,[b] Ángela Sastre-Santos,[b] Paul A. Karr,[c] and Francis D'Souza[a]

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BODIPY's optical and redox properties can be easily tuned by peripheral substitution and extended π-conjugation.[1-2] In fact, BODIPYs carrying extended π-conjugation have been used in biomedical applications such as tissue imaging and photodynamic therapy due to their absorption and fluorescence in the near-IR region of the electromagnetic spectrum.[3-4] Two wide-band-capturing donor-acceptor conjugates featuring bis-styrylBODIPY and perylenediimide (PDI) have been newly synthesized, and the occurrence of ultrafast excitation transfer from the ^{1}PDI* to BODIPY, and a subsequent electron transfer from the ^{1}BODIPY* to PDI have been demonstrated. Optical absorption studies revealed panchromatic light capture but offered no evidence of ground-state interactions between the donor and acceptor entities. Steady-state fluorescence and excitation spectral recordings provided evidence of singlet singlet energy transfer in these dyads, and quenched fluorescence of bis-styrylBODIPY emission in the dyads suggested additional photo-events. The facile oxidation of bis-styrylBODIPY and facile reduction of PDI, establishing their relative roles of electron donor and acceptor, was born out of electrochemical studies. The electrostatic potential surfaces of the S_1 and S_2 states, derived from time-dependent DFT calculations, supported excited charge transfer in these dyads. Spectro-electrochemical studies on one-electron-oxidized and one-electron-reduced dyads and the monomeric precursor compounds were also performed in a thin-layer optical cell under corresponding applied potentials. From this study, both bis-styrylBODIPY$^{\cdot+}$ and PDI$^{\cdot-}$ could be spectrally characterized and were subsequently used in characterizing the electron transfer products. Finally, pump–probe spectral studies were performed in dichlorobenzene under selective PDI and bis-styrylBODIPY excitation to secure energy and electron-transfer evidence. The measured rate constants for energy transfer, k_{ENT}, were in the range of 10^{11} s^{-1}, while the electron transfer rate constants, k_{ET}, were in the range of 10^{10} s^{-1}, thus highlighting their potential use in solar energy harvesting and optoelectronic applications.

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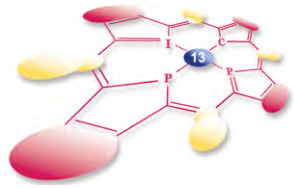

Cryo-EM structure of monomeric *bovine* cytochrome *c* oxidase in a lipid Nanodisc

Izumi Ishigami[a], Joshua H. Mendez[b], Ana B. Asenjo[a], Hernando J. Sosa[a], Syun-Ru Yeh[a] and Denis L. Rousseau[a]

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Cytochrome *c* oxidase (C*c*O) is an essential enzyme in mitochondrial and bacterial respiration. It catalyzes the four-electron reduction of molecular oxygen to water and harnesses the chemical energy to translocate four protons across biological membranes, thereby establishing the proton gradient required for ATP synthesis. X-ray crystallographic structure analyses of *bovine* C*c*O (bC*c*O) have been based mainly on the dimeric form of the enzyme[1]. Recent cryogenic-electron microscopy (cryo-EM) structures revealed that C*c*O exists in its monomeric form in the respiratory supercomplex[2,3]. By treating the enzyme with TritonX-100, we generated the monomeric form of bC*c*O in solution and embedded it into nanodiscs for cryo-EM imaging. The nanodisc is comprised of a membrane scaffold protein (MSP), which encircles a lipid center providing a native-like environment for membrane proteins, like bC*c*O. We obtained a single particle cryo-EM structure of bC*c*O and resolved it to a resolution of 2.19 Å (Fig. 1). Here we will compare this single particle monomeric cryo-EM structure to those of the monomeric and dimeric structures of bC*c*O obtained by X-ray crystallography, and compare the resonance Raman spectra of monomeric bC*c*O embedded in a nanodisc to those obtained in solution.

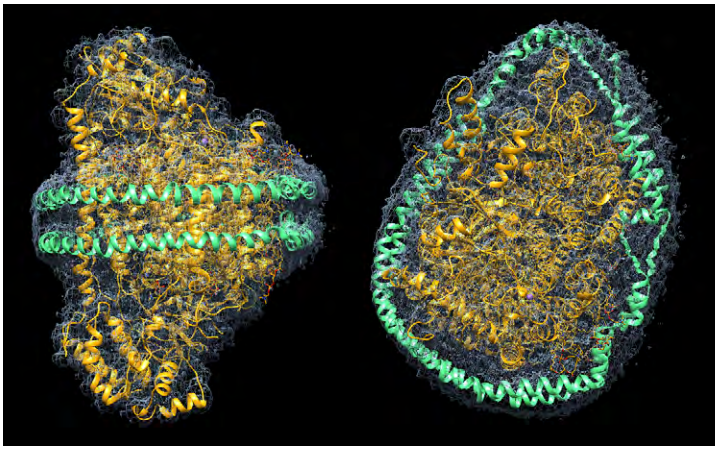

Fig. 1 Cryo-EM structure of monomeric bC*c*O Nanodisc.

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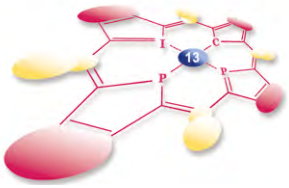

Visible Light Mediated Photocatalysis by Corroles: Green Approach for Organic Transformations

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In recent years, photocatalysis has emerged as a good alternative for organic transformations; it is a green and sustainable approach which uses visible light/sunlight as energy source [1]. Popularly, Ru(II), Ir(III) polypyridyl complexes and organic dyes have been used for photocatalyzed organic transformations [2]. Corroles are tetrapyrrolic macrocycles with strong absorption in the visible region and rich electrochemical properties. Thus, corroles can serve as photocatalyst in the visible light mediated C-H activation reactions. In the past few decades, corrole-metal complexes (Fe, Co, Ni, Sb, Ir, Ru etc.) have been used extensively for catalysing organic transformations such as oxidations, epoxidation, cyclopropanation, hydroxylation of alkene and halogenation reactions [3].

Our group at IIT Gandhinagar is working on the photocatalytic applications of corroles, porphyrins and metal dipyrrinato complexes [4, 5]. This poster presents the synthesis and characterization of a series of A_3 and A_2B type corroles having heterocyclic moieties at their *meso*-positions. The work describes a non-toxic, efficient method for the C-H arylation under blue light or sunlight and desired products were obtained in good yields. The results of TD-DFT calculations will also be discussed to explain the reaction mechanism.

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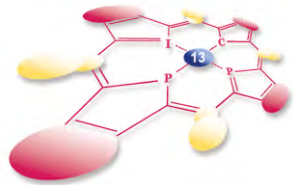

Photoredox Catalysis by Porphyrins: C-H Activation of Organic Substrates

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Porphyrins are tetrapyrrolic compounds commonly found in cytochromes, heme group, chlorophyll, enzymes, etc. These moieties play a significant role in various life processes like oxygen transport, electron transport, photosynthesis, and catalytic activity in many enzymes [1]. Photocatalysis is an environmentally friendly and sustainable approach. Photocatalysis employs a safe and inexpensive renewable source of energy. Similar to photosynthesis, porphyrin can capture light energy and this energy can be used for organic transformations. In recent years, there has been notable progress in the development of metalloporphyrins (Mg, Fe, Co, Ni, Zn, Rh, Pd, Sn, Pt, etc.) based catalysis for organic transformations such as oxidations, reductions, epoxidation, carbon−carbon, and carbon-heteroatom bond formations [2].

Our group at IIT Gandhinagar is working on the photocatalytic applications of porphyrins. A_3B and A_2B_2 type palladium porphyrins have been used for the photo-oxidation of aldehydes to carboxylic acids [3, 4]. This poster presents the synthesis and characterization of a series of zinc porphyrins and 21-thiaporphyrins having heterocyclic moieties at *meso*-positions [5]. A light-induced, non-toxic, efficient method was developed for the C-H activation under blue light, and products were obtained in good yields. To get a deeper insight, excited state redox potentials were calculated and mechanistic studies were done using TD-DFT.

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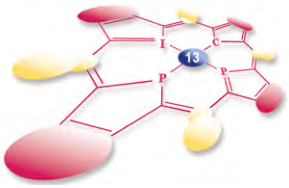

The effect of TiO_2 nanoparticles on the catalytic activity of a porphyrin towards electrochemical sensing and photoelectrodegradation of pentachlorophenol

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Sensing and degrading pollutants is crucial for identifying and removing pollutants in water and air. To improve sensitivity and selectivity, an electroactive catalyst is applied at the surface of an electrode. Metal porphyrins (MPs) have been applied in sensing as catalysts, the modification of MPs can improve properties such as electron transfer and redox processes. For improved catalytic effect, TiO_2 nanoparticles are employed as supports for porphyrins for electrochemical sensing and degradation of organic pollutants. This is due to their physical and chemical properties in various states, nontoxicity, conductivity, easy preparation and high stability. The conjugation of metal porphyrin to TiO_2 extends the light absorption of wide band gap TiO_2 into the visible light region [1]. This improves the photocatalytic properties of the TiO_2 which makes them ideal catalysts for photo-electrodegradation (Fig. 1) since sunlight can be used to initiate the degradation of organic pollutants in water or air. In this study, TiO_2 nanoparticles are conjugated to a metal porphyrin (structure shown in Fig. 1) to improve the detection and degradation of pentachlorophenol using electrochemical sensing and photoelectrodegradation.

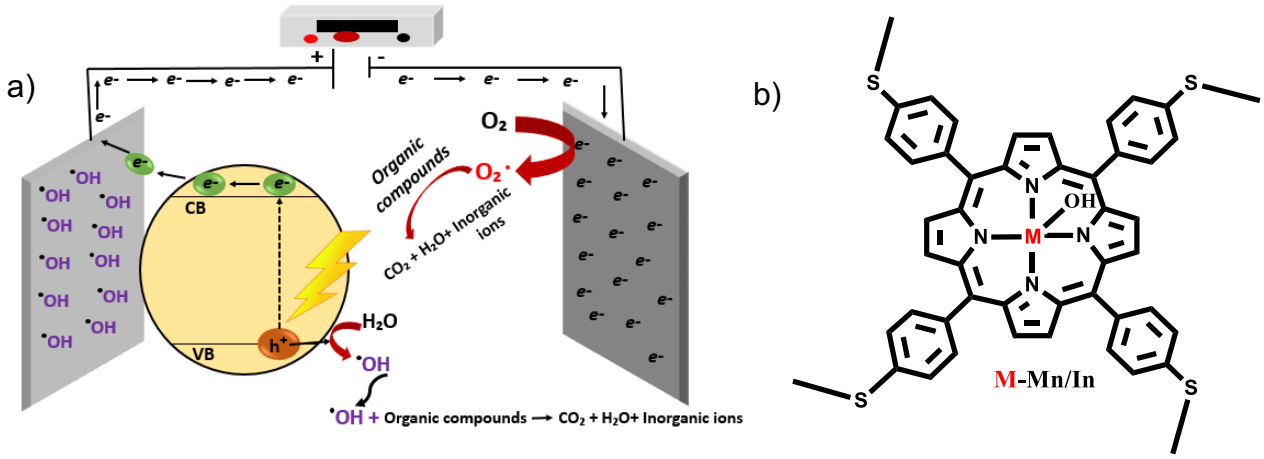

Figure 1: (a) Photoelectrochatalysis mechanism of degradation and (b) the structure of the porphyrins used.

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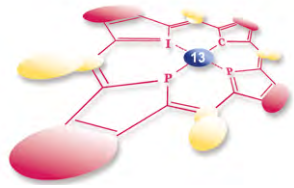

Photodynamic antimicrobial activity of selected metal-free and tin porphyrins

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Photosensitization is considered nowadays as one of the alternatives for antimicrobial and photodynamic therapy treatment by researchers. Different dyes such as bodipy, phthalocyanines and porphyrins are used for this purpose. In this study selected metal-free porphyrins and tin 5 10 15 20 -tetrakis (4-bromophenyl) porphyrin and meso-tetra (4-carboxyphenyl) tetramethyl ester porphyrins were synthesized and used for the inhibition of *staphylococcus aureus* and *Salmonella* including *E.Coli.* Irradiation was performed using 530 nm and 650 nm LED lamps. Dyes used in this work showed good results for metalated compared to free base.

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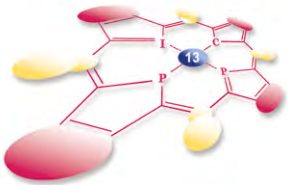

Photocatalysis with Adsorbed Fluorinated Phthalocyanines

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The adsorption and photocatalytic properties of fluorinated phthalocyanines (F_{64}PcZn[1]) on metal oxide solid supports were investigated. The supported F_{64}PcZn complexes were characterized by diffuse reflectance, infra-red and fluorescence spectroscopies and with SEM, TEM and EDS imaging. Pcs act as photosensitizers to generate singlet oxygen ($^1O_2$) using visible light.[2] $^1O_2$ can react to form other reactive oxygen species (ROS), possibly including hydroxyl ($HO\cdot$) and superoxide ($O_2^{-\cdot}$) radicals.[3] The metal oxide adsorbed F_{64}PcZn was shown to be capable of generating ROS using only visible light and air: an environmentally friendly, green photo-oxidation catalyst.

The degradation of organic sulfides was investigated under several conditions: homogeneous photocatalysis using F_{64}PcZn and heterogeneous photocatalysis using F_{64}PcZn adsorbed on alumina, titania, and zirconia nanoparticles. Heterogeneous photocatalysis was performed in solvent-rich and solvent-less systems. Different light wavelengths and intensities were used to investigate the kinetics and stability of the supported catalyst. GC-MS was used to identify degradation products and the reaction kinetics were determined using GC-FID. Photocatalysis in solvent-rich systems (homogeneous or heterogeneous) followed first-order kinetics while solvent-free systems followed zero-order kinetics. No degradation products were observed in the absence of phthalocyanine. Catalyst stability was confirmed by diffuse reflectance and IR spectroscopy, and catalyst re-usability was demonstrated.

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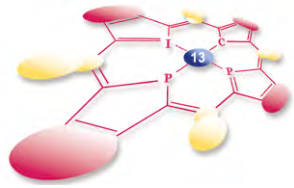

Synthesis and Photophysical Properties of Annulated Mono and Dinuclear Phthalocyanines

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Washington State University, Department of Chemistry, Pullman, USA

Metal-free mononuclear, dinuclear, and phenoxy phthalocyanines were prepared through a mixed cyclotetramerization process involving a 1,2,4,5-tetracyanobenzene derivative (Pyrrolo[3,4-f]isoindole-1,3,5,7(2H,6H)-tetraimine) and 4,5-diphenoxyphthalonitrile. Notably, a pi-electron-conjugated phenoxy binuclear phthalocyanine was synthesized for the first time, with phthalocyanine units connected by commonly annulated benzene rings. This binuclear phthalocyanine stands out for its distinctive structure and its suitability for STM studies.

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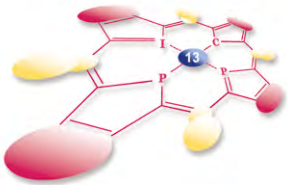

Synthesis of osmium-containing porphyrinoids: metallaporphyrins and multinuclear complexes

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In a classical metalloporphyrin, a metal ion is bound in the coordination cavity, or slightly above it, often with axial ligands. A completely new way of metal binding in porphyrin is the construction of a so-called **metallaporphyrin** in which the nitrogen atom is replaced by a metal atom. Thus, metallaporphyrins may be classified as organometallic heteroporphyrins with metallic heteroatoms. To date, metallaporphyrins containing palladium(II), platinum(II), platinum(IV), and rhodium(III) centers have been obtained and described [1-4]. These compounds were synthesized by substituting a metal atom for tellurium atom(s) in 21,23-ditelluraporphyrin.
The characteristic feature of most metallaporphyrins is the specific rhomboidal in-plane deformation of the macrocyclic skeleton and the fluxional behavior.
Here we present the studies of metallaporphyrins containing the osmacyclopentadiene motif. In addition to its position in the periodic table, close to the elements mentioned above, the choice of this metal for the study was determined by the previously observed reactivity of $[Os_3(CO)_{12}]$ towards tellurophene [5]. The reaction of 21,23-ditelluraporphyrin with an osmium, source yielded several products: 21-osma-23-telluraporphyrin and 21,23-diosmaporphyrin, as representatives of a metallaporphyrin group, and trinuclear osmium complex of 21,23-ditelluraporphyrin. Hybrids of 21-osma-23-telluraporphyrin and metal clusters were detected as well. The products were characterized by NMR and UV-Vis spectroscopy, mass spectrometry, and X-ray.

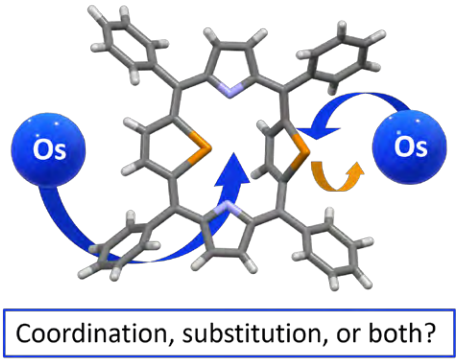

Figure 1. Possible pathways for the reactivity of ditelluraporphyrin with osmium reagent.

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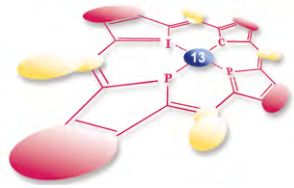

Excited-State Charge Transfer in Push−Pull Zinc(II) π-Extended Porphyrins Fused with Tetracyanopentacene

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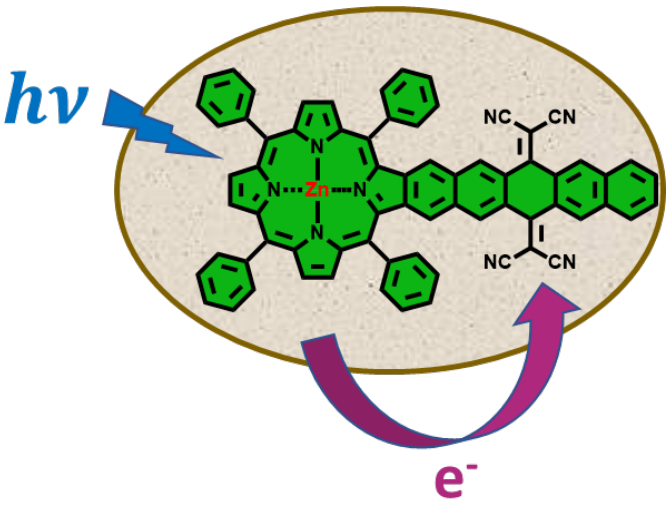
We have designed, synthesized, and characterized a dyad system that consists of a zinc porphyrin (ZnP) as a donor and tetracyano-pentacene (TCPC) as an acceptor in donor-acceptor (ZnP-TCPC) approach to generate the long-lived charge separated species. Ground-state optical studies were performed to choose the excitation wavelength for transient absorption spectroscopy. The redox properties suggest that the zinc porphyrin is easy to oxidize and the tetracyano part of the dyad is very easy to reduce. Spectro-electrochemical studies on one-electron-oxidized and one-electron-reduced dyads were also performed in a thin-layer optical cell under corresponding applied potentials. From this study, both $ZnP^{\cdot+}$ and $TCPC^{\cdot-}$ could be spectrally characterized and were subsequently used in characterizing the electron-transfer product. Later, DFT calculations were performed to support the redox properties that the electron density of the highest molecular orbital (HOMO) is distributed on the zinc porphyrin donor part and while the lowest unoccupied molecular orbital (LUMO) is distributed on the acceptor tetracyano-pentacene. Finally, time-resolved transient absorption studies were performed to identify the photoinduced electron transfer from the singlet excited porphyrin to tetracyano-pentacene entity in different polar solvents like benzonitrile, and *o*-dichlorobenzene. Data analysis by Glotaran revealed the lifetime of charge-separated species 18 ps and 159 ps in benzonitrile and *o*-dichlorobenzene, respectively.



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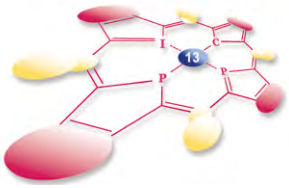

Synthesis of face-to-face sandwiched hexaphyrin-cyclodextrin hybrids for unorthodox π-type interactions

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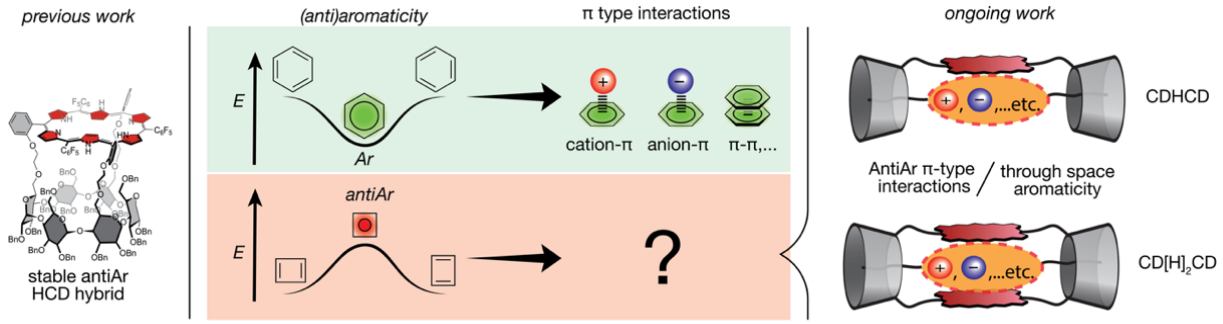
Aromaticity is a stabilizing property of cyclic molecules resulting from the delocalization of conjugated π electrons. [1] This stability allows these molecules to interact with other molecules *via* several kinds of π-type interactions (π-π stacking, anion/cation-π, and CH-π). On the contrary, altering the electron number, topology and/or excitation state of these same molecules can lead to a destabilizing antiaromatic character. [1] However, this destabilizing character can be stabilized by porphyrinoid macrocycles such as norcorroles, [2] or hexaphyrins, [3] allowing to explore attractive anti-aromaticity-based properties such as electronic communication with molecular junctions or weak interactions within nanospaces. [4]
Recently, we have synthesized hybrid molecules (HCD) composed of cyclodextrin (CD) and hexaphyrin (H) subunits stabilizing both aromatic and antiaromatic states. [5] We are currently synthesizing a sandwich of hybrid molecules composed of two cyclodextrins and two hexaphyrins subunits aiming to use it as a tool to further explore π-type interactions of antiaromatic compounds and through-space aromaticity.



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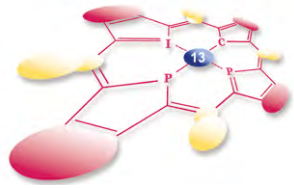

Nanoparticles for tumor immunotherapy using combined treatment of photodynamic therapy and metallic immunotherapy

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PDT employs a combination of photosensitizer (PS) and light energy to generate active oxygen species, effectively eliciting cancer cell death and provoking immune activation [1,2]. However, PS exhibits hydrophobic properties, rendering it unstable when exposed to the aqueous phase [3]. Additionally, limitations such as the absence of site-specific targeting underscore the indispensability of a suitable drug delivery carrier for the successful implementation of PS in human applications. Here, I introduce a novel approach involving the utilization of metal-organic framework nanoparticles containing pheophobide A (MOFP), which exhibits targeted recognition of the tumor microenvironment. This allows for a rapid rise in metal ion concentration while promoting the controlled release of the encapsulated pheophobide A. At physiological pH 7.4, MOFP exhibits a size of approximately 170 nm, which significantly decreases to less than 10 nm under acidic conditions at pH 6.5. Acid-induced degradation of MOFP causes a rapid increase in metal ion concentration, leading to potent cytotoxic effects against colon, breast, and pancreatic cancer. Additionally, upon laser irradiation, the encapsulated photosensitizer within the MOFP initiates the generation of reactive oxygen species, which synergistically increases the cytotoxicity induced by metal ions. In a tumor-bearing mouse model, intravenous administration of MOFP resulted in a significant expansion of helper T cells and cytotoxic T cells, accompanied by a decrease in the regulatory T cell population. These changes resulted in significant inhibition of tumor growth, highlighting the efficacy of MOFP in this experimental model. Importantly, MOFP exhibits favorable safety properties, is not toxic to vital organs, and does not cause weight loss. Therefore, MOFP holds tremendous promise, highlighting its potential in the field of anticancer immunotherapy, either as a standalone treatment or in combination with various anticancer immunotherapies.

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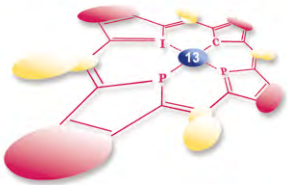

Complexation of Porphyrin Oligomers and Hemoproteins toward Constructing Rigid Protein Dimers

Sukyeong Kim[a], Garyo Ueda[a], Hiroaki Inaba[a], Shinya Ariyasu[a], Yuichiro Aiba[a], Osami Shoji[a]

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Hemoproteins are one of the most versatile metalloproteins and are also used for structural units in artificial protein assemblies [1]. To provide additional functions into hemoproteins for composing such protein assemblies, heme substitution is frequently utilized. However, the structures of the incorporated synthetic complexes are generally limited to those like heme because heme-binding sites of hemoproteins are highly optimized to heme. For this reason, structures of reconstituted protein assemblies often lack rigidity due to the flexibility of a heme-like scaffold.

In contrast, heme acquisition system protein A (HasA), secreted by gram-negative bacteria, has a unique heme-binding site that is highly exposed to the solvent (Fig 1-a). We have found that HasA can capture various rigid metal complexes different from heme, such as diphenylporphyrins (DPPs) (Fig 1-b) [2] and tetra-phenylporphyrins (TPPs) (Fig 1-c) [3]. These porphyrin derivatives have been utilized as rigid scaffolds within the field of coordination chemistry. Therefore, utilizing this unique property of HasA, it seems possible to construct rigid structural units for composing HasA assemblies using porphyrin oligomers as scaffolds and to control the distances between HasAs based on the design of guest molecules.

In this work, we first focused on the construction of rigid HasA dimers, representing an initial investigation for constructing artificial assemblies of HasA (Fig 1-d). We investigated the incorporation of several porphyrin oligomers into HasA through the heme substitution method. We have found that rigid porphyrin oligomer can be incorporated into HasA, and be scaffold for HasA dimers.

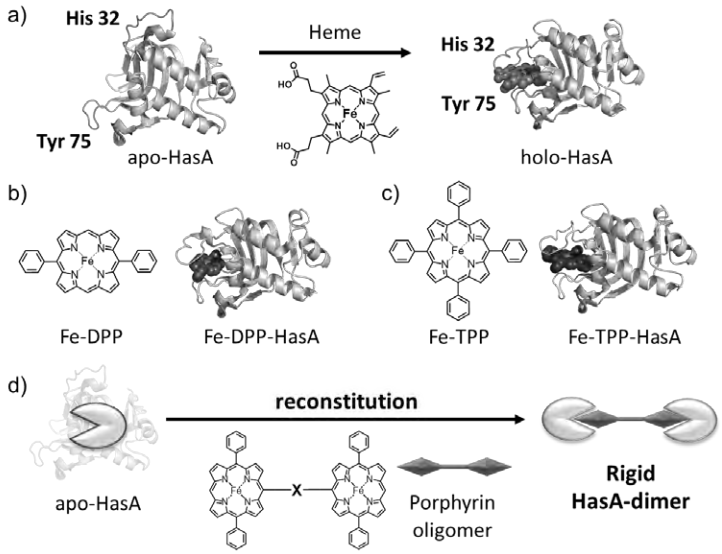

Figure 1: a) The crystal structures of the heme-free form (apo form) and the heme-bound form (holo form) of heme acquisition system protein A (HasA), b) The crystal structure of Fe-DPP HasA (PDB: 5XIB) and c) Fe-TPP HasA (PDB: 7EMO), d) Overview of this research.

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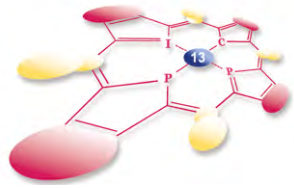

Rational pathway for the synthesis of morpholinobacteriolactone and related bis-modified chromophores

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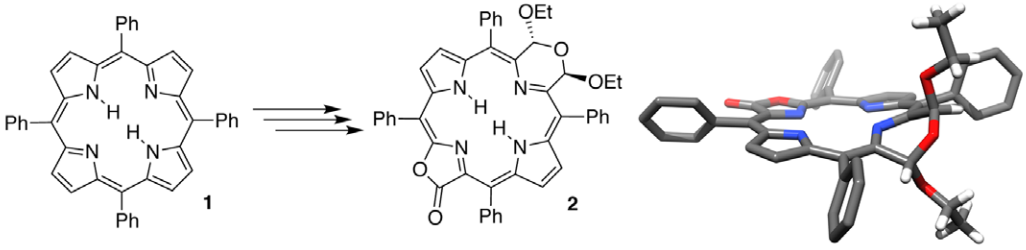
The conversion of pyrrolic building blocks in porphyrins or chlorins to a non-pyrrolic moiety has often drastic consequences on their optical properties [1], but structure-function relationships are not always clear. Morpholinochlorins and morpholinobacteriochlorins are chlorin- and bacteriochlorin-like pyrrole-modified porphyrins in which one or two pyrrolic building blocks were replaced by morpholine moieties, respectively, and for which some structure-function relationships were developed [2, 3]. Porpholactones are pyrrole-modified porphyrins with porphyrin-like optical properties carrying an oxazolinone moiety. The optical properties of the bis-modified (iso)bacteriodilactones are not (iso)bacteriochlorin-like [4].
The work presented here explores the synthesis and optical properties of bis-modified pyrrole-modified porphyrins that combine a morpholine building block with a range of pyrroline and oxazolone building blocks opposite to the morpholine. Different synthetic pathways toward the morpholinobacteriolactone **2** are tested, all relying on the manipulation of *meso*-tetraarylporphyrins, such as **1**. The influence of the *meso*-aryl groups was tried. Preliminary structure-optical properties relationships are reported.



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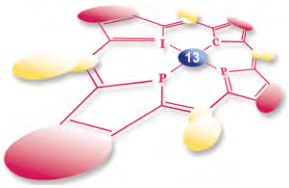

Creation of Supramolecular Assemblies Using TTF-Annulated Subphthalocyanine

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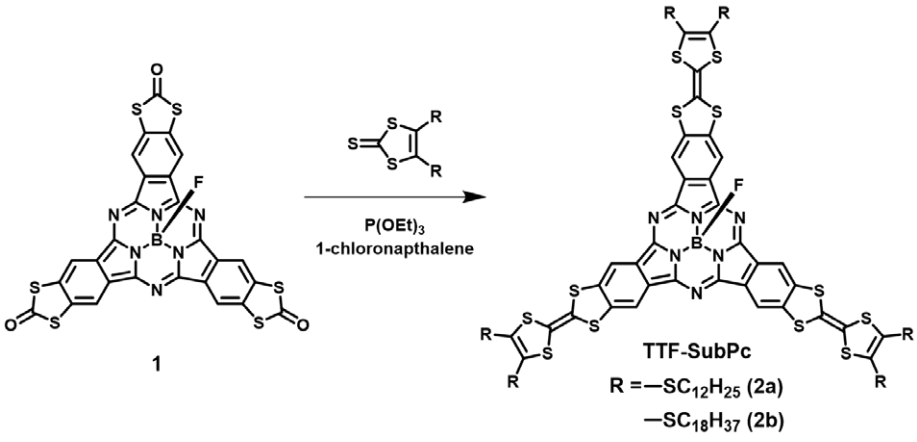
Due to the bowl-shaped structure, subphthalocyanine tends to form stacked columnar self-assemblies when the axial ligand of the central boron is substituted with a less-sterically hindering fluorine atom. In our previous study, we developed tetrathiafulvalene-annulated SubPc (TTF-SubPc)[1,2] and successfully controlled this stacking behavior using redox-responsive intermolecular interactions of the TTF moieties. Due to the π-π stacking interactions, TTF-SubPc also formed stacked structures in apolar solvents or by lowering temperatures. The variable-temperature ^{1}H NMR study revealed an isodesmic self-assembly process with an association constant of 180 M^{-1} and a degree of polymerization of ca. 1.3 at 25 °C. Because of the small association constant, the supramolecular assemblies of TTF-SubPc could not be observed by atomic force microscopy (AFM).
In this study, to enhance the intermolecular interactions at the neutral state, long thioalkyl chains were introduced to the periphery of TTF-SubPc. The association constant of TTF-SubPc bearing thiododecyl groups (**2a**) was improved to be 5.0 x 10^4 M^{-1} at 25 °C. In addition, a robust stacking structure of TTF-SubPc bearing thiooctadecyl groups (**2b**) enabled the observation of supramolecular wire structures by AFM.
In this poster presentation, the synthesis of **2a** and **2b** and their supramolecular polymer formation will be discussed.



Scheme. Synthesis of TTF-SubPcs (**2a** and **2b**) bearing long thioalkyl chains

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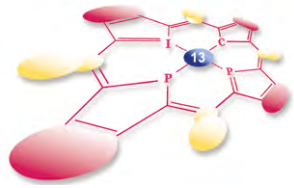

Photochemical internalization mediated by amphiphilic phthalocyanine photosensitizers

Magdaléna Kozlíková[a], Monika Rohlíčková[a], Dominika Daničová[a], Kateřina Vlková[a], Veronika Nováková[b], Petr Zimčík[b], Miloslav Macháček[a]

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Failure of some treatments may be caused by the limited ability of drugs to cross cell membranes and find their intracellular targets. The plasma membrane is permeable to small lipophilic molecules. In most cases, large or charged molecules are transported by endocytosis to lysosomes with their subsequent degradation [1]. This effect is not desirable with some biologically active compounds and drugs and contributes significantly to their ineffectiveness. Photochemical internalization (PCI) can be used to increase the biological activity of these drugs reluctantly crossing the plasma membrane. PCI is based on the principles of photodynamic therapy [2]. Amphiphilic photosensitizers (PS) are used for their easy incorporation into the cell membrane. After endocytosis, those PSs are trapped in the same vesicles as the drugs. After irradiation with a specific wavelength, reactive oxygen species are formed, leading to vesicle disruption and subsequent release of the drug into the cytoplasm to find its intracellular target. Drugs typically used in PCI include type I ribosome-inactivating proteins (RIPs), gene-encoding plasmids, adenoviruses and oligonucleotides and certain chemotherapeutics, such as bleomycin. Examples of type I RIPs are saporin and gelonin which can also be conjugated with antibodies that recognize antigens overexpressed in tumor tissue, which, in combination with PCI, increases the selectivity of anticancer treatment [1,3]. In our project, we selected original phthalocyanine PSs, which were compared with commercially available PSs ($AlPcS_{2a}$ and $TPPS_{2a}$) and saporin. The human cervical carcinoma cell line (HeLa) was used for all experiments. First, the cytotoxic effect of PS and saporin after irradiation was evaluated. The IC_{50} values obtained were used to generate a concentration series corresponding to $IC_{50}/8$, $IC_{50}/4$, $IC_{50}/2$, IC_{50}, $2\times IC_{50}$ and $4\times IC_{50}$ values for each compound. Subsequently, cytotoxicity was evaluated for PSs and saporin, and also for their combination using the Chou-Talalay methodology. In most cases, strong synergism was found. Also, these original phthalocyanine PSs achieved a similar or better effect in combination with saporin as $AlPcS_{2a}$ and $TPPS_{2a}$.

Acknowledgments: This project was funded by Charles University Grant Agency grant no. 1312220 and the results of this project were obtained with financial support from the Ministry of Education, Youth and Sports under the ERC CZ programme (Grant No. LL2318).

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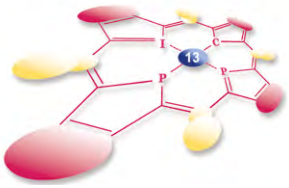

Photoinduced Electron and Energy Transfer Processes in Ruthenium(II) Phthalocyanine-Subporphyrazine Conjugates

Swathi Krishna[a], Elena Cañizares-Espada[b], David Guzmán[b], M. Salomé Rodríguez-Morgade[b,c], Tomás Torres[b,c,d], Dirk M. Guldi[a]

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Over the last few years, solar energy conversion has gained prominence due to diminishing fossil fuel reserves. In this regard, electron donor-acceptor (D-A) systems have garnered attention for their capacity to generate long-lived charge-separated states, convertible into useful forms of energy upon photon capture.[1] A growing interest in the exploration of non-fullerene acceptors has been deciphered in the field of artificial photosynthesis. Porphyrinoids, renowned for their pivotal role in nature, are frequently chosen as chromophores in photovoltaic devices and artificial photosynthetic systems. They have emerged as perfect candidates for incorporation into D-A arrays, owing to their exceptional optoelectronic properties, rapid energy/electron transfer capabilities, and the possibility to tune their properties through peripheral substitutions or synthetic derivatizations.[2]

Subporphyrazines (SubPzs), a class of 14 π-electron porphyrinoids, are unique chromophores that exhibit outstanding optoelectronic properties that can be tailored through axial or peripheral functionalization.[3] Phthalocyanines, on the other hand, are 18 π-electron porphyrinoids, well-known for their strong absorption across the visible range of the solar spectrum, small reorganization energy in electron transfer reactions, and rich redox chemistry. Ruthenium(II) phthalocyanines (RuPcs), in particular, are incorporated in D-A systems since they form strongly coordinated assemblies, promote rapid charge separation, and feature slow charge recombination.[4] RuPcs, in combination with SubPzs, cover a wide range of solar radiation spectra, with absorption spanning between 300 to 800 nm. In this context, we report on a series of RuPc-SubPz conjugates, which display either electron or energy transfer reactions depending on the structural design of SubPzs, showcasing their potential for advancing the efficiency and versatility of artificial photosynthetic systems.

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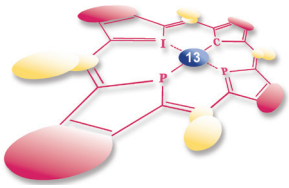

How many metal atoms can one porphyrin bind? Synthesis of porphyrin-cluster hybrids

Paulina Krzyszowska[a*], Emilia Ganczar[a], Ewa Pacholska-Dudziak[a]

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Telluraporphyrinoids show exceptional properties through the presence of tellurophene subunit(s) in the macrocycle. Tellurium-centered reactivity, such as chlorination or oxidation, has been observed for telluraporphyrins, including 21-telluraporphyrin [1, 2] and 23-tellura-21-carbaporphyrin [3]. Upon reaction of 21,23-ditelluraporphyrin with hydrochloric acid [4] the extrusion of tellurium atoms occurred, leading to the transformation of the macrocycle into 21,23-divacataporphyrin [5], a porphyrin-annulene hybrid. Furthermore, in the presence of metal salts (Pd, Pt, Rh), the tellurophene ring(s) of the 21,23-ditelluraporphyrin can be transformed into metallacyclopentadiene unit(s) embedded within the macrocycle. Thus, 21-metalla-23-telluraporphyrins and 21,23-dimetallaporphyrins were the first porphyrins to include transition metal(s) in their macrocycle skeletons [6-9]. Here, we will show that the use of ruthenium, which is a metal capable of forming clusters, proves that 21,23-ditelluraporphyrin can produce compounds incorporating more than two metal ions. The reaction of 21,23-ditelluraporphyrin with a ruthenium source yielded, in addition to the classical 21-rutena-23-telluraporphyrin, several multinuclear compounds that are porphyrin-metal cluster hybrids. The ruthenium atoms located at positions 21 and 23 of the porphyrin skeleton, and the remaining metal atoms, in number from one to five, are bonded above or/and below the macrocyclic plane. The synthesized porphyrin-cluster hybrids were characterized using NMR, IR, and UV-Vis spectroscopy, MS, and X-ray.

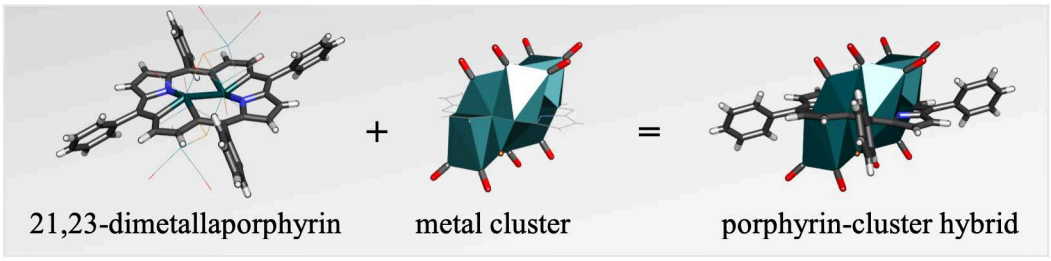

Figure 1. Exemplary structure of a porphyrin-cluster hybrid.

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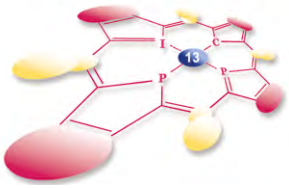

Non-Metals Chelated by Redox-Active Chelators as Electrocatalysts for Hydrogen Evolution Reaction (HER)

Sachin Kumar[a], and Zeev Gross[a]

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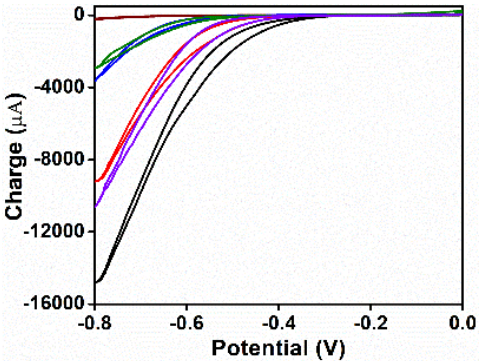
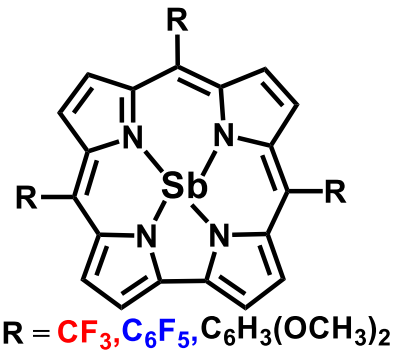
Global energy consumption and its environmental consequences emphasize the need for the development of non-polluting methodologies for energy production from renewable sources. The utilization of hydrogen as a fuel is most attractive since it has a high energy density of 140 MJ/Kj and produces only water as a byproduct. Despite the "simplicity" of the H-H bond, a catalyst is required to make its formation process efficient and economical. Although platinum group metals (PGM) are the best catalysts for the Hydrogen Evolution Reaction (HER) to date, they are rare and expensive. We now report antimony corroles [1] and boron subphthalocyanines [2] as HER electrocatalysts. Two new corroles with electron donating and electron withdrawing *meso*-substituents were fully characterized by X-ray crystallography, NMR, electronic spectra, and electrochemistry. It revealed that is the electron-poor complexes perform best under homogeneous catalysis and that the most electron-rich complexes display the most benefit under substituted heterogeneous catalysis likely tris di-methoxy onset potential and faradaic efficiency due to the secondary sphere present in it.





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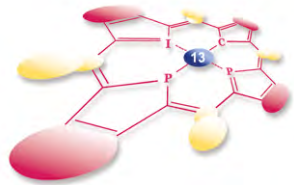

Post Transition and Non-PGMs as Efficient Electrocatalysis for HER

Sachin Kumar[a], and Zeev Gross[a]

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Global energy consumption and its environmental consequences emphasize the need for the development of non-polluting methodologies for energy production from renewable sources. The utilization of hydrogen as a fuel is most attractive since it has a high energy density of 140 MJ/Kj and produces only water as a byproduct. Despite the "simplicity" of the H-H bond, a catalyst is required to make its formation process efficient and economical. Although platinum group metals (PGM) are the best catalysts for the Hydrogen Evolution Reaction (HER) to date, they are rare and expensive. We now report antimony corroles [1] and boron subphthalocyanines [2] as HER electrocatalysts. Two new corroles with electron donating and electron withdrawing *meso*-substituents were fully characterized by X-ray crystallography, NMR, electronic spectra, and electrochemistry. It revealed that is the electron-poor complexes perform best under homogeneous catalysis and that the most electron-rich complexes display the most benefit under substituted heterogeneous catalysis likely tris di-methoxy onset potential and faradaic efficiency due to the secondary sphere present in it.

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A Clickable Azaphthalocyanine Derivative for Ternary Complexes Facilitated by Cucurbit[8]uril

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Cucurbit[*n*]urils, are widely used water-soluble macrocyclic hosts. They can bind various types of guests (metallocene derivatives, adamantane derivatives, pyridinium derivatives); however, their prototypical guests are endowed with ammonium substituents.[1, 2] Interestingly, the size of the cucurbit[8]uril cavity allows the binding of two identical or different guests at the same time. For a successful formation of a ternary complex, an electron-deficient and an electron-rich arene are required.[3] A very common electron-deficient compound used for this purpose is a viologen cation. A typical motive for the complementary electron-rich guest is 2,6-naphthalenediol. In our case, one of the guests is attached to an azaphthalocyanine derivative – a nitrogen analogue of phthalocyanine – that can be used as a photosensitiser for photodynamic therapy or as a fluorescence sensor. By the formation of ternary complexes (see Figure 1), we plan to study the possibilities of influencing the photophysical properties of the azaphthalocyanine, such as quenching the fluorescence by photoinduced electron transfer.[4] Copper-catalyzed azide-alkyne cycloaddition was used to prepare the conjugate of the azaphthalocyanine and the cucurbit[8]uril guest to allow easy modification of our compound. In this poster, we present the design and synthesis of this unique supramolecular system, as well as the first photophysical studies testing our hypothesis.

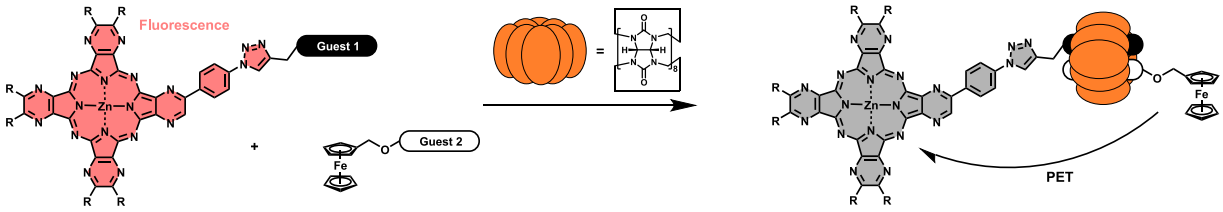

Figure 1. Graphical representation of the fluorescence quenching by formation of a ternary complex.

Acknowledgments: This project was financially supported by the Charles University Grant Agency (170223) and the Czech Science Foundation (23-06177S).

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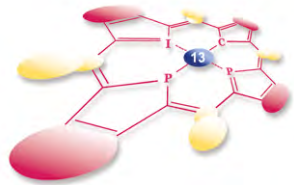

Porphyrin Analogues with Fused Heteroaromatic Rings: Synthesis and Aromatic Character of Phenanthroline, Quinoline and Isoquinoline-fused Porphyrinoids

Timothy D. Lash, Victoria C. Ujah, Jane M. Hostert and Trang N. Nguyen

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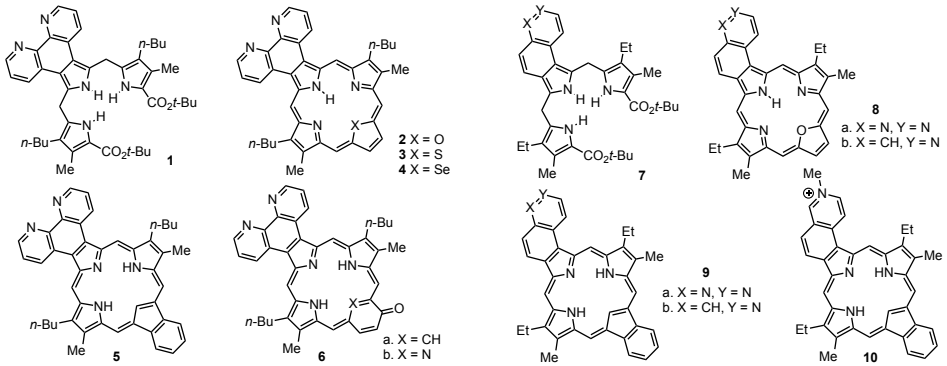
Numerous strategies have been applied to adjust the properties of porphyrinoid systems, including core modification [1] and ring fusion [2]. A combination of these strategies enables further alterations to be made [3]. Previously, we reported an efficient route to porphyrins with fused phenanthroline units [4,5] but this intriguing system has not been well studied. Tripyrrane **4** was synthesized in 3 steps from 5-nitro-1,10-phenanthroline. Cleavage of the *tert*-butyl ester protective groups with trifluoroacetic acid, followed by condensation with furan, thiophene or selenophene dialdehydes gave phenanthroline-fused heteroporphyrins **2**-**4** in 44-79% yield. Similarly, reaction with an indene dialdehyde gave carbaporphyrin **5**, while hydroxybenzene or pyridine dialdehydes afforded oxybenzi- and oxypyriporphyrins **6a** and **6b**, respectively. The proton NMR spectra gave seemingly contradictory results as both the internal and external protons were shifted upfield. For instance, the internal C-H resonance for carbaporphyrin **5** was observed at nearly -9 ppm, approximately 2 ppm upfield from the expected value for carbaporphyrins [6], but the *meso*-protons gave far less deshielded values than related structures. Quinoline and isoquinoline-fused tripyrranes **7** [7] reacted with furan and indene dialdehydes to give **8** and **9**, respectively. Although the proton NMR spectra for these derivatives showed far smaller effects, these annulated porphyrinoids readily underwent external methylation to give pyridinium derivatives **10**.



Research supported by the National Science Foundation (CHE-2247214).

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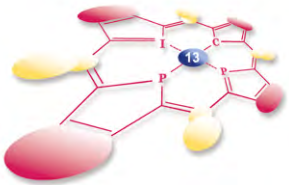

Towards Novel Porphyrinoid Architectures: Synthesis of Porphyrin Analogues with Two Exocyclic Rings

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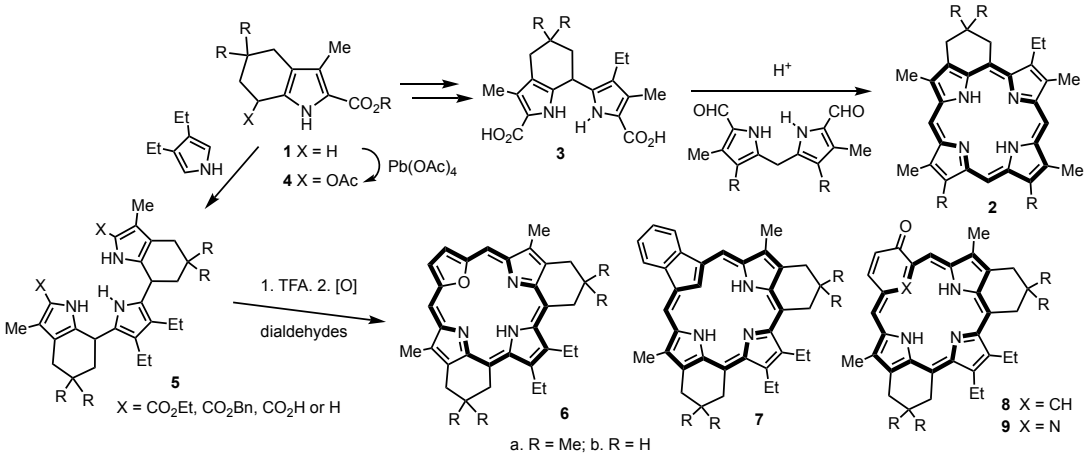
Multistep routes to porphyrin analogues provide the opportunity to determine how structural modifications affect diverse families of porphyrinoids [1]. The construction of intermediates that incorporate carbocyclic rings allows these units to be introduced into a series of analogues, including heteroporphyrins [2], carbaporphyrins [3], oxybenziporphyrins [4] and oxypyriporphyrins [5]. Cycloalka[*b*]pyrroles such as tetrahydroindoles (THIs) **1** have been used to prepare cycloalkanoporphyrins (CAPs) **2** via dipyrrolic intermediates **3** using the MacDonald '2 + 2' strategy [6]. Adaptation of this approach enabled synthetic access to several geochemically significant CAPs, including deoxophylloerythroetioporphyrin. Oxidation of THIs **1** with lead tetraacetate regioselectively afforded acetoxy derivatives **4** and these were condensed with 3,4-diethylpyrrole under mildly acidic conditions to generate tripyrranes **5**. Cleavage of terminal ester groups with NaOH in ethylene glycol, or benzyl esters with H_2-Pd/C, followed by condensation with a series of dialdehydes gave oxaporphyrins **6**, carbaporphyrins **7**, oxybenziporphyrins **8** and oxypyriporphyrins **9**. Although the spectroscopic properties of these porphyrinoids were only mildly influenced by the presence of the exocyclic rings, the study provides proof of concept for the methodology, and this will enable the preparation of further modified porphyrinoid architectures.



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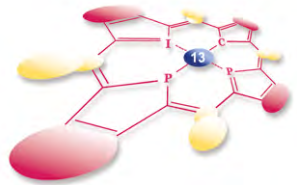

Porphyrin Star Mesogens and the Supramolecular Click Process – a Success Story?

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The supramolecular click process is a self-assembly, in which two complementary star molecules – including a shape-amphiphile - generate dimers optimizing the space-filling in soft mesogenic materials. This procedure operates perfectly for zinc phthalocyanine star-mesogens (Pc) with and without fullerene pseudo guests, which results in ordered phthalocyanine columns with quadruple fullerene helices. Such donor-acceptor structures are of interest for photovoltaic applications, however, the correct alignment between electrodes has to be achieved in future devices. The high clearing temperatures of the Pc materials prevent the conventional preparation of the accurately ordered thin films.[1,2] Owing to their structural similarity, porphyrins are also attractive liquid crystal target molecules possessing typically lower clearing temperatures and a more symmetric molecular structure.[3, 4] Therefore, unconventional porphyrin oligo(thienyl) discotic molecules were synthesized without and with fullerene attached to the conjugated arms to explore their potential for the click procedure.
In this contribution, the challenging synthesis and molecular analysis of the unsubstituted compounds **1**, **3** and fullerene-substituted zinc porphyrin oligo(thienyl) molecules **2**, **4** are highlighted. The thermotropic properties of the neat compounds and their 1 : 1 mixtures are explored using polarized optical microscopy, differential scanning calorimetry and comprehensive X-ray scattering.

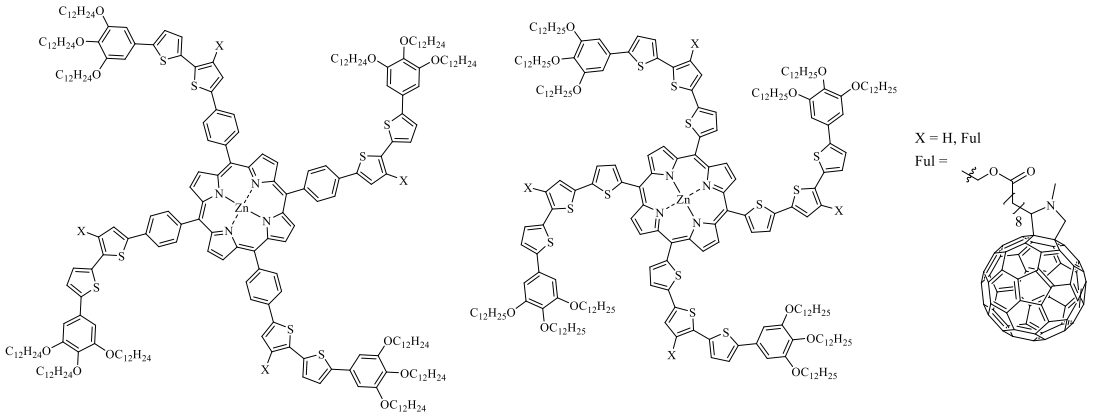

Figure. Star-shaped porphyrin target molecules.

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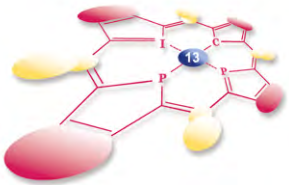

Original fluorescent probes for use in microscopy on a model organism: *Caenorhabditis elegans*

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Following an active substance within an organism is a major stake. Indeed, this allows, among other things, to facilitate the discovery of new targets of interest. To do this, fluorescence microscopy is a particularly well-suited tool. Our research work aims to develop a novel fluorescent labelling technique to follow the fate of a molecule or a microorganism *in vivo*, in the intestine of the nematode *Caenorhabditis elegans* [1]. For this purpose, several fluorescent probes have been designed and synthetized to be coupled to a molecule or a microorganism of interest *via* a potentially cleavable link. The intent would be for the active substance to be released after irradiation to a set wavelength.

Scheme 1. Schematic depiction of a fluorescent probe

After ingestion, the vector's path can be followed thanks to the nematode's transparency, at the bodipy's fluorescence wavelength [2]. Then, after an irradiation at another specific wavelength, the active substance will be released, allowing the study of its fate and impact *in vivo*. This approach will allow the following of the effect of a drug *in vivo*, or could be used as an innovative screening process.

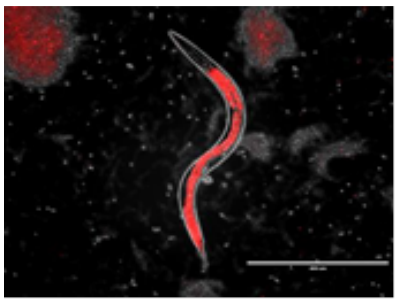

Figure 1. Example of an image obtained by microscopy on *C. Elegans*

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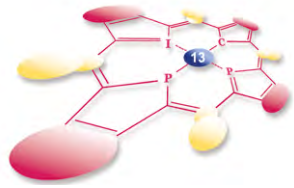

Porphyrin core and triphenylamine connected by azomethine link: Synthesis and characterization.

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[a] *Laboratoire de Chimie et Physique des Matériaux (LCPM), UFR Sciences et Technologies, Département de Chimie, Université Assane Seck de Ziguinchor, Ziguinchor, Sénégal*
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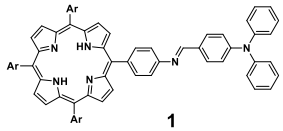
Since the demonstration of the photovoltaic effect on conjugated organic compounds by Professor Pope's group, research on the development of organic or inorganic solar cells has experienced considerable growth [1]. Nowadays, organic solar cells, with an efficiency of over 10%, have several advantages over their inorganic counterparts: they are cheaper, less polluting, and more environmentally friendly during their manufacturing process. In practice, an organic solar cell is composed of an active organic layer sandwiched between the anode and the cathode. The organic layer consists of p-type materials, which are organic electron-donating compounds, and n-type materials, which are predominantly organic electron-acceptor compounds [2].
In this context, our main research objective is the synthesis of polyconjugated molecules containing both an electron-donating core and an electron-accepting core [3]. To achieve this, we have chosen two molecules: a free-base porphyrin (as an electron acceptor) and triphenylamine (as an electron donor). The two molecules will be fused through an azomethine linkage to create a series of three new porphyrin chromophores that are potential candidates for use in organic solar cells.



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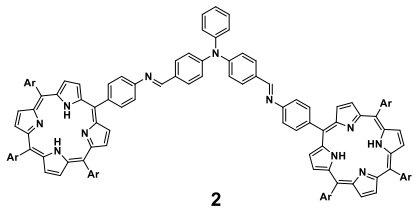

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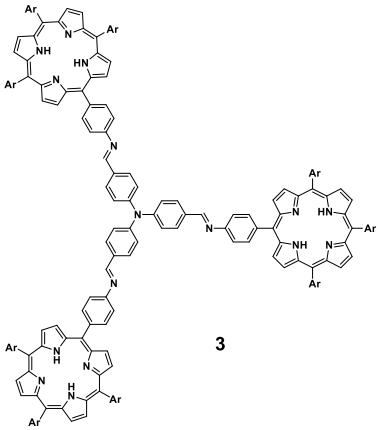

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Combined studies using high-resolution NMR spectroscopy and mass spectrometry have unequivocally confirmed the formation of the three porphyrin chromophores. The initial results obtained from photophysical and electrochemical studies will be discussed in this presentation.

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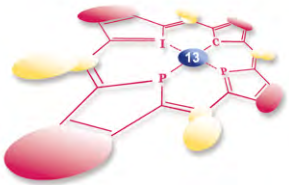

Porphyrin-based lipid nanoparticles vaccine for adjuvants screening and rapid induction of tumoricidal CD8+ T cells

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CoPoP liposomes containing cobalt porphyrin–phospholipids are demonstrated as a potent delivery system for cancer vaccines. His-tagged short peptides can be displayed on its surface and co-delivered with adjuvants to induce an anti-tumor effect. Herein, we iteratively screen a panel of 22 varying lipid-phase immunostimulatory vaccine adjuvants in mice for the capacity to induce rapid T cell induction based on CoPoP liposome. CL401, a dual TLR2/7 adjuvant was identified to induce T cells faster than others based on improving drainage and uptake to immune cells in lymph nodes. Additional rounds of adjuvant screening identified CL401-complementary TLR4 (3D6A- PHAD) and TLR8 (motolimod), and inflammasome (QS21) adjuvants that further enhanced T cell responses and combined to yield synergistic cytokine secretion patterns in antigen-presenting cells. Co-delivery of adjuvants and antigens was found to be critical for potent immune responses. The integrated adjuvant-peptide-lipid nanoparticles gave rise to immune responses that regress large established tumors, inhibit metastatic disease, and synergize with immune checkpoint blockade without overt toxicity or reactogenicity. The use of adjuvant screening holds considerable upside for cancer vaccines and the development of new active immunotherapy approaches.

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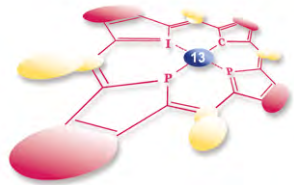

Photodynamic therapy of Sn-tetra pentafluorophenyl porphyrin loaded onto spermine modified carbon nanospheres for enhanced cancer selectivity

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Photodynamic therapy (PDT) is a minimally invasive treatment modality for diseased cancer cells, which uses laser light of appropriate wavelength and a photosensitizer to generate cytotoxic reactive oxygen species (ROS) including singlet oxygen, that eradicate diseased cells [1,2]. Sn 5,10,15,20-tetra pentafluorophenyl porphyrin containing 3-hydroxypyridine axial ligands, Fig. 1, are used for PDT against triple negative breast cancer cells (MDA-MB-231) when alone or when conjugated to spermine modified carbon nanospheres (sper-CNS) through nondestructive noncovalent interaction namely π-π stacking, Fig. 1 to form porphyrin – sper-CNS. The conjugate resulted in the lowest viability of 16.1% when compared to individual components. The cellular uptake studies were also performed, and it was observed that spermine enhances the cellular uptake of conjugates. The sper-CNS enhanced the singlet oxygen genarating ability of the porphyrin.

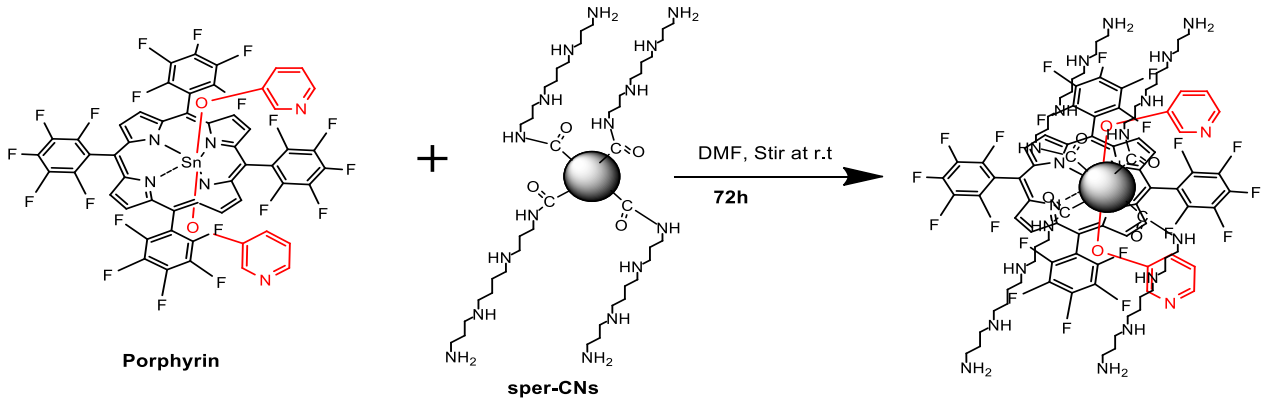

Fig. 1. π-π stacking of the porphyrin onto sper-CNS

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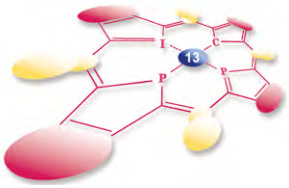

Fabrication and Characterization of Open-shell [3]Triangulene-fused Porphyrins

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On-surface synthesis under ultra-high vacuum conditions has emerged as an appealing strategy for the fabrication of surface-supported nanostructures [1], which can directly be accessed by local-probe techniques such as scanning probe microscopy, allowing for their *in situ* structural and electronic characterization with sub-molecular resolution. Among such nanostructures, π-extended porphyrins (Pors) represent an interesting target due to their unique structural and optoelectronic features.

Recently, our group has reported the fabrication and atomic-scale characterization of some novel open-shell phenalenyl-based π-extended Pors [2] which were obtained on Au(111) *via* on-surface cyclodehydrogenation reaction at 300 ºC from suitable Por precursors. Interestingly, further thermal annealing (i.e., 325 ºC) of the latter surface-supported monomeric Pors triggered an *inter*molecular coupling reaction leading to the formation of π-extended Por nanotapes which retained the open-shell character of the π-extended Por precursors [3].

As an extension of that work, we investigated here the effect of further increasing the π-extension of the surface-supported Pors by "fusing" them into two (Figure 1a) and four (Figure 1b) [3]triangulene moieties. Such nanostructures, which were fabricated through cyclodehydrogenation reaction of adequate Por precursors bearing two or four 9-(2,6-dimethylphenyl)anthryl moieties at their *meso* position, were characterized by STM and nc-AFM. These novel nanostructures present an open-shell character which makes them promising nanomaterials for future-applications in molecular electronics and spintronics.

Figure 1

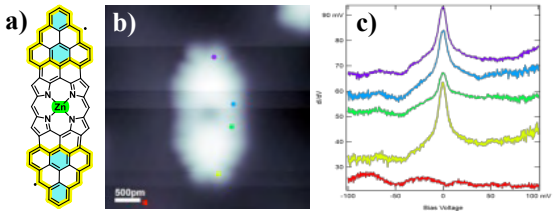
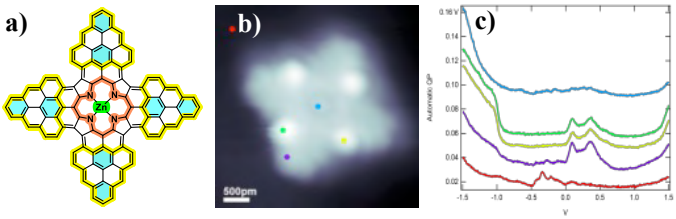


Figure 2



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POSTERS

Optical Oxygen Sensing with Luminescent (Surface-Anchored) Metal Organic Frameworks

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Porphyrin derivates belong to the most prominent luminescent indicators for optical sensing of molecular oxygen. Additionally, they constitute excellent building blocks for Metal Organic Frameworks (MOFs), providing thermal stability, permanent porosity and high accessibility to gases in combination with typical photophysical properties of the porphyrins. Porphyrinic and other MOFs have emerged as a promising class of sensing materials, including those for oxygen measurement. Especially PCN-224, built of Zr_6 clusters and metal(II)-tetrakis-(4-carboxyphenyl) porphyrin (M(II)TCPP, M = Pt, Pd), was found to have promising oxygen sensing properties.(1)

Herein we report new crystalline MOFs with partly fluorinated porphyrinic blocks and significantly improved photostability due to electron-withdrawing substituents and less reactivity towards singlet oxygen. Since immobilization of the MOF crystals is crucial to provide a competitive sensor material, Surface-Anchored MOFs (SURMOFs) have been fabricated on functionalized glass and flexible poly(ethylene terephthalate) support coated with a thin Indium-Thin-Oxide layer. The layer-by-layer dipping procedure provided SURMOFs with a homogenous surface and adequate stability. The SURMOF composed of Pt(II)TCPP and Indium-Oxo-Clusters shows optimal sensitivity at ambient conditions, whereas trace sensors can be manufactured by substituting Pt(II) with Pd(II) in the porphyrin core.

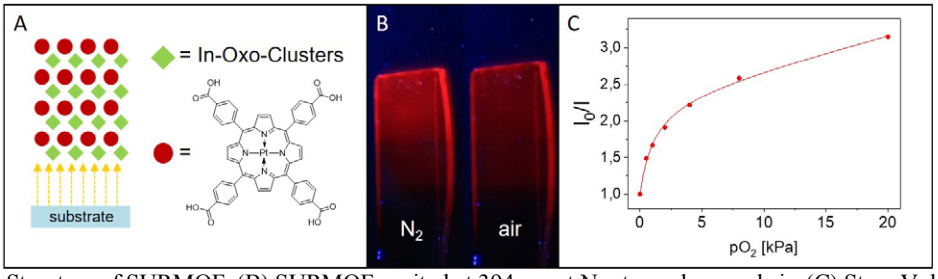

Figure 1: (A) Structure of SURMOF. (B) SURMOF excited at 394 nm at N_2 atmosphere and air. (C) Stern Volmer plots for SURMOF at dry gas atmosphere.

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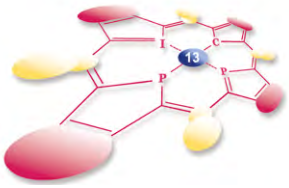

Vitamin B_{12} Conjugates for Targeted Cancer Therapy

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Despite the high efficacy offered by modern therapeutic and diagnostic treatments for cancer, a key obstacle continues to be severe secondary effects. These side effects are mostly caused by a lack of selectivity towards tumor cells over healthy tissue. [1] Hereby, we report the synthesis and analysis of differently modified bioconjugates of Cbls with therapeutic or diagnostic agents. [2] The binding of these conjugates to proteins such as transcobalamin II (TCII) is reported. Radiolabelling studies are discussed to apply promising B_{12}-conjugates for *in vivo* studies in mice.[3]

Acknowledgment: We thank the Forschungskredit (Grant Number: *FK-20-096*) and the Graduate School of Chemical and Molecular Sciences Zurich (CMSZH) for their financial support.

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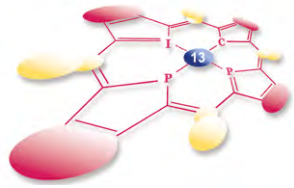

Carboxylate BODIPY functional zinc-based metal-organic frameworks: Towards solid state luminescence

Clément Michelin[a], Marion Leroux[a], Alexis Tran[a], Damien Boyer[a], Federico Cisnetti[a]

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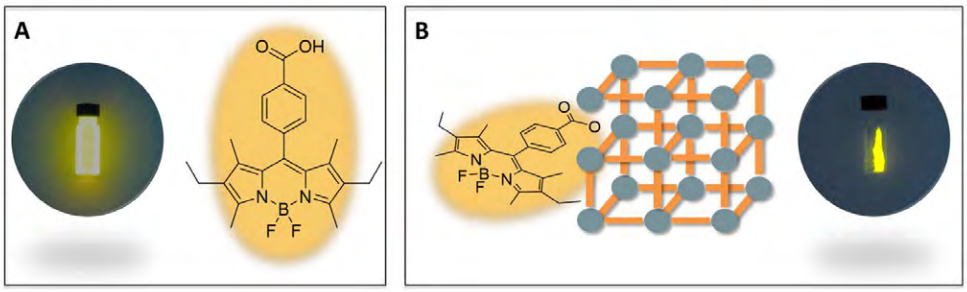
BODIPYs are widely used organic fluorophores thanks to their excellent fluorescence properties. They have very good quantum yields, extinction coefficients, thermo- and photo-stability properties, and tuneable fluorescence emission from the visible to the near-infrared. As a result, these molecules are used in a wide range of fields, from bioimaging to photoactive materials or even as sensors.[1],[2] However, they do have certain limitations. Indeed, their low Stokes shift (around 30 nm) is an intrinsic one. In addition, due to intermolecular interactions such as π-π stacking most BODIPYs suffer from the Aggregation-Caused Quenching (ACQ) phenomenon, which prevents their fluorescence emission in the solid state. To overcome the latter problem, the idea of dispersing Bodipys in a crystalline structure has emerged. Several studies have already demonstrated the possibility of integrating these compounds into polymeric structures or Metal-Organic Frameworks (MOFs).[3]

MOFs are considered versatile self-assembled porous crystalline solids. The zinc-based MOF with a terephthalate ligand, called MOF-5, is the most described in the literature due to its simple access and low precursor cost. Among other conditions, this MOF is accessible at room temperature within a few hours using bases to accelerate the crystallization mechanism. These mild conditions are compatible with organic molecules such as BODIPYs.

Here we report an easy, room-temperature method for incorporating carboxylated BODIPYs into MOF-5 by replacing a certain amount of the ligand with the luminescent molecule.[4] We demonstrated the successful integration of BODIPYs into the MOF structure and this made it possible to observe solid state fluorescence.



Bodipy structure and solution fluorescence (Fig A), Bodipy/MOF structure and solid state fluorescence (Fig B)

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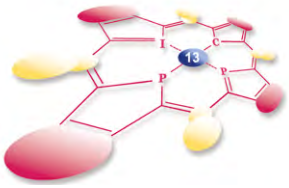

Nickel Corrole Catalyst for Hydrogen Evolution Reaction: Reactivity and Spectroscopy

Sruti Mondal[a], and Zeev Gross[a]

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Developing catalysts not based on expensive metals is still a major challenging research area worldwide, particularly in hydrogen gas production. There has been a significant increase in the application of metallocorroles [1] with first-row transition metal as electrocatalyst over the past decade. Herein, we report two new nickel corrole complexes as electrocatalysts for hydrogen evolution reaction (HER) [2]. In the present work, two nickel corrole complexes were synthesized with electron-withdrawing *meso*-substituents and with two sulfonamide substituents on the most reactive β-position of the corrole macrocycle. Both complexes were spectroscopically characterized by NMR, electronic spectra, ESI-MS and electrochemistry. It revealed that the electron-poor nickel corrole complexes perform better as electrocatalysts for HER under homogeneous catalysis.

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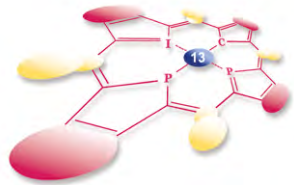

Intriguing Selectivity and Flexibility of an Expanded Porphyrinoid Ligand

Viola Munzert[a], **Doris Kunz**[a]

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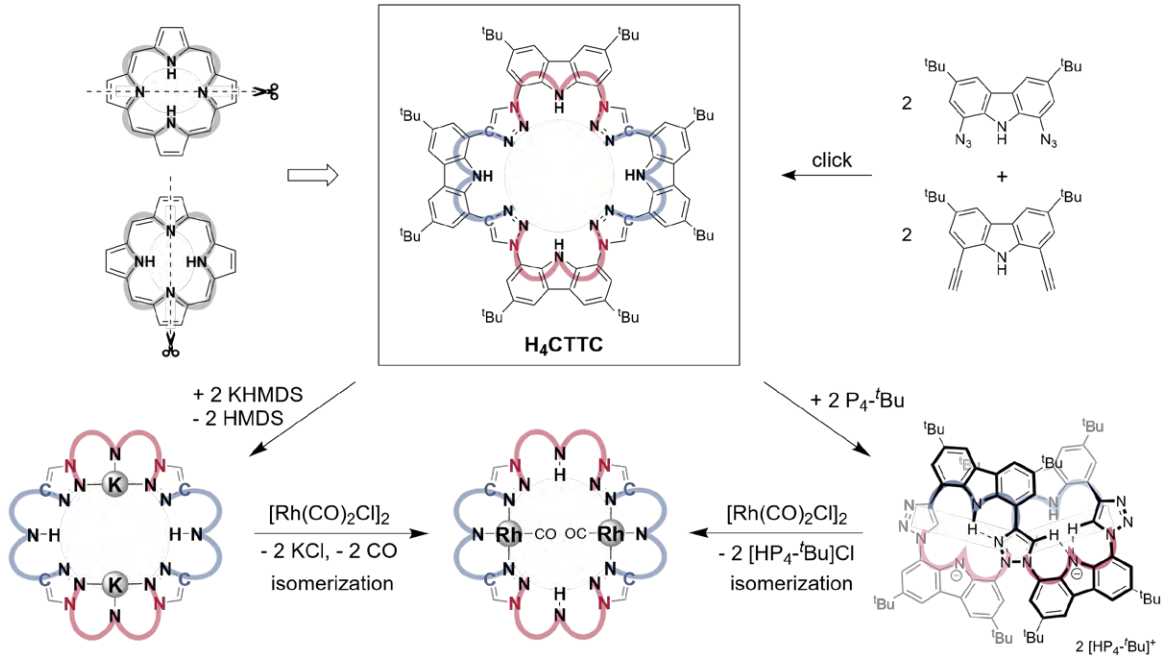

The synthesis of a new expanded porphyrinoid macrocycle (*cyclo*-tetra(triazolyl carbazole), H_4CTTC) in a copper-catalyzed click reaction was developed in our group.[1] Due to the binding of the triazole via either the C or N atom to the carbazole moieties, two different pairs of NNN-pincer-like pockets (N-linked pocket (red), C-linked pocket (blue)) are formed, which can be regarded as half a porphyrin each. After deprotonation of the carbazole-NH units, the saddle-shaped quatrefoil CTTC ligand allows the complexation of up to four metal cations nearby. To investigate possible cooperative effects in multimetallic CTTC complexes, we monitored the metalation of the pincer-like pockets. Despite isomerization and equilibria between different metalated states, we succeeded in obtaining some complexes selectively. Li and K exhibit a clear preference to occupy the N-pocket, whereas after transmetallation the dimetallic rhodium complex isomerizes from the N- to the C-linked pockets as elucidated by NMR studies. In the solid state, we observed intriguing structures of saddle-shaped stacked dimers for the mono- and dipotassium complexes as well as a figure-eight motif for the [H_2CTTC]-dianion with weakly coordinating cations.

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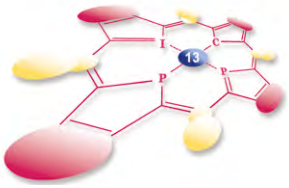

Vacuum Deposition of Porphyrins *via* Electrospray Ionization Ion Beam Technique

Florian Münster[a], Lukas Heuplick[a], Grigori Pasko[a], Jan Herritsch[a], J. Michael Gottfried[a]

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Developing novel and complex porphyrins poses an exciting challenge, yet their stability often remains a limiting factor. The controlled surface environment in a vacuum can provide a stabilizing effect, thus facilitating the synthesis and exploration of these molecules. However, depositing suitable precursor molecules for exotic tetrapyrroles, such as the 'embryo' corrole or tetrapyrroles with large substituents, can be challenging. A viable strategy to overcome these preparation-related limitations is electrospray ionization ion beam deposition (ESI-IBD), which allows for the deposition of mass-filtered ions. While this technique is becoming increasingly popular, for example for the deposition of large biomolecules, the precise chemical state of the deposited molecules often remains elusive. For this study, we chose meso-tetraphenylporphyrin as a well-established model system to investigate the deposition process of such tetrapyrroles as well as the chemical state of the molecule after deposition via ESI-IBD. X-ray photoelectron spectroscopy (XPS) revealed the presence of an N-protonated species. Additionally, utilizing scanning tunneling microscopy (STM), we observed self-assembled islands composed of multiple distinguishable species, in agreement with the existence of N-protonated porphyrin molecules.

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Modular Setup for Broadband Magnetic Resonance Studies at THz-frequencies

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We report on the recent development of a high-frequency rapid scan electron spin resonance (FRASCAN) spectrometer at the Brno University of Technology. The basic principle of frequency rapid scan will be explained and compared to conventional methods. The FRASCAN operates in induction mode using quasi-optics with a superheterodyne detection scheme. Fast frequency sweeps of the order of 1000 THz/s allow access to spin relaxation of the order of 1 ns [1,2], in a frequency range of 80 GHz to 1100 GHz [3], at temperatures from 1.8 K to 300 K, and at magnetic fields up to 16 T. We developed several sample holders for performing measurements on liquids, single crystals, and air-sensitive samples, including the possibility of photoexcitation [3,4]. In addition, we developed a carousel sample holder for pressed powders that accommodates up to 6 samples, avoiding the time-consuming event of loading the probe into the cryostat and cooling down process. The carousel holder can be used for quantitative ESR. The FRASCAN is controlled by home-written software in LabView, allowing it to run experiments in an automatic mode controlled by scripts [5]. Frequency rapid scan experiments on an oriented single crystal of LiPc will be presented along with a simulation for the calculation of the relaxation times. Furthermore, additional capabilities of FRASCAN are demonstrated using frequency-detected magnetic resonance spectra as a function of the orientation for a single-crystal of copper acetate [6] and frequency-field ESR maps for Mn12 and TEMPO [7]. The FRASCAN is built on a remotely controllable movable table on trails that can be fully removed, exchanging the quasi-optics ESR table with a desk on trails containing a Bruker Vertex 80v spectrometer with adapted coupling mirrors and optical pipes in a probe to perform Fourier-transform infrared magnetic spectroscopy (FIRMS) in transmission mode, using as detectors either an external bolometer or a composite silicon bolometer placed right under the sample within the superconducting coil [8].

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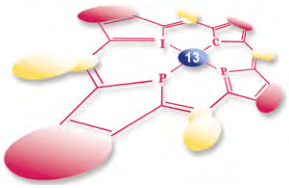

Solvent-Free Synthesis of Alkali Metal Porphyrins and Corroles

Leonard Neuhaus[a], Florian Münster[a], Kassandra Zoltner[a], Stefan R. Kachel[a], Jan Herritsch[a], Lukas Heuplick[a], Peter Schweyen[b], Martin Bröring[b], J. Michael Gottfried[a]

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Tetrapyrroles such as porphyrins and their metal complexes play important roles in living organisms and in modern technologies, e.g., in energy storage, (electro-)catalysis, and sensor systems. Since their properties are heavily influenced by the central metal atoms, the synthesis of new tetrapyrrole complexes has been intensely researched for several decades. Reactions in thin molecular films under vacuum conditions allow the solvent-free synthesis of new metal tetrapyrrole complexes. While various transition metal complexes have been synthesized in this way, much less is known about their alkali metal analogues.
Here, we report the thin-film vacuum synthesis of Li and Cs alkali metal complexes of tetraphenylporphyrin (H_2TPP) and an oktaalkylcorrole (H_3HEDMC). The reaction progress is monitored by X-ray photoelectron spectroscopy (XPS). Using Temperature-programmed reaction (TPR) experiments combined with mass spectrometry, we were able to unambiguously identify the reaction products. With caesium, H_2TPP and H_3HEDMC form dicaesium complexes (Cs_2TPP and HCs_2HEDMC), which are stable up to at least 550 K. The smaller Li atoms react with H_3HEDMC forming a series of complexes containing 1 to 4 Li atoms. DFT calculations indicate that the Cs_2TPP complex has a bipyramidal structure with Cs on both sides of the molecular plane, whereas in Li_4HEDMC the Li atoms assume a tetrahedral arrangement.

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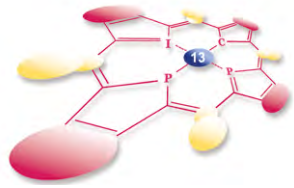

Recognition of atomic-level difference in porphyrin dyads for self-sorted supramolecular polymer growth

Sangyoon Oh[a], Woo-Dong Jang[a]

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Porphyrin dyads (PD_MS, where M = Zn and Cu) composed of diphenylporphyrin and tetraphenylporphyrin units, designated as $^{D}PD_MS$and $^{T}PD_MS$, respectively, exhibited remarkable differences in the molecular assemblies depending on the coordination metal ion. Furthermore, $^{T}PD_MS$ showed self-sorting behavior during the formation of supramolecular assemblies through the recognition of atomic-level differences.

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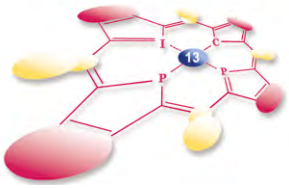

Design of a Coupled Polymerization and Depolymerization Cycles System Based on Nucleophilic Aromatic Ring-Opening Polymerization/Fused-Porphyrin project

Uka Oji, Wang Hong

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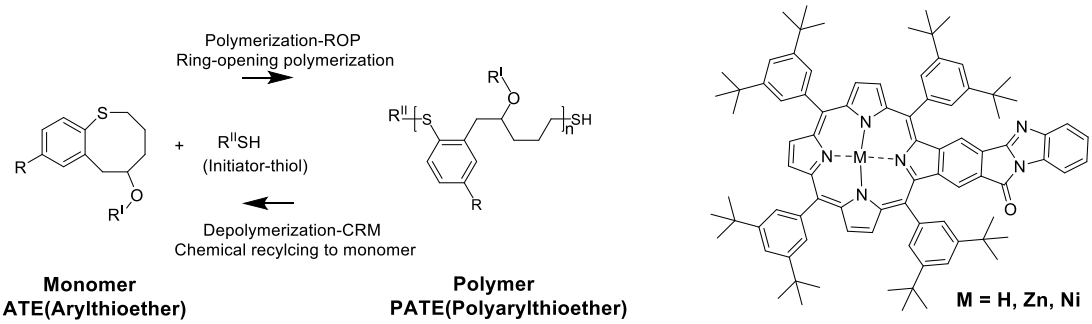
Ranging from traditional food packaging and clothing to current small and large electronic devices and automobiles, plastics serve to fulfill diverse demands in our daily lives. However, global plastic waste generation is dramatically escalating and contributes to huge plastic pollution at the end of the life cycle of plastics. Mechanical recycling is a common method of recycling plastics but has some shortcomings. Chemical recycling is emerging as a promising alternative method due to its high efficiency, simple preliminary steps and ability to retain the intrinsic properties of the polymer [1]. My research proposal aims to present a chemically recyclable polymer system, where polymers (poly arylthioethers) can be efficiently synthesized through ring-opening polymerization (ROP) and later recycled to monomers by ring-closing depolymerization, in an efficient circular-type system. It is anticipated that this practical approach of a closed-loop method will address the end-of-use problem of polymer materials. Another project involves the synthesis of pi-extended porphyrins where the porphyrin is fused with different functional groups at the β,β' position eg. Imidazole group derivative as shown below. Such fused porphyrin molecules have been shown to have distinct optical and electronic properties [2]. The goal is to investigate the synthesis, characterization and metal (M) coordination abilities of the porphyrin core.



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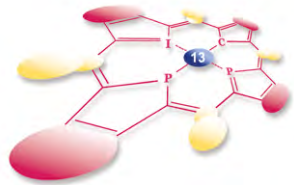

Synthesis and evaluation of aza-BODIPY conjugates

Mistura Olajuwon[a], Simran Dhingra[a], Seetharama D. Jois[b], Frank Fronczek[a] and Maria da Graça H. Vicente[a]

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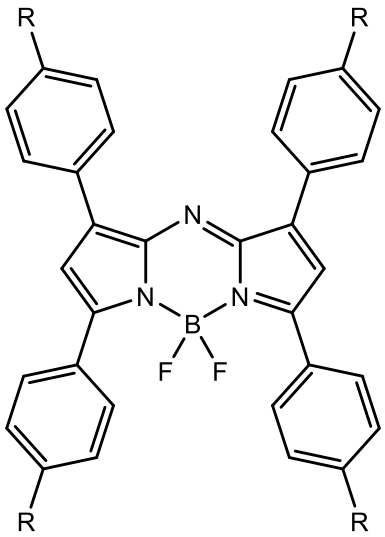
Aza-BODIPYs are structural analogues of BODIPYs that are obtained by replacing the meso-carbon of the boron dipyrromethene core with an aza-bridge [1]. We will present the synthesis of a new series of aza-BODIPYs bearing up to two amino and/or isothiocyanate groups [2]. The conjugation of these aza-BODIPYs to peptides and tyrosine kinase inhibitors (TKI) will be discussed, and the properties of the resulting conjugates will be evaluated and compared.



R = H, NH_2 or NCS

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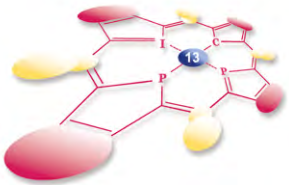

Synthesis and Physicochemical Properties of Tetrafluorobenzo-[α]-fused BOPYPY Dyes

Sebastian Oloo,[a] Guanyu Zhang,[a] Petia Bobadova-Parvanova[b], Seleen Al Horani,[b] Masa Al Horani,[b] Frank Fronczek[a], Kevin M. Smith[a] and Maria da Graça H. Vicente[a]

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Novel unsymmetrical [α]-benzo-fused BOPYPY dyes are synthesized from 4,5,6,7- tetrafluoroisoindole [1] and 2-hydrazinopyrazine or 2-hydrazinopyridine. To investigate the reactivity and properties of the dyes, regioselective substitution reactions at the periphery of the tetra-fluorinated BOPYPYs were performed using various nucleophiles [2]. α-Substituted derivatives were also produced from Pd-catalyzed reaction with the α-bromo BOPYPY derivative. The spectroscopic properties of these new dyes were investigated and compared with those previously reported for non-fluorinated analogs [3, 4].

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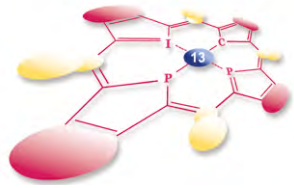

Photochemical Magnetic Switch of Homoleptic Metal (II) Complexes of azadipyrromethene and their Corresponding aza-BODIPY

Morris Oyelowo[a], Jacob Schaffner,[b] David Blank,[b] Christopher Ziegler,[c] Viktor Nemykin,[a]

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[c] *Department of Chemistry, University of Akron - Akron, OH USA*

The 1,7-bis(2,6-ditert-butylphenyloxy)-3,5-diphenyl aza-BODIPY, 1,7-bis (2,6-ditert- butylphenyloxy)-3,5-(4-bromophenyl) aza-BODIPY and their respective homoleptic transition metal DIPY were prepared by oxidizing their respective diphenol and tetraphenol derivatives (Figure 1). The diradicaloid nature of these compounds was investigated using a wide range of spectroscopic methods, including NMR, mass spectrometry, EPR, UV-Vis, fluorescence, IR spectroscopy, transient absorption spectroscopy as well as variable-temperature X-ray crystallography. DFT and TDDFT calculations, variable-temperature NMR and EPR data suggest a singlet ground state for the aza-BODIPY based diradicaloids. Electrochemical and spectroelectrochemical data indicate several processes in these systems. Transient absorption spectroscopy shows a dramatic decrease in the excited state lifetime of the diradicaloids compared to that of the phenols. DFT and TDDFT calculations were used to explain the unusual spectroscopy observed in the target compounds.

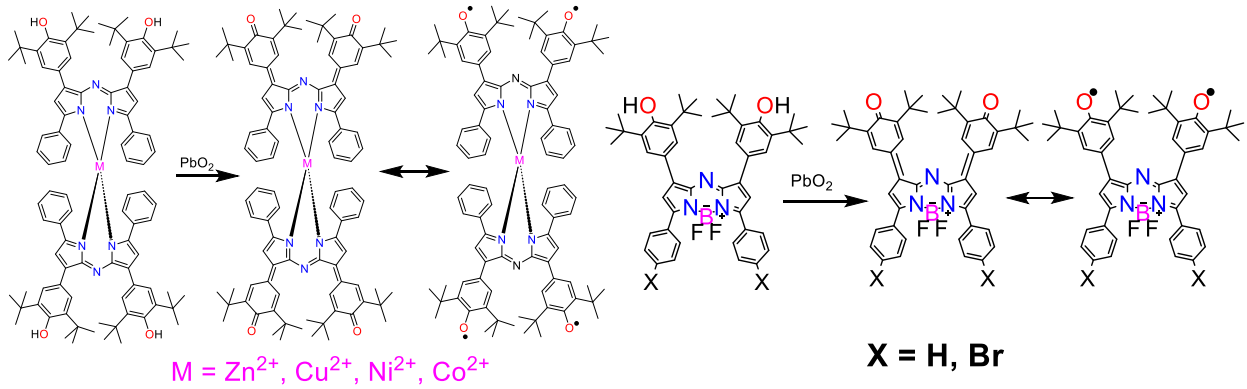

Fig.1. Representative example of transition metal DIPY and their chemically oxidized quinone in resonance with tetraradicaloid and aza-BODIPY based diradicaloid.

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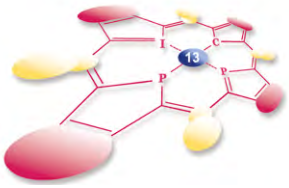

Expanding the Horizons of Photodynamic Therapy: Indium Metalated Pyridinyl-based *trans*-A_2B_2 Porphyrins as Novel Anti-biofilm Agents

James Oyim[a], Edith Amuhaya[b], Tebello Nyokong[a*]

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Modern medicine faces numerous challenges with regards to antibiotic-resistant bacteria and formation of biofilms [1]. To address this urgent issue, researchers are examining novel biofilm-fighting techniques to replace or enhance antibiotics. Photodynamic therapy (PDT) is a pioneering technique that can eliminate biofilms with minimal resistance [2]. In this study, we shed light on the remarkable properties of some indium-metalated pyridinyl-based *trans*-A_2B_2 Porphyrins (**1, 2, 3** and **4,** structure shown in **Fig. 1.**), which, due to their unique structures and photophysical properties, displayed enhanced PDT activity against both planktonic cells and *S. aureus* biofilms.

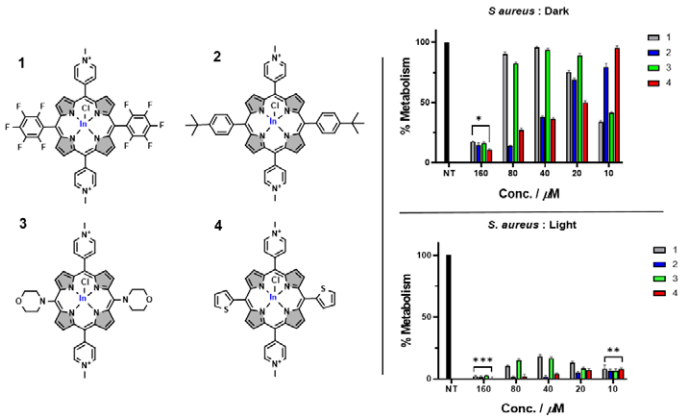

Fig. 1. Porphyrin structures (**1-4**) and biofilm viability of *S. aureus* in the dark and upon treatment with gradient concentrations of **1-4** and after illumination with 415 nm LED light at a constant irradiance of 240 mW·cm^{-2} at a constant dose of 524 J cm^{-2} for 30 minutes. Cell viability was determined using resazurin cell viability assay with none-treated samples abbreviated by **NT**.

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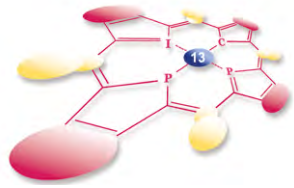

New alternative reaction media for the sustainable synthesis of metallophthalocyanines in solution

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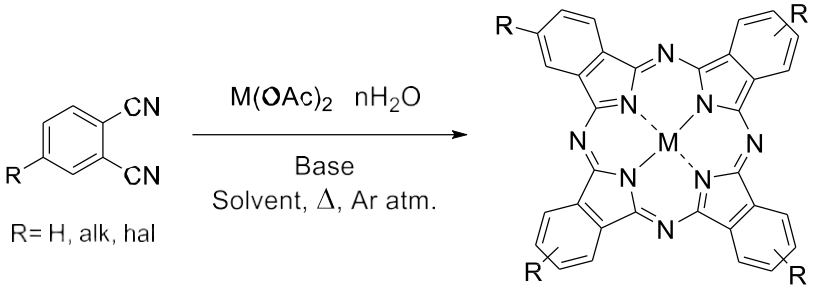
Over the past two decades, in order to address the growing environmental awareness, scientific efforts have been focused on minimizing the production of waste of chemical processes, as well as developing new and environmental friendly approaches in organic synthesis. In this context, the use of alternative and cost-effective reaction media with respect to conventional solvents provides a promising strategy for more sustainable synthetic approaches [1-3]. This contribution explores the use of non-toxic, low cost, biodegradable, and potentially recyclable solvents, such as anisole, glycerol, propane-1,2-diol, and polyethylene glycol (PEG) as reaction media for the metal-templated cyclotetramerization of several phthalonitriles to obtain the related metallophthalocyanines. The environmental and economic sustainability of the syntheses herein displayed will be evaluated by calculating the E-factor, a green chemistry metric defined as the ratio of the mass of waste generated per mass of product obtained in the process, and by estimating the cost of each derivative.



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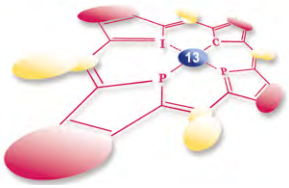

Synthesis and photoinmunotherapeutic abilities of antibody-Aza-BODIPY bioconjugates

Irene Paramio[a], Mireia Jordà-Redondo[b], Tomás Torres[a,c,d], Santi Nonell[b], and Gema de la Torre[a,c]

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Photodynamic Therapy (PDT) is a photochemistry-based cancer treatment modality that uses a photosensitizer (PS) and high-penetrating light to generate reactive oxygen species (ROS). These reactive products can oxidize the key components within the illuminated tissue, causing a local cytotoxic effect.[1] Immunotherapy, also a revolutionary cancer treatment, relies on the activation of the immune system to eliminate cancer.[2]
Combining PDT with immunotherapy (photoimmunotherapy, PIT) may trigger a synergistic effect that can, on one hand, enhance the selectivity towards tumour tissues and, on the other hand, further the therapeutic efficacy to prevent tumour metastasis and recurrence.[2] An approximation to this combined therapy consists in forming a bioconjugate by covalent linkage of a PS to a monoclonal antibody (mAb). In PIT, the PS imparts phototoxic properties to the hybrid, while monoclonal antibodies act as targeting molecules, directing the PS to the desired cells or tissues. [3]
Here, we have selected the Aza-BODIPY dye as PS to prepare the targeted bioconjugate with a mAb, since this dye shows excellent optical and thermal stability and especially, NIR absorption and emission maxima within the therapeutic window [4]. The designed Aza-BODIPYs must have i) a long spacer between the PS and the mAb, to preserve the recognition of the antibody by specific receptors, and ii) hydrophilic substituents around the PS core, to prevent aggregation issues and increase its water solubility. The PSs are functionalized with N-hydroxysuccinimide (NHS) activated ester for the conjugation to mAbs. The targeting specificity and therapeutic effects of the bioconjugates over breast cancer cells have been evaluated.

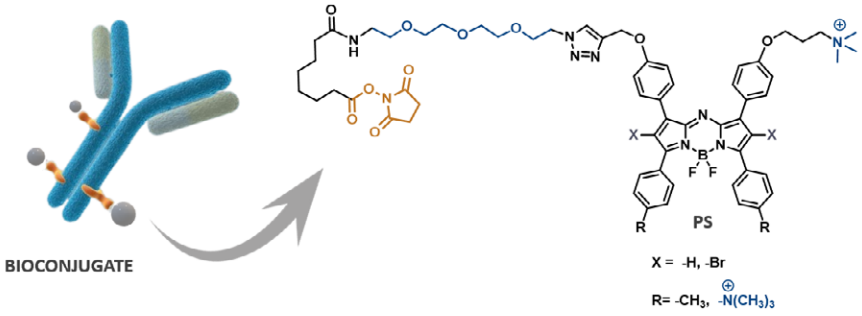

Figure 1: Illustration of bioconjugate and Aza-BODIPY chemical structure.

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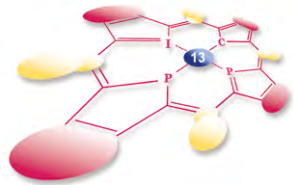

Design and Synthesis of conjugated Donor-Acceptor Covalent Organic Frameworks based on pi-extended porphyrin and phthalocyanine

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Covalent Organic Frameworks (COFs) are a type of porous and crystalline materials that possess a unique structure consisting of organic building blocks connected by robust covalent bonds. These frameworks possess fascinating characteristics because of their clearly defined structures and adjustable and tuneable functionality [1]. Therefore, these COFs show great potential for practical applications in catalysis, energy conversion and storage, gas storage, and separation. The pore size of the COFs, which was restricted within 2-5 nm at earlier time, is a primary factor to consider for these applications. Yet, Jin et.al.,2013 [2] reported that conjugated COFs, formed through a donor-acceptor process, exhibited a pore size of 5.3 nm. In the conjugated COFs, the π-electrons are arranged in a stacked and interconnected manner to create two-dimensional COFs. Larger pore size results in better stability, better gas separation and charge transfer [3]. The objective of this research is to develop a synthetic approach for building a conjugated donor-acceptor COF using pi-extended Porphyrin and Phthalocyanine. Porphyrins are known for their high electron density and their 18 π-electron aromatic macrocyclic structure and often serve as electron donors in molecular dyads. However, when a transition metal is introduced, its function can be changed to an electron acceptor. Phthalocyanines usually function as electron donors. It is expected that the constitution of COFs using pi-extended porphyrins and phthalocyanines will offer distinct structures and properties. The photophysical properties including photoinduced electron transfer and charge separation will also be investigated.

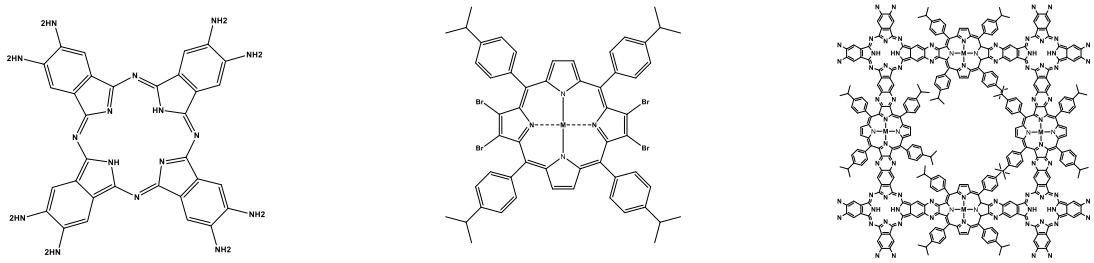

Fig: Schematic illustration of proposed conjugated COF

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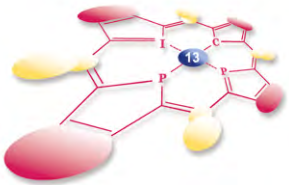

Separation, spectroscopy, and applications of perfluoroalkyl phthalocyanines with different degrees of substitution

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The reaction of two different, but symmetrical phthalonitriles (A and B), could yield up to 4 low (C_2 axes) and 2 high-symmetry (C_4 axes) phthalocyanines (Pcs): A_4, A_3B, AABB, ABAB, AB_3 and B_4, *Figure 1*. Separating complex mixtures of Pcs requires structural analysis (where symmetry and hydrophobicity play a big role), coupled with a range of purification and isolation techniques, including trituration, fractional crystallization, and chromatography. We report purification strategies, spectroscopy, and applications of fluoro- and perfluoroalkyl A_nB_m (n + m = 4, n, m ≥ 0) Pcs. The F_{64}PcCu, *cis*-F_{40}PcCu, and F_{16}PcCu Pcs were used for obtaining conductive films, while some of their anions crystallized as salts and were characterized using X-ray crystallography. [1, 2, 3]

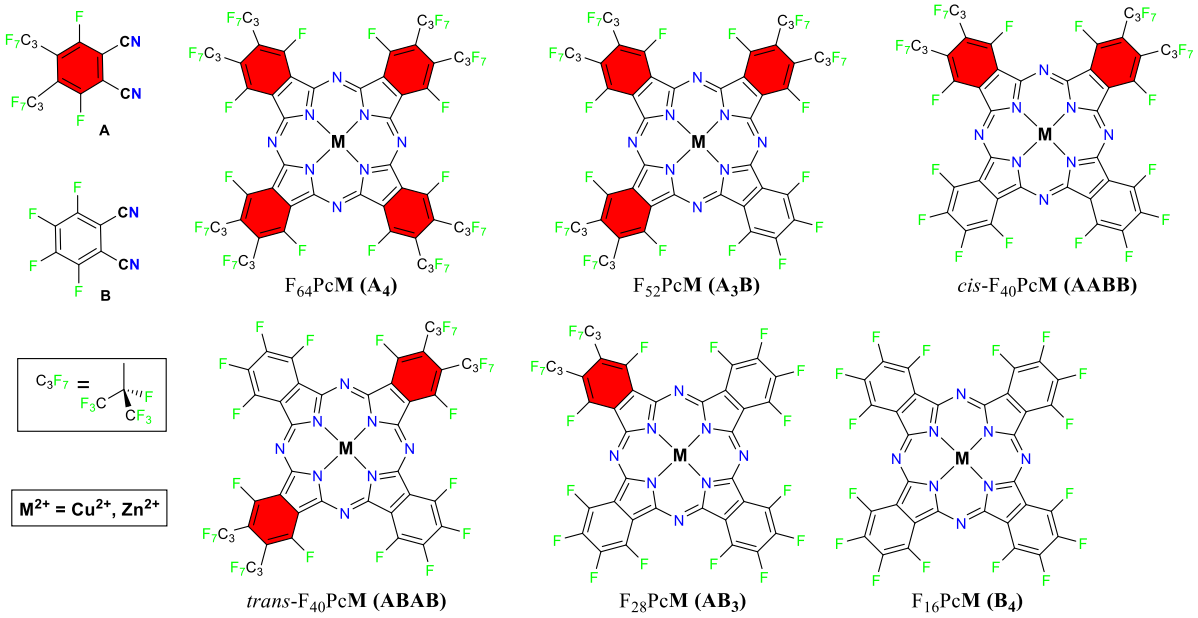

Figure 1. Chemical structures of the perfluorinated Pcs with different degrees of perfluoroalkyl substituents.

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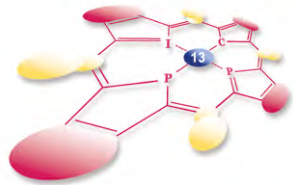

BOIMPYs as new photosensitizers in $^1O_2$ storage and release systems

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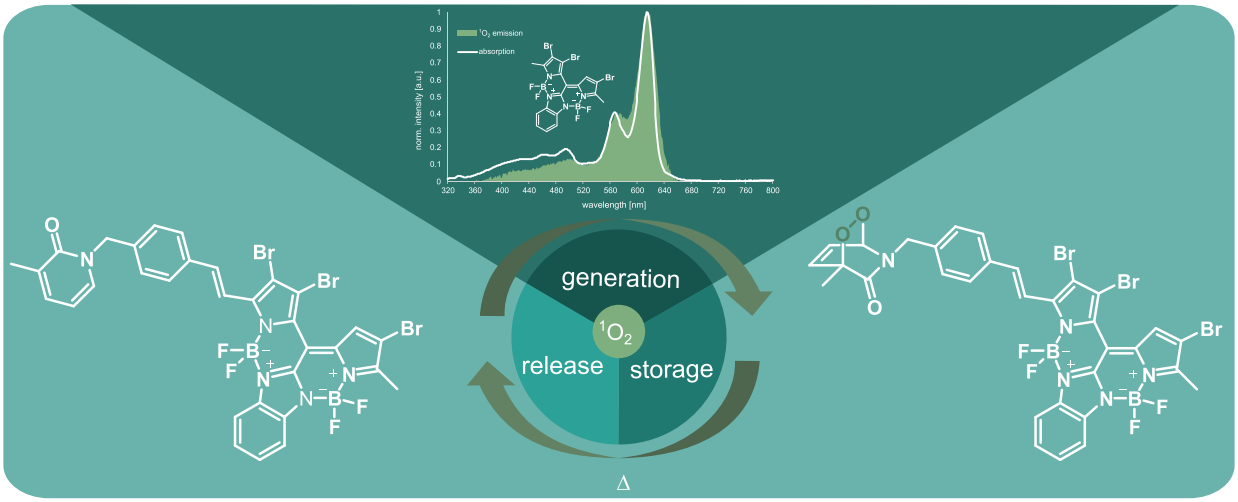
BOIMPYs have recently become available as alternatives to the more established boron dipyrromethene (BODIPYs) that have been investigated as photosensitizers for photodynamic therapy.[1-2] BOIMPYs are structurally characterized by a benzimidazole unit in the *meso* position of dipyrromethene. As such, the framework of BOIMPY can chelate two BF_2 fragments via the pyrrole and the benzimidazole nitrogen atoms, respectively. This structural variation leads to absorptions and emissions in the BOIMPYs that are significantly shifted to longer wavelengths compared to those of the BODIPYs. Hence the optical properties of the BOIMPYs address a region of interest for photosensitization and PDT applications. [2-4]

Supported by theoretical investigations of DE SIMONE *et al.*[4] we have initially investigated brominated BOIMPYs for their ability to act as a $^1O_2$-photosensitizer. Furthermore, we have explored the potential of BOIMPYs to be incorporated into a $^1O_2$ capture, storage and release system. To this end, we have prepared 2-pyridone-functionalized BOIMPYs that are capable of reversible $^1O_2$ binding.[5] We will report here the synthesis and the photochemical properties of these dyads and will confirm their suitability as actors in the time-delayed $^1O_2$-provision for PDT applications.



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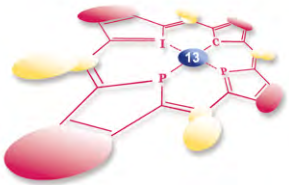

Photo-oxidation with Fluorinated Phthalocyanine Materials: Metal Oxide Supports and Polymer Coatings

Brandon Pineda[a], Reva Pavithran[a], Abdul Azeez[a], Sergiu M. Gorun[a,b], James E. Hanson[a]

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[b] *Center for Functional Materials, Seton Hall University. USA*

Phthalocyanines are versatile and complex structures that have attracted much interest as catalysts. The phthalocyanine F_{64}PcZn[1] was supported on a variety of metal oxides and then embedded in various polymer coatings. These coatings were applied to different surfaces and were then characterized and evaluated as catalysts. The characterization techniques performed on the materials included IR spectroscopy, contact angle, fluorescence, and reflectance UV/Vis. GC analysis was used to evaluate catalysis. These techniques highlighted the characteristics of the materials in their different permutations of support, coating, and substrate. A common factor in all these materials was the phthalocyanine and its chemical behavior when introduced to high-intensity light sources.[2] The catalysis results demonstrated the ability of the phthalocyanine-containing materials to generate singlet oxygen and degrade a variety of organic compounds. The scope of the presentation highlights the characteristics of the different structures and their overall ability to degrade molecules that are susceptible to oxidation.

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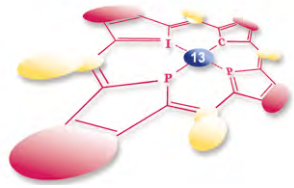

Encapsulation of Perfluorinated Zinc Phthalocyanines in Mesoporous Silicas and Silicates

Jonathan Z Pinnock, Kai N. Hansen, Alexander Y. Fadeev

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This work reports the preparation and characterization of the encapsulated perfluorinated zinc phthalocyanines with general formula F_nPcZn (n=16 and 64) in ordered mesoporous silicas (SBA-15 and SBA-16) and Halloysite mineral and the use of these materials as oxidation photocatalysts. To encapsulate the phthalocyanines, we employed the "bottle-around-the-ship" strategy by conducting the synthesis of the SBA's in the presence of F_nPcZn. For Halloysite mineral, the encapsulation was done differently, via the "pore filling technique" followed by the polycondensation of TEOS. The phthalocyanine-encapsulated solids were characterized through solid-state UV-Vis spectroscopy, TGA, TEM, and confocal fluorescent microscopy. According to nitrogen adsorption, the encapsulation preserved the mesoporous structures and maintained the open pores of the parental silicas. The catalysts prepared demonstrated good activity in the room temperature photo-oxidations of the model compounds. The kinetics of (i) oxidation of the methyl orange dye in aqueous solutions and (ii) neat 2-chloroethyl ethyl sulphide (CEES) was reported. The authors acknowledge support by DTRA.

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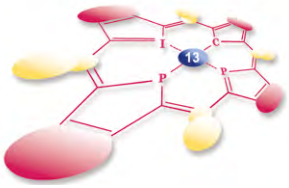

N-alkyl Corrole metal complexes as Catalysts.

Francesco Pizzoli[a], Alessia Fata[a], Sara Nardis[a] and Roberto Paolesse[a]

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In the large family of porphyrinoid, corrole represents a category that has aroused great synthetic and applicative interest in various fields, ranging from sensors to pharmaceutics. Among the numerous derivatives developed in recent years, one class, in particular, has been somehow neglected: N-substituted corroles. These compounds, having chirality induced by the alkylation of the inner core nitrogens, were first synthesized in 1965 by Johnson and Kay [1], but a small number of studies have been published since then, possibly due to low yields and the difficulties in isomers separation [2, 3]. For this reason, we have developed an effective alkylation synthetic strategy starting with the simplest N-methyl derivate, obtaining an increase of two N-methylated isomers as a racemate of 5,10,15-tri-p-tolylcorrole (TTC), decreasing the presence of the unwanted di-methylated corroles [4]. The products were separated into their respective enantiomers by chiral chromatography and then characterized by UV, NMR, X-ray diffractometry analysis and Circular Dichroism. At this point, numerous alkylation tests were carried out changing the chain length, and their complexation reaction has been studied using palladium, cobalt, manganese, copper and iron. Among the numerous possibilities of use of these new compounds, their application as catalysts for coupling reactions of diazo compounds has aroused our interest. There are not numerous examples reported in the literature of corroles used for this type of catalysis, while there are no examples of the use of porphyrinoids in general as enantioselective chiral catalysts[5]. For this reason, methylated TTC complexes were examined to be tested as catalysts in different types of reactions, specifically N-H, S-H insertions and Ylide Formation, comparing yields, recoverability and enantioselectivity.

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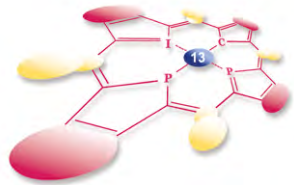

Electronic, steric and catalytic properties of N-heterocyclic carbene rhodium(I) complexes linked to (metallo)porphyrins

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N-heterocyclic carbenes (NHCs) are relevant ligands both in the fields of coordination and organometallic chemistry.[1-2] During the last decade, several molecular systems combining porphyrins and NHC ligands were reported in the literature.[3] Merging metalloporphyrins and NHC-metal complexes within unimolecular systems may lead to multimetallic species with new catalytic properties such as cooperative effects between inner and outer metal cations. Here, we present the synthesis and characterization of some molecular systems combining porphyrins and NHC-rhodium(I) complexes (see below). The catalytic properties of these complexes were investigated for the conjugated addition of phenylboronic acid to cyclohexen-2-one.[4-6] We have notably highlighted the effect of the inner metal cations on the catalytic properties of the outer rhodium(I) complexes. According to the structure of the ligand and the distance between the two metal centers, we show a cooperative effect between the two metal centers for complexes with short M-Rh distances. When porphyrins are used as NHC-wingtips, the nickel(II) in the macrocycle significantly improves the catalytic activity of the neighbouring NHC-Rh(I) complex in the conjugate addition of phenylboronic acid to cyclohexen-2-one.

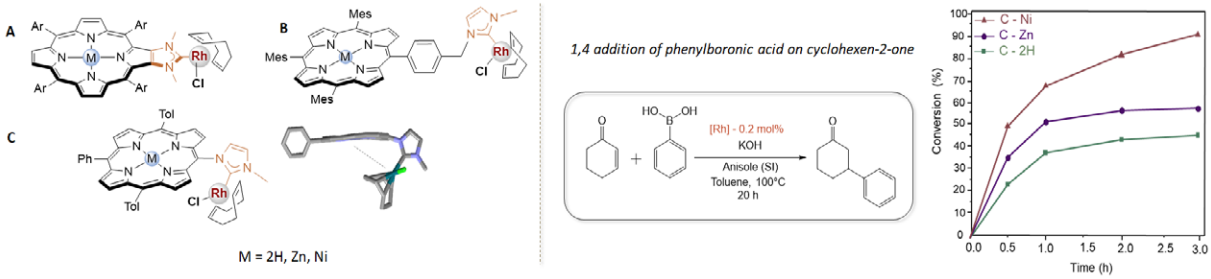

Figure: Structures of the synthesised porphyrin-Rh(I) complexes with DFT optimized structures of complex C-Zn (left). Conjugate addition of phenylboronic acid to cyclohexen-2-one reaction and catalytic profile obtained after 3h for complex C.

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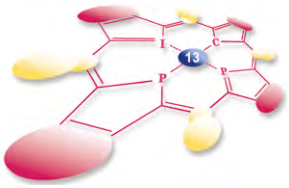

Synthesis of 2-Pyridone[α]-Fused BOPHYs *via* Cyclocondensation Reaction

Dijo Prasannan[a], **Victor N. Nemykin**[a]

[a]*Department of Chemistry, University of Tennessee Knoxville, TN 37996, USA. Email: vnemykin@utk.edu.*

Among the recently developed -BF_2 based flurophores, bis(difluoroboron)1,2-bis((1H-pyrrol-2-yl)methylene)hydrazines (BOPHYs) [1] with its fascinating properties is well-received and has attracted the researchers for various applications [2]. Herein, we describe a regioselective heterocyclyzation reaction [3] to afford 2-pyridone[α]-fused BOPHY derivatives. We present a facile synthetic strategy involving the preparation of enamine derivative in the first step followed by intramolecular cyclocondensation with an ester group in the second step to obtain the target compounds (Figure 1). The post-modification of the BOPHY core to obtain a fused-ring has been challenging since BOPHY suffers from the loss of one of the -BF_2 units. Two series of compounds were prepared and characterized by UV-Vis, fluorescence, NMR, HRMS, and X-ray crystallography. The structural and electronic properties of the pyridone derived BOPHYs were explored theoretically by DFT calculations. The pyridone fused BOPHYs exhibit significant red-shifted absorption and emission, excellent fluorescence quantum yields (ϕ_f = 0.92) as well as high chemical stability compared to the parent BOPHY. Furthermore, we have investigated the interaction of terminal pyridine in BOPHY with metalloporphyrin via axial coordination speculating that such interactions can play significant role in developing supramolecular architectures.

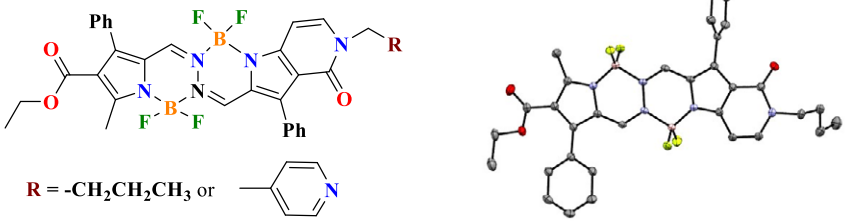

Figure 1. Structures of 2-pyridone[α]-fused BOPHYs

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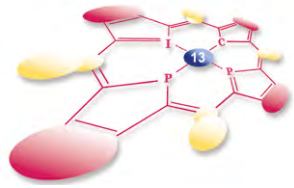

Silver(III) and Iron(III) 21-Carbaporphyrins – Formation and Transformations

Monika Przewoźnik[a], Bartosz Szyszko[a], Emilia Ganczar[a] and Lechosław Latos-Grażyński[a]

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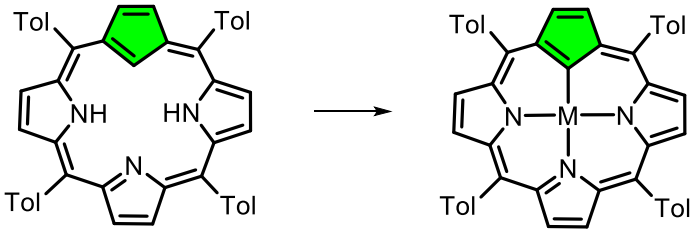
Carbaporphyrinoids are a special case of heteroporphyrins in which one of the pyrrolic nitrogen atoms is replaced by a carbon atom [1], as shown for *meso*-tetraaryl-21-carbaporphyrin **1** [2], or 21-carba-23-selenaporphyrin [3]. The latter shows an interesting reactivity forming a series of dyads using an azepine unit as a merging motif [3]. An interesting insight into 21-carbaporphyrin chemistry was provided by metal-mediated contractions of *p*-benziporphyrin providing 21-carbaporphyrin complexes with gold(III), rhodium(III) and palladium(II) [1].
The synthesis of *meso*-tetraaryl-21-carbaporphyrin **1**, the first macrocycle with a cyclopentadiene subunit entrapped in the *meso*-tetraarylporphyrin architecture [2], provides significant motivation for further exploration of the chemistry of 21-carbaporphyrin and its derivatives.



The study focuses on the coordination chemistry of *meso*-tetraaryl-21-carbaporphyrin **1** with metals binding with the inner core, such as silver or iron. Although these compounds may seem quite basic, their subsequent reactivity is rather nontrivial. The silver (III) complex of 21-carbaporphyrin undergoes further oxidation leading to a novel compound 21-carbaporphyrin-2,3,21-trione, which in the solid state and solution in lower temperature forms the chiral dimeric structure with two subunits linked by a network of hydrogen bonds. Moreover, 21-carbaporphyrin with iron metal inside its core yields an μ-oxodimer with interesting antiferromagnetic properties reflected by its ^{1}H NMR spectra.

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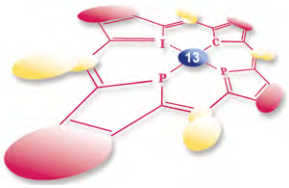

Synthesis, Structural, Spectral and Electrochemical Redox Properties of *β*-Acetamidoporphyrins

Reena, and Muniappan Sankar*

Department of Chemistry, Indian Institute of Technology Roorkee, Uttrakhand, India, 247667

The *β*-functionalization of *meso*-tetraarylporphyrins is of significant interest as it can alter the electronic and electrochemical redox properties of the porphyrin macrocycle with small changes in the substituents. The introduction of formyl, nitro, bromo, or acyl substituents *via* aromatic electrophilic substitution at *β*-position(s) of *meso*-tetraarylporphyrins is a crucial synthetic step for synthesizing a wide range of *β*-functionalized porphyrins for diverse applications.[1] Further exploring the reactivity of nitro substitution in various reactions leads to the development of new porphyrins through Michael addition and the reduction of nitro into amine or acetamide. Notably, acetamide appended molecules and their derivatives showed potential medicinal applications.[1c] Herein, we are substituting the *β*-position with the carboxylamino (acetamide) functional group by the reduction of the nitro group.[1d] Mono *β*-functionalized porphyrins, MTPP(NHCOMe) (M= 2H, Co, Ni, Cu, Zn, V(IV), Mn(III)) were synthesized and characterized by various spectroscopic techniques including UV-vis, fluorescence, NMR, MALDI-TOF mass spectrometry, SCXRD, and electrochemical and DFT studies. Synthesized porphyrins showed bathochromic shifts in B as well as in Q-bands as compared to the precursor. Further, these porphyrins exhibited an intriguing redox behavior due to the *β*-acetamido substitution. In this presentation, we will discuss the synthesis, photophysical, and intriguing electrochemical redox properties of the synthesized porphyrins.

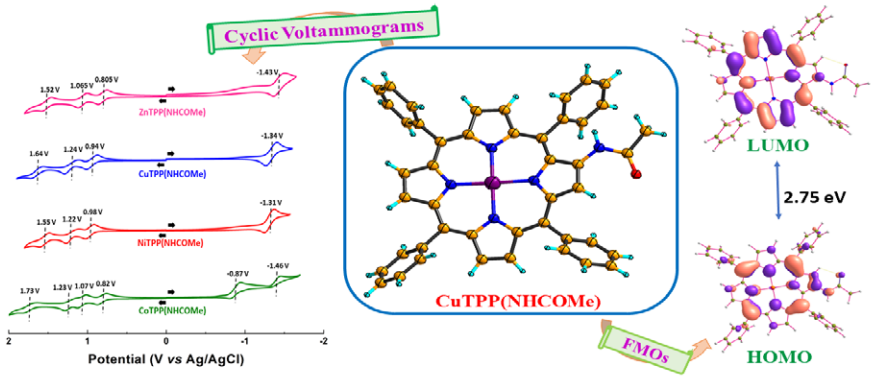

Figure 1. SCXRD structure and FMOs of CuTPP(NHCOMe) and Cyclic Voltammograms of MTPP(NHCOMe) where M = Co(II), Ni(II), Cu(II) and Zn(II).

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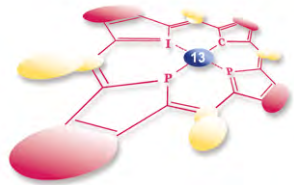
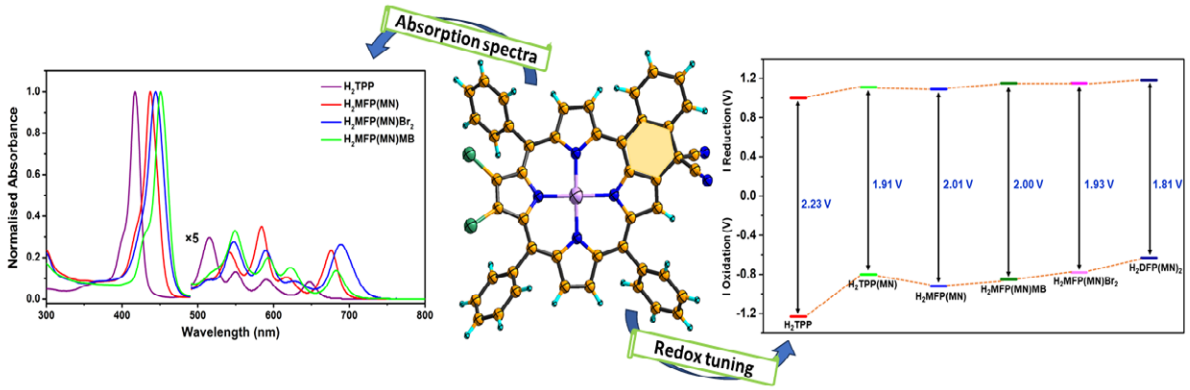


Synthesis, Structural, Spectral, and Electrochemical Redox Properties of mono-*β* Fused Porphyrins

Reena and Muniappan Sankar*

Department of Chemistry, Indian Institute of Technology Roorkee, Uttrakhand, India−247667

The intramolecular fusion of a porphyrin aromatic system has been an intriguing area of research due to its distinctive photophysical and electrochemical redox properties shown by the fused π-conjugated system.[1] Changing the degree of π-conjugation and substituting suitable donor-acceptor groups at the *β*-position results in reducing the HOMO-LUMO gap, changes in electrochemical redox properties, and high ground state dipole moment.[2] The fused porphyrin systems with incredible electronic and optical properties make them fascinating candidates for applications like photoacoustic imaging, dye-sensitized solar cells, material, and two-photon absorption.[3] The present study demonstrates the facile synthesis of the mono *meso-β* fused porphyrins, MMFP(MN)MB, MMFP(MN)$(X)_2$, [M = 2H, Co^{II}, Cu^{II}, Zn^{II} & X = H, Br] and their characterization by various spectroscopic techniques including UV-vis, fluorescence, NMR, MALDI-TOF mass spectrometry, SCXRD. Further, we have explored their electrochemical redox properties and energy correlation with frontier molecular orbitals (FMOs) by DFT calculation. All the synthesized porphyrins showed bathochromic shifts in B as well as in the Q-bands as compared to their precursor. The first-ring reduction potential of MMFP(MN)MB, MMFP(MN)$(X)_2$ [X = H, Br] showed 110-455 mV anodic shift, whereas 50-150 mV positive shift was observed for the first-ring oxidation potential compared to their corresponding MTPPs, except for Co derivatives, showed 60-130 mV cathodic shift in the first ring oxidation potential. Systematic and comparative studies among monofused, difused, and trifused porphyrins along with their parent MTPPs have been carried out in terms of their photophysical, structural, and electrochemical redox properties.



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Two-Dimensional Oxidative Polymerization of Zn Porphyrin to Porphene: Mechanism

Saghar Rezaie[a], Thomas F. Magnera[a], Igor Rončević[b,c], and Josef Michl[a,b]

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[b]*Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences; Prague, Czech Republic*
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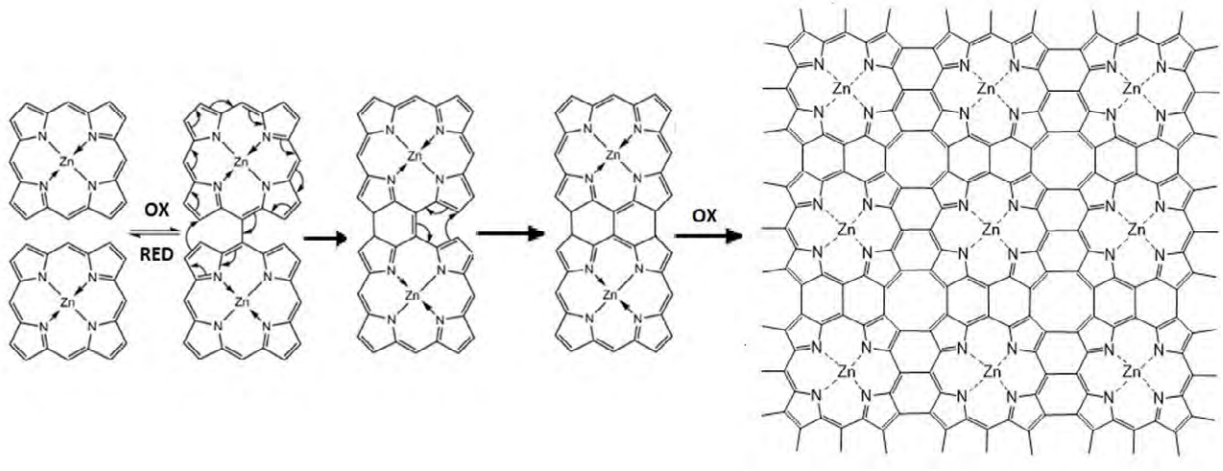
Two-dimensional (2D) materials have emerged as a fascinating class of structures with unique properties and promising applications across various fields. They exhibit extraordinary mechanical, electrical, optical, and thermal properties due to their atomic-scale thickness and high surface-to-volume ratio. In multilayer porphene, a new family of two-dimensional organic materials, each layer can contain metal ions of a different kind, offering a nearly continuous tuning of properties.

We study the oxidative polymerization of monomeric zinc porphyrin in two dimensions to yield porphene. Monomeric Zn porphyrin was spread on the surface of a Langmuir-Blodgett trough, on an aqueous subphase containing K_2IrCl_6, which converts the three CH bonds on each of the four sides of the square-shaped porphyrin into three C-C bonds to the neighbors on all four sides, thus producing porphene. The polymer sheet can be transferred onto different substrates as a monolayer or multilayer for ex-situ characterization methods such as XPS and Raman. We also investigate the polymerization kinetics using in-situ methods (Brewster's angle microscopy, transmission UV-vis-NIR and reflectance FTIR). UV-vis-NIR shows a fast conversion of the meso CH bonds into C-C bonds at the meso positions between neighboring monomers, believed to be reversible. This is followed by a slower disappearance of the beta CH bonds, producing two additional CC bonds between each pair of neighbors. Our current hypothesis for the overall mechanism, heavily dependent on DFT calculations, is shown below.



Acknowledgment: This work was supported by grants from the NSF (CHE-2247956), USARO (23-05-0007), and GACR (20-03691X).

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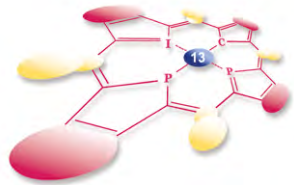


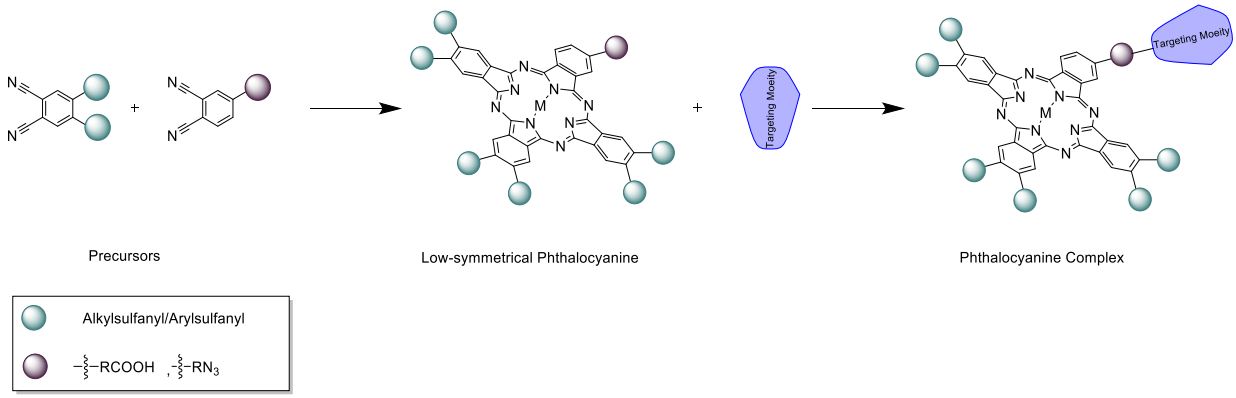
Low-symmetrical phthalocyanines for photodynamic therapy

Leon David Rodrigues, Veronika Novakova

Department of Pharmaceutical Chemistry and Pharmaceutical Analysis, Faculty of Pharmacy in Hradec Kralove, Charles University, Ak. Heyrovskeho 1203, Hradec Kralove 500 03, Czech Republic. rodrigule@faf.cuni.cz

Photodynamic therapy is an effective form of cancer therapy involving a photochemical reaction with a light-activatable molecule – a photosensitizer, light and molecular oxygen. However, the optimal photosensitizer is yet to be developed. Phthalocyanines are aromatic macrocycles having 18 π-electron and are optimal photosensitizers from the spectral and photophysical point of view [1]. The macrocyclic core can be modified to achieve better targeting, enhanced water solubility and increased singlet oxygen production.

In this project, we aim to synthesize low-symmetrical phthalocyanine through the Linstead method using Mg(BuO)2 as the initiator of the reaction with phthalonitrile-bearing alkylsulfanyl or arylsulfanyl groups of different bulkiness as one of the precursors. Another precursor carries a carboxyl or azide group. The introduction of one such functional group into phthalocyanine can be used for attaching to a targeting moiety. The alkylsulfanyl groups are known to have better shifts in the absorption spectra and also improved singlet oxygen production [2].



Acknowledgment: The work was supported by the Ministry of Education, Youth and Sports (ERC-CZ, grant Nr. LL2318).

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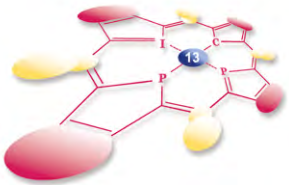
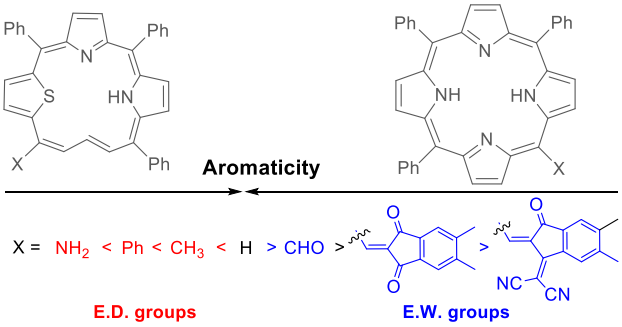


Effects of Electron-Withdrawing and Electron-Donating Groups on Aromaticity in Cyclic Conjugated Polyenes

Tae-Ho Roh, Min-Sung Ko and Dong-Gyu Cho*

Department of Chemistry and Chemical Engineering, Inha University, Incheon 22212, Republic of Korea

Determining the aromaticity of various fluorinated benzenes is challenging,[1] as easily obtained experimental aromaticity ($\Delta\delta(H_{outer}–H_{inner})$) necessitate the chemical shifts of inner and outer protons. This issue was addressed in porphyrinoids by replacing the electron-withdrawing (E.W.) groups at the *meso*-positions of porphyrins and allyliporphyrins. Electronic effects on aromaticity in porphyrinoids has not been thoughtfully examined in the literature. In porphyrins, the effect of E.W. groups is minimal, making it difficult to establish a clear relationship between aromaticity strength and E.W. groups. Conversely, in allyliporphyrins,[2] stronger E.W. groups such as indanedione (IND) derivatives significantly reduce the aromaticity of the parent structure. The IND derivatives disrupted the aromatic pathway of allyliporphyrin more effectively than those attached to porphyrins. This is attributed to the absence of β-carbons in allyliporphyrins. The effect of electron-donating (E.D.) groups on porphyrins and allyliporphyrins was further investigated. Contrary to the initial assumption that the E.D. groups might enhance aromaticity owing to their ability to increase electron density, as the strength of the E.D. groups increased, the aromaticity of the porphyrinoids decreased. Despite the modest reduction in aromaticity, any form of electron perturbation reduces aromaticity. The aromaticity of various fluorinated benzenes should parallel our observations of porphyrinoids as representative aromatic polyenes.



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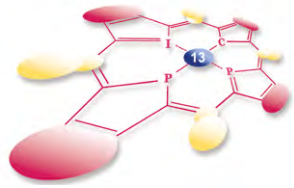

A Novel Approach towards Nitrile-Substituted Corrole: Versatile Precursor for Click Chemistry and Beyond

Azad Saini[a], Zeev Gross*[a]

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Corroles, i.e., contracted porphyrins, have gained substantial attention due to their unique electronic and photophysical properties, making them a suitable choice for catalysis and medical applications.[1-2] Upon systematically adjusting the electronic effects via substitution at *meso*- or *β*-positions on corrole macrocycle, the fine-tuning of fundamental properties (*absorbance, emission, redox potential, HOMO-LUMO gap etc.*) for the corresponding metal complexes can be achieved.[3-4] We now introduce a versatile precursor of the azide-nitrile click chemistry for potential chemical modifications. While there have been no previously reported examples of corroles with *meso*-C substituted nitriles, we now present a facile approach for the synthesis of 5,10,15-triscyanocorrole, (H_3-**1**). Hydrolysis of 5,10,15-tris(trifluoromethyl)corrole by an aqueous ammonia solution afforded H_3-**1**, due to a rare CF_3 to CN transformation. The free base corrole and several of its metal complexes were characterized by UV-Vis, IR, and NMR spectroscopy. This allows for investigating how the physical and chemical properties of corroles are affected by C_6F_5, CF_3, and CN substitution of the *meso*-C position.

The structure of the redox-active cobalt and photoactive phosphorus complexes **1**-$Co^{III}(py)_2$ and **1**-$P^{V}(OH)_2$, respectively, were determined by X-ray crystallography. Electrochemical characterization of **1**-$Co^{III}(py)_2$ with a strongly red shifted Soret band unveiled the reversible Co^{II}/Co^{I} couple at -1.1 V vs. Ag/AgCl, more facile by 460 mV and less facile by 320 mV as the *meso*-C substituent is varied from C_6F_5 to CN to CF_3. The photophysical property of **1**-$P^{V}(OH)_2$ was analyzed using fluorescence emission spectroscopy, with excitation at 423 nm, revealing a highly intense band at 598 nm. The quantum yields of H_3-**1** and **1**-$P^{V}(OH)_2$ were measured using tetraphenylporphyrin as a reference and were found to be 13% and 24% respectively.

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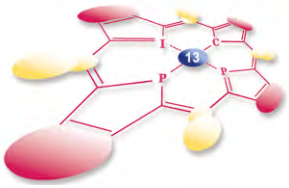

Cobalt complexes of the substituent-free corrole with a variety of axial ligands

Irena Saltsman[a], **Marcelo Fernandez-Dela-Mora**[a], **Zeev Gross**[a]

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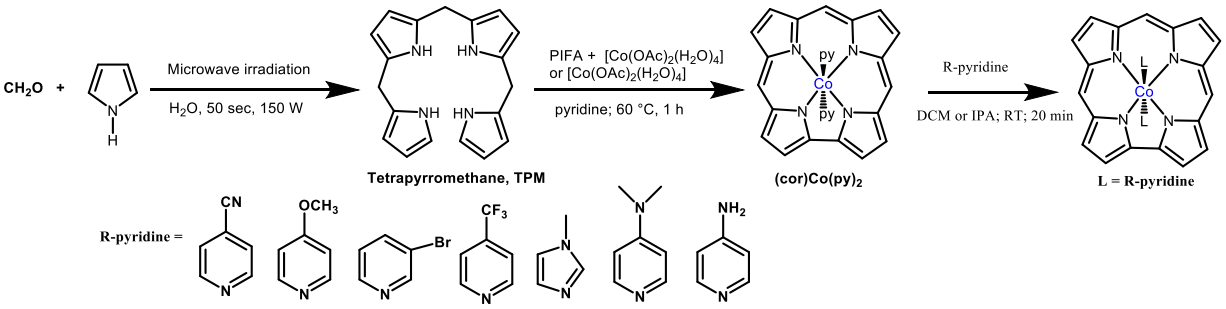
The science and technology of corroles, macrocycles that share structural similarity with the cobalt chelating prosthetic group of Vitamin B12 and numerous features with the iron chelating porphyrin present in heme proteins/enzymes, constantly crosses new horizons ever since stable derivatives became easily accessible. Particularly important is the increased utilization of corroles and the corresponding metal complexes for the benefit of mankind, in terms of new drug candidates for treating various diseases and as catalysts for sustainable energy relevant processes [1]. One challenge was to gain access to the parent macrocycle, which we have achieved by conceptually different pathways [2]. We now present the corresponding cobalt complexes coordinated with a large variety of axial amines for understanding if and how they affect the most fundamental properties.



Scheme 1. One-pot synthesis of (cor)Co via one-pot oxidative cyclization of TPM and metalation by cobalt(II) acetate; and the preparation of (cor)Co(L)$_2$ complexes with various axial ligands (L).

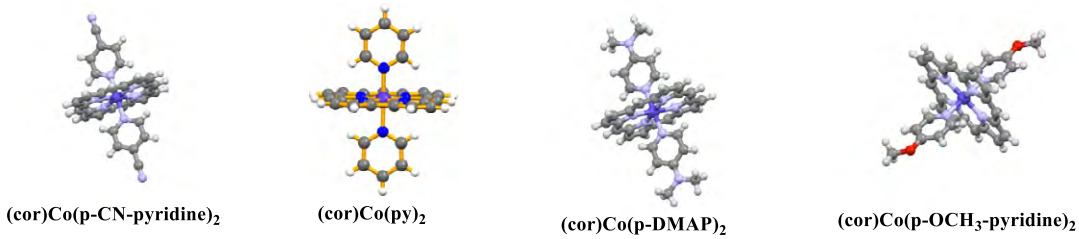


Figure 1. X-ray structures of parent-corrole complexes with different substituted pyridines as axial ligands.

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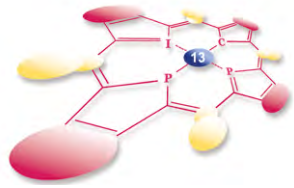

Adsorption and reactivity of carboxy and ester functionalized fluoro phthalocyanines immobilized on solid-state supports

Sean Scally[a], Marius Pelmuş[a], Sergiu M. Gorun[a]*

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Fluorinated phthalocyanines (F_xPcM) are strong electron-deficient compounds. Those that bear electron-withdrawing perfluoroalkyl substituents, exhibit enhanced photosensitizing properties. [1] Perfluoroalkyl, R_f, and substituted phthalocyanines are very thermally robust materials, chemically inert, and exhibiting enhanced stability to electrophilic, nucleophilic, and reactive oxygen species with radical character. [2] The adsorption and interactions of $(R_f)_yF_xPcMetal$ with different functional groups on solid supports are of interest given their applications in heterogenous photo- and catalysis. We report the synthesis of $F_{48}H_7(COOEt)PcZn$, the ester of the carboxy-functionalized Pc, $F_{48}H_7(COOH)PcZn$. The esterification induces small but identifiable shifts in the electronic and ^{19}F NMR spectroscopic characteristics of the common macrocyclic moiety. Significant differences are observed in adsorption/desorption equilibria and immobilization on oxidic supports, which may occur via a single point, the metal center for both complexes, but via two points only in the presence of the free carboxylic group, $F_{48}H_7(COOH)PcZn$. Oxygenations of thioethers are noted.

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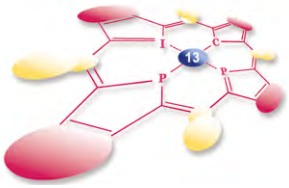

Photo-oxidation with Fluorinated Phthalocyanines Adsorbed on γ-Alumina

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The adsorption and photocatalytic properties of fluorinated phthalocyanines (F_{64}PcZn and F_{16}PcZn [1, 2]) on γ aluminum oxide solid support were investigated. The respective phthalocyanines along with their metal oxide complexes were characterized by diffuse reflectance, infrared and fluorescence spectroscopies along with thermogravimetric analysis. Phthalocyanines act as photosensitizers using visible light to generate singlet oxygen ($^1O_2$) which can react to form other reactive oxygen species (ROS).[3]

The degradation of organic sulfides of interest was investigated under several conditions: homogenous photocatalysis using F_{16}PcZn and F_{64}PcZn; heterogeneous photocatalysis using F_{16}PcZn and F_{64}PcZn respectively adsorbed on γ- alumina. The biological activity of the phthalocyanine and phthalocyanine-metal oxide complex was investigated by way of photodegradation of giant unilamellar vesicles acting as a cellular mimic.[4] Supported catalyst kinetics were analyzed using UV-Vis. Degradation products were confirmed using GC-MS and reaction kinetics were analyzed using GC-FID. Complexes in solvent-rich systems followed first-order kinetics. Ongoing work is being performed to analyze the degradation and interaction of these supported catalysts within the mock vesicle system.

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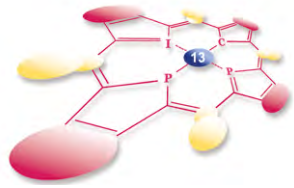

Cyclooctatetraene attached π conjugated porphyrins and optoelectronic studies on their conformational planarization state.

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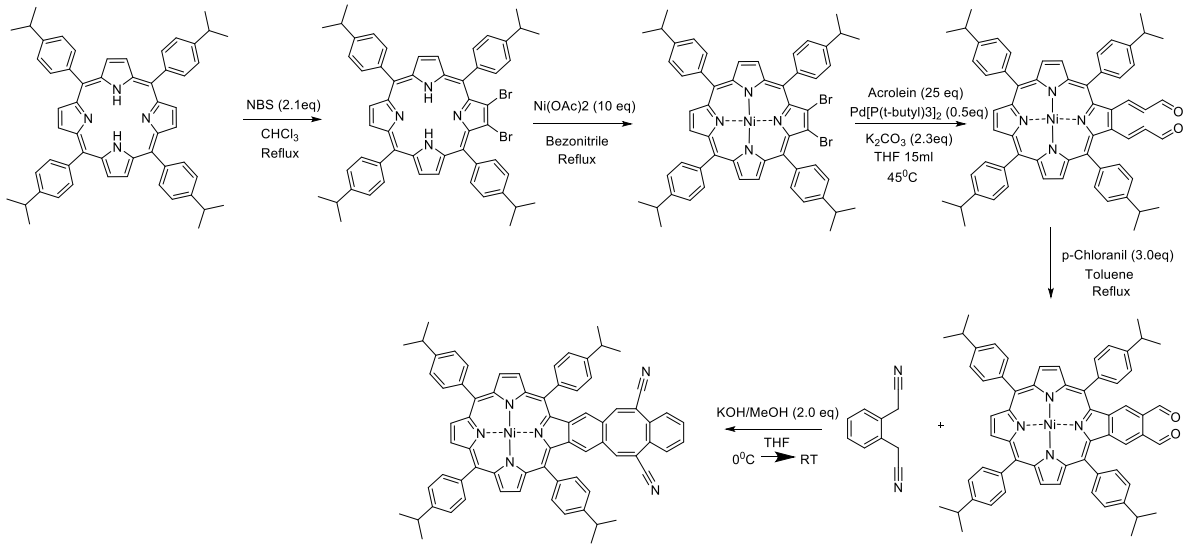
Cyclooctatetraene with 8π electron system is non-aromatic failing to satisfy the important Hückel's criteria. The energetically favored tub-shaped conformation allows this molecule to avoid conjugation with the alternate double bonds within the ring. Upon excitation, cyclooctatetraene will be planarized due to aromatization, and it is thus of interest in fundamental research because of its 4nπ excited-state aromaticity relevant to extended Baird's rule [1]. Baird's rules suggest that annulenes that follow 4n and 4n+2 criteria in their ground state switch their aromaticity in their excited state. There has been growing interest in studying aromaticity reversal phenomena using aromatic and antiaromatic annulene systems and the non-aromatic cyclooctatetraene molecule. In this work, cyclooctatetraene moieties were incorporated into porphyrins to construct cyclooctatetraene-porphyrin fused π-systems. The impact of the exotic cycles on the electronic, optical, and aromatic properties of porphyrins was investigated using UV-Vis spectroscopy, fluorescence, transient absorption spectroscopy and spectro-electrochemistry.



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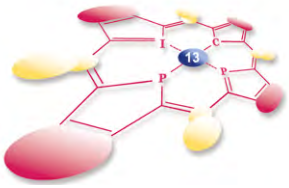

Intramolecular Charge Transfer (ICT) in Main Group Porphyrin-Based Push-Pull Systems

Jatan K. Sharma[a], Brandon J. Bayard, Nick Zosel, Syeda Ali, Noah Holzer, Steven Peterson, Vladimir N. Nesterov, Paul A. Karr, Francis D'Souza[a], Prashanth K. Poddutoori[b]

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Donor-acceptor (D-A) constructs with "push−pull" architecture have gained a lot of attention in recent years because of their impressive properties in a variety of applications. For instance, a porphyrin comprised of a push-pull system with an electron-donating group at the peripheral position and an electron-withdrawing group at the opposite led to remarkably improved solar energy conversion efficiencies in dye-sensitized solar cells. This property not only minimizes the energy-wasting electron recombination in electron transfer reactions but also provides directionality to electron flow thus increasing the efficiencies of the photoinduced processes. In this presentation, push-pull style intramolecular charge transfer (ICT) in an elegantly designed main group porphyrins peripherally decorated with electron-rich methoxy substituents will be demonstrated. We have demonstrated that the ICT is strongly dependent on the position of the methoxy groups on the phenyl ring and the polarity of the employed solvent in phosphorous porphyrins [1] and hypervalent Antimony porphyrins. [2] Steady-state and time-resolved emission, and transient absorption spectroscopic techniques have been employed to establish the tunable ICT in the studied systems. Furthermore, time-dependent density functional theory (TD-DFT) calculations have been performed to complement the experimental results. The systematic study of hypervalent porphyrins, especially the observed tunable ICT is expected to play an important role in prompting high-yield charge-separated states in multi-modular donor-acceptor systems comprised of hypervalent porphyrins for solar energy conversion and molecular electronic and photonic applications.

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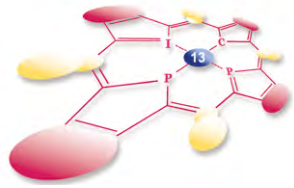

Zinc Tetrapyrrole Coordinated to Imidazole Functionalized Tetracyanobutadiene or Cyclohexa-2,5-diene-1,4-diylidene-expanded-tetracyanobutadiene Conjugates: Dark vs. Light-Induced Electron Transfer

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[b]*Indian Institute of Technology Indore, India*

Using the popular metal-ligand axial coordination self-assembly approach, donor-acceptor conjugates have been constructed using zinc tetrapyrroles (porphyrin (ZnP), phthalocyanine (ZnPc), and naphthalocyanine (ZnNc)) as electron donors and imidazole functionalized tetracyanobutadiene (Im-TCBD) and cyclohexa-2,5-diene-1,4-diylidene-expanded-tetracyanobutadiene (Im-DCNQ) as electron acceptors.[1] The newly formed donor-acceptor conjugates were fully characterized by a suite of physicochemical methods, including absorption and emission, electrochemistry, and computational methods. The measured binding constants for the 1 : 1 complexes were in the order of 10^4–10^5 M^{-1} in o-dichlorobenzene. Free-energy calculations and the energy level diagrams revealed the high exergonicity for the excited state electron transfer reactions. However, in the case of the ZnNc:Im-DCNQ complex, owing to the facile oxidation of ZnNc and facile reduction of Im-DCNQ, slow electron transfer was witnessed in the dark without the aid of light. Systematic transient pump-probe studies were performed to secure evidence of excited state charge separation and gather their kinetic parameters. The rate of charge separation was as high as 10^{11} s^{-1} suggesting efficient processes. These findings show that the present self-assembly approach could be utilized to build donor-acceptor constructs with powerful electron acceptors, TCBD and DCNQ, to witness ground and excited state charge transfer, fundamental events required in energy harvesting, and building optoelectronic devices.

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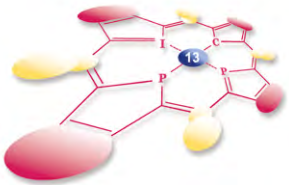

Synthesis, Characterization and Aromatic Effect of Dihydrobenzopyrroloindole-Fused Porphyrin Based on Beta Functionalization

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The π-Extension of porphyrins enhances their electrical and photophysical properties, making them suitable for biomedical imaging and organo-electronics. Their properties can be tuned by modification of structure, for instance, linearly extending conjugation via β-β' pyrrolic position and meso position[1]. Meso tetraaryl porphyrins are also extensively studied due to their simple synthesis, bright fluorescence, deep colors and great photochemical stability with their ability to bind metal ions[2]. Introducing aromatic heterocycles to a π-conjugated structure could be another possible strategy for modifying the electrical and aromatic characteristics of organic compounds. In a previous work, thiophenes, naphtho[2,1-b:3,4-b']dithiophene (**F2VTP**) and its isomeric structure naphtho[1,2-b:4,3-b']dithiophene (**F3VTP**) were fused to the porphyrin periphery, giving a unique set of optical and electronic properties that resulted in ~20% and ~30% increase in fluorescence lifetime, respectively. A more than two-fold decline in emission quantum yield (φ=0.018) for **F2VTP** and a 1.5-fold increase in fluorescence quantum yield for **F3VTP** were observed, suggesting an unusual trend[2]. In this work, we introduce a pyrrolic unit to the porphyrin β-β' position. We plan to investigate how their optical and electronic properties change upon structural modification. The Heck reaction will be employed to synthesize 1,2-di(1H-pyrrol-2-yl)benzene fused porphyrin (**a**) followed by 6π cyclization and aromatization, using *in situ* prepared Pd^0 catalyst[3]. The subsequential Scholl reaction on (**a**) will lead to the formation of dihydrobenzopyrroloindole fused porphyrin (**b**)[2]. The characterization of (**a**) and (**b**) will be done using UV-Vis and Fluorescence spectroscopy.

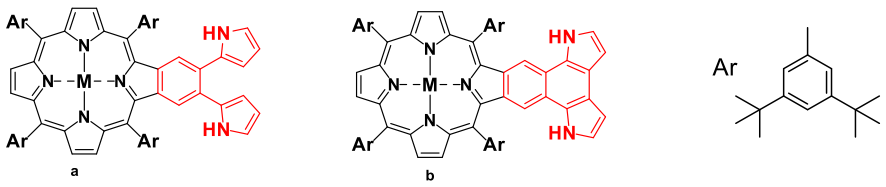

Figure 1. Meso and β-β' functionalized porphyrin derivatives

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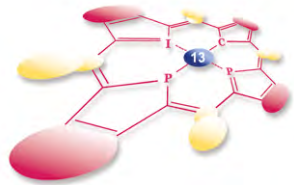

Sufficiently enriched dual-ion batteries with ferrocenyl-substituted NiNc organic electrodes

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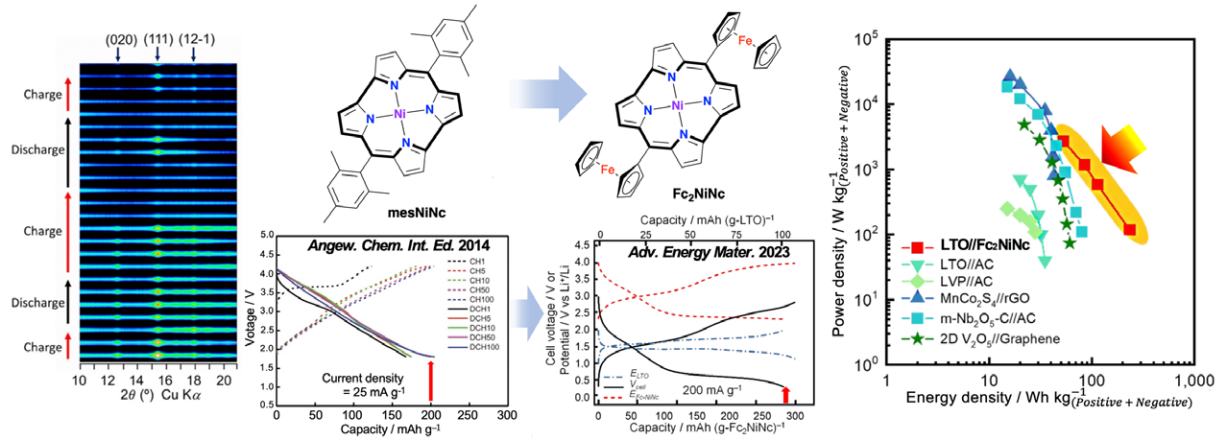
Nickel(II) norcorrole (NiNc) frameworks exhibit sufficient electrochemical properties based on their antiaromatic nature, capable of application to secondary organic batteries as active electrode materials. The reversible multi-redox passages of NiNc with the appropriate chemical durability have successfully operated long-term charge-discharge processes and exposed superb Coulombic efficiencies in both Li-organic and symmetric organic batteries [1]. Furthermore, optimization approaches with various battery electrolytes improved dual ionic modulations of liquid electrolytes efficiently, fasting the charge-discharge speeds and inhibiting the damage of dissolution from electrode materials [2]. Facile redox conversions of the electrode material and the mechanical kinesis of electrolyte ions were carefully interpreted with in-situ XRD and ex-situ Raman spectroscopic analyses and monitoring dual-ion behaviors of three-electrode cells [3]. Ferrocenyl-substituted NiNc, prepared to explore an advanced organic battery electrode material, precisely enhanced the battery behavior, manipulating pseudocapacitive processes with fast and stable charge-discharge performances, superior battery capacity, and high Coulombic efficiency [4].



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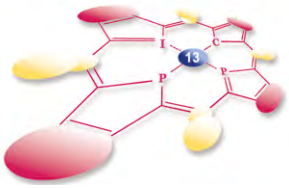

Synthesis of new derivatives of purpurine imide with functional group

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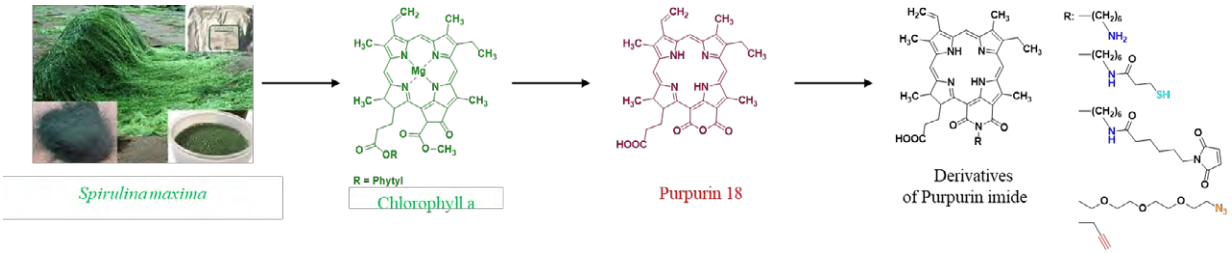
Chlorins are among the most interesting photosensitizers for photodynamic therapy because they exhibit a high quantum yield of singlet oxygen generation and absorbance in the near-infrared. Indeed the penetration depth of light into skin increases with wavelength from the UV to the near-infrared light range. Even if chlorins can be synthesized, they are present in nature and the most abundant natural chlorin is chlorophyll. After aceton extraction of chlorophyll a from *spirulana maxima*, it is possible to synthesize a derivative, the purpurin 18, which has an absorbance of around 700 nm thanks to an additional anhydride exocyclic ring compared to the chlorin p6 whose maximum absorbance wavelength is at 650 nm.[1] The disadvantage is that this anhydride exocyclic ring is very reactive and can be easily opened by a nucleophile to lead to a derivative of chlorin p6. To preserve a cycle and thus the absorbance around 700 nm, previous work has shown that it is possible to open purpurin 18 with an amine and to recyclize to lead to purpurin imide derivatives which have also shown very important phototoxicity.[2] In this work we have therefore synthesized different derivatives of purpurine imide, which have different reactive functional groups such as amino, sulfhydryl, maleimide, azide and alkyne to allow subsequent functionalization and open up the possibilities of using them. The structures of all new derivatives of purpurine imide were characterized by NMR and UV-visible spectroscopy and mass spectrometry.



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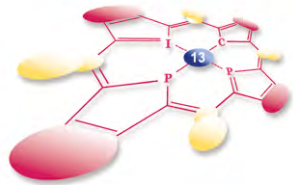

Green Dye Molecules Using Phthalocyanine: Molecular Design, Synthesis and Measurement in Ink and High-Visibility Applications

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Green dye molecules play a crucial role in various applications, including printing inks and high-visibility materials. In this study, we focus on the design, synthesis, and property measurement of green dye molecules based on phthalocyanine derivatives, aiming for their effective utilization in ink and high-visibility applications.
The molecular design phase involves the strategic modification of the phthalocyanine core structure to impart desired optical properties, such as absorption and emission spectra, color purity, and stability. Rational design strategies, including the introduction of electron-donating or -withdrawing substituents, are employed to tailor the molecular properties to meet the requirements of ink and high-visibility applications.
The synthesized green dye molecules are thoroughly characterized using spectroscopic and analytical techniques, including UV-Vis absorption spectroscopy, fluorescence spectroscopy, mass spectrometry, and chromatography. These analyses provide valuable insights into the molecular structure, purity, and optical properties of the synthesized dyes.
The application phase involves the formulation of green phthalocyanines incorporating the synthesized dye molecules and their evaluation in terms of color intensity, stability, and printability.
Overall, this study highlights the importance of molecular design, synthesis, analysis, and application in developing green dye molecules based on phthalocyanine derivatives for ink and high-visibility applications. The findings contribute to the advancement of sustainable and high-performance dye materials in the field of printing and visibility enhancement.

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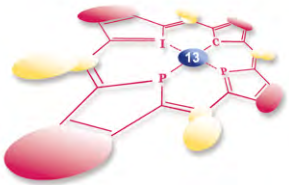

Redox-Active Dihydroindolo(2,3a)carbazole-Based Macrocycles and their [b]-Annulated BODIPY Complexes Exhibiting Near-IR Electrochromism

Aswini Spergen, Arumugam Kalaiselvan and Sabapathi Gokulnath*

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Materials exhibiting near-IR electrochromism are promising candidates for developing variable optical attenuators in optical telecommunication, smart windows, energy storage devices, etc.[1] Over the past few decades, seminal reports have documented inorganic, polymer, and organic electrochromic materials. Whereas, organic materials have advantages such as flexibility, easy tunability, high color contrast, etc. In particular, porphyrinoids are excellent chromophores that show a high molar absorption coefficient, low energy gap, good stability, and form stable radicals during electrochemical redox processes. In this work, a new class of redox-active dihydroindolo(2,3a)carbazole (InC)-based porphyrin-like macrocycles and their [b]-annulated BODIPY complexes are reported with a facile synthetic methodology.[2] In these macrocycles, InC acts as a donor, and an azafulvene-extended with π-conjugated fragment (thiophene or *p*-phenylene) acts as an acceptor. Further, the acceptor character of the macrocycle was enhanced by BF_2 complexation. The free macrocycles and their BF_2 complexes display intriguing near-IR electrochromic properties with reversible multi-color switching upon cathodic scans at room temperature. Interestingly, the radical anionic species of BODIPY complex (InCT·BF_2) shows high stability upon reduction with a radical comproportionation constant (K_c) of 1.22×10^6 (Figure 1).

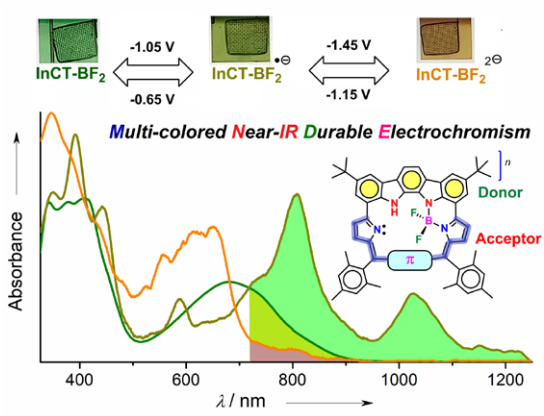

Figure 1: UV−vis−NIR absorption profile of macrocycle InCT·BF_2 upon applying a range of potentials.

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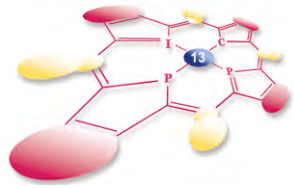

Influence of Charged Moieties on the Performance of Porphyrin Photocatalysts for CO_2 Reduction

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Porphyrins with a positively charged moiety in the second coordination sphere have shown great promise for photocatalytic CO_2 reduction [1]. To further investigate the influence of charged groups, a library of iron porphyrins with two, four and eight positively charged groups in differing positions on the porphyrin ligand, were synthesized and their performance under typical photochemical CO_2 reduction conditions was evaluated.

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Si(IV) complexes of octaaryl-substituted porphyrazine and corrolazine

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Corrolazines are porphyrazine analogs with contracted macrocycles in which one *meso*-nitrogen is missed. They show very strong light absorption in both the blue and the red regions and have photophysical and photochemical properties which are easily tunable by chemical modification. Consequently, corrolazines can find important applications in such fields as photovoltaics and photodynamic therapy (PDT) [1].

In this work, Si(IV) complexes of octaaryl-substituted porphyrazine ($(HO)_2SiPzAr_8$, Ar=Ph, ^{t}BuPh) were obtained using both template cyclomerization [2] and complexation methods, and a comparison of these approaches is given. In the case of the octaphenyl substituted derivative, the cyclomerization of the corresponding diiminoimide is accompanied by its 1,3-dipolar cycloaddition to one of the pyrrole fragments and the formation of the chlorin-type byproduct ($SiPzPh_{10}$), the structure of which was identified by a single crystal X-ray analysis.

The treatment of $(HO)_2SiPzAr_8$ with tripropylchlorosilane in the presence of magnesium in pyridine leads to the formation of axially siloxylated porphyrazines $(Pr_3SiO)_2SiPzAr_8$, followed by the reductive contraction of the macrocycle and formation of the corresponding corrolazine complexes $(Pr_3SiO)SiCzAr_8$. Sulfochlorination of phenyl fragments and subsequent hydrolysis leads to the formation of water-soluble sulfonated derivatives $(HO)_2SiPz(PhSO_3H)_8$ and $(HO)SiCz(PhSO_3H)_8$.

The effects of the macrocyclic ligand contraction and the nature of the axial ligand on the absorption spectral, fluorescence and acid-base properties, as well as the ability to generate singlet oxygen, are discussed.

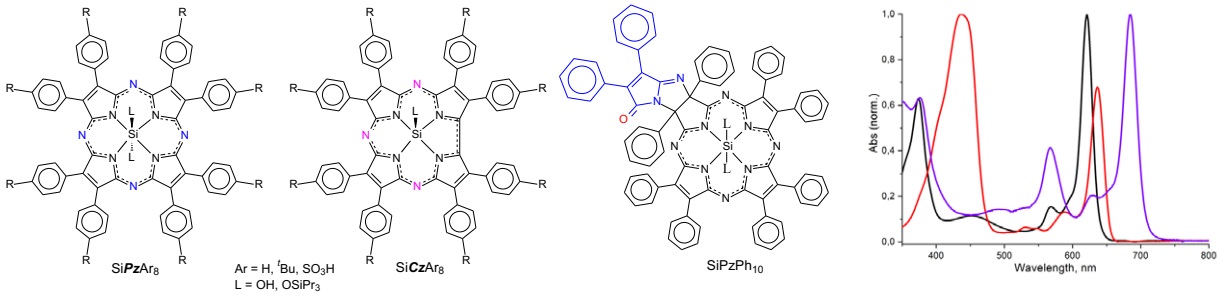

Figure 1. The structures of the obtained Si^{IV} complexes and UV-vis spectra of $(L)_2SiPzPh_8$ (black), $(L)SiCzPh_8$ (red) and $SiPzPh_{10}$ (purple) in CH_2Cl_2

Acknowledgment: This study was supported by the Russian Foundation of Basic Research (grant No. 20-53-26004).

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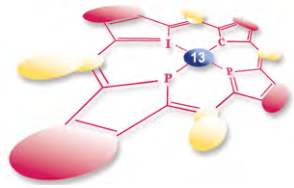

Hydrolytic scission of P^V octaphenylporphyrazine and formation of novel diazatripyrrinedione complex

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In recent years, complexes of porphyrazines and phthalocyanines with phosphorus(V) have attracted increasing attention due to their unusual photophysical and chemical properties [1-2]. The presence of a positive charge on the central atom in dihydroxo- or dialkoxophosphorus(V) complexes has a strong impact on the chemical properties of the macrocyclic ligand. Recently a reversible nucleophilic addition to the α-pyrrolic carbon atom of P^V phthalocyanine was shown with distortion of macrocyclic conjugated system [3]. Tripyrrolic compounds are known as cyclic (subporphyrazines and subphthalocyanines, subporphyrins) and non-cyclic tripyrrines. The last one is quite rare because of the low stability of tripyrrine ligand. However, these compounds can be stabilized by metal introduction [4]. Recently we have observed that octaphenyl substituted porphyrazine macrocycle in dihyrsoxophosphorus(V) complex can undergo hydrolytic excission of one pyrrolic fragment with the formation of the stable hexaphenyldiazadipyrrinone phosphorus(V) complex.

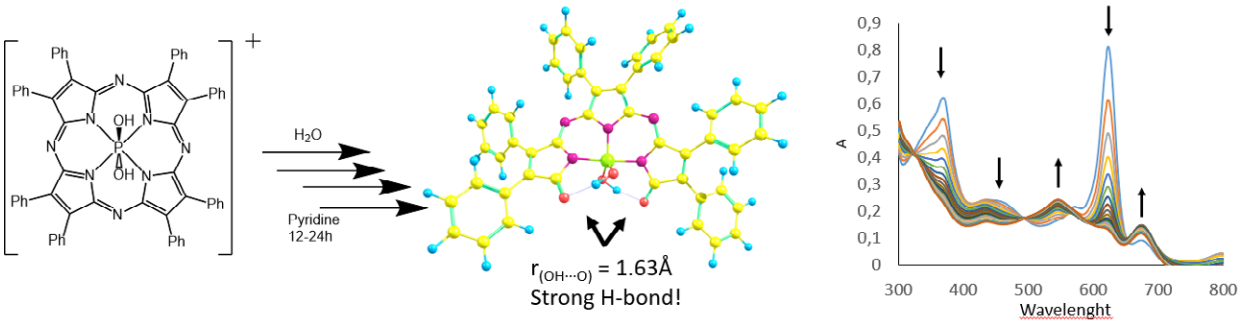

Fig. 1. Scheme (left) and spectral changes (right) upon hydrolysis of P^V octaphenylporphyrazine in pyridine

The process of hydrolysis was investigated in organic solvents, such as pyridine, acetone, DMSO and CH_2Cl_2. The structure of this product was confirmed using MALDI-TOF mass-spectrometry, IR, ^1H and ^{31}P NMR spectroscopy. DFT calculations reveal that the molecular structure of the obtained tripyrrolic P^V complex is stabilized by intramolecular hydrogen bonds POH…O=C between hydroxy groups attached to the phosphorus atom and pyrrolic keto groups. The thermodynamics of this process is also described using DFT calculations.

Acknowledgment: This study was supported by the Russian Foundation of Basic Research (grant No. 20-53-26004).

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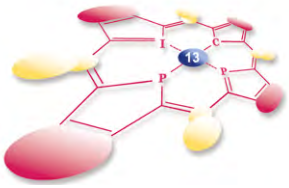

Phosphorescent Membrane-Anchored Probes for Oxygen

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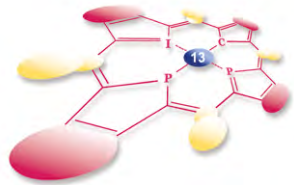
Department of Biochemistry and Biophysics, Perelman School of Medicine, and Department of Chemistry, School of Arts and Sciences, University of Pennsylvania, Philadelphia

Molecular membrane-anchored probes (MAP) are a useful tool for measurements of analyte concentrations in the immediate environment of the cell without perturbing cellular physiology. When combined with in vivo imaging, such probes can enable measurements of analytes in areas where soluble probes cannot reach, making it possible to monitor cellular environments for prolonged periods while avoiding invasiveness and tissue damage. Here, we report the development of a water-soluble amphiphilic phosphorescent MAP for oxygen. Oxygen MAP will be used for longitudinal oxygen quantification in the niche of transplanted hematopoietic stem cells and leukemic cells (HSCs and LCs) in living mice to help understand the role of the environment on the SC dormancy, self-renewal and proliferation.



Type-I Conformation of Hexaphyrins(1.1.1.1.1.1) caused by Electron-Withdrawing Properties of *meso*-Aryl Substituents

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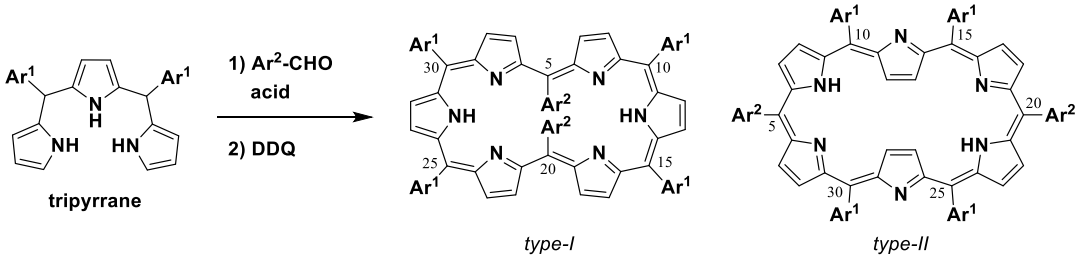
Graduate School of Natural Sciences and Technology, Shimane University

Expanded porphyrins, higher homologues of porphyrins, possess flexible frameworks due to their elongated pyrrole-methine arrays.[1] Among these, hexaphyrin(1.1.1.1.1.1) shows intriguing molecular thermal motions such as caterpillar-like macrocyclic revolutions and conformational exchanges, which allow effective comparisons between distinguishable structures of the same molecules themselves.[2a] The key issue of these investigations is preparation of oligo-pyrrole precursors like tripyrranes, which enable us to handle A_4B_2-type symmetric patterns.[2] Type-I (a dumbbell form) and type-II (a rectangle form) conformations of hexaphyrin(1.1.1.1.1.1) are the original structure and the general one, respectively, and they are mainly controlled by the steric hindrances around the *meso*-positions (particularly 5,20-positions). However, for synthetic reasons, the other *meso*-aryl groups should have moderate steric hindrances by electron-withdrawing *ortho*-substituents. On the other hand, when all the *meso*-substituents are sufficiently electron-withdrawing like 3,5-bis(trifluoromethl)phenyl group, only the type-I conformer is obtained.[3] Nevertheless, a hexaphyrin(1.1.1.1.1.1) skeleton tends to take the type-I conformation in the any cases and such a tendency causes unique skeletal transformations giving unprecedented functional frameworks.[2b,c] In this context, intentional control of these frameworks can be provide indispensable chances to utilize chemistry of hexaphyrins.

In this study, introduction of a series of *meso*-aryl groups as the Ar^2 substituents was investigated for the sake of comprehension of the boundary between the conformations from the view point of the electron-withdrawing natures of the substituents. When 4-cyanopehyl, 3-nitrophenyl, and 4-nitrophenyl groups were introduced at the 5,20-positions, type-I and type-II conformers were found to be equilibrated as mixtures in the cases of Ar^1 = pentafluorophenyl group, while the 3,5-dintrophenyl derivative afforded the sole type-I conformer judging from ^{1}H NMR measurements.[4]



Scheme 1. Synthesis of A_4B_2-type hexaphyrins(1.1.1.1.1.1) by reactions of tripyrrane with aryl aldehydes.

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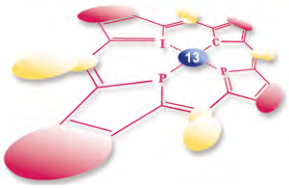

Zwitterion interacting systems based on imidazo[1,5]carbachlorin

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N-confused porphyrin (**NCP**) is one of the isomers of porphyrins, in which one of the four pyrrole rings is incorporated in the macrocycle with a single β-*meso* linkage instead of all α-*meso* bonds [1]. Compounds with additional rings on the perimeter of the tetrapyrrole allow the introduction of another donor atom as a fragment of the fused ring. An example of a system in which an imidazole fragment has been fused to the NCP structure is imidazole-conjugated carbachlorin (**ICC**). Due to the rare tris(anionic) nature of the macrocyclic system, ICC enables the stabilization of different oxidation states of metal ions, for example, silver ions in the +III oxidation state (**AgICC**) [2]. Alkylation of **AgICC** leads to cationic complexes. Such alkylated individuals are precursors of zwitterionic complexes, in which a metal ion on the +III oxidation state (Ag^{III}) is replaced by a metal ion on the +II oxidation state (Pd^{II}, Pt^{II}). The structures of porphyrins and porphyrinoids, in which the charge is delocalized onto the core units, make it possible to combine molecules with opposite charges, thus forming ionic pairs. The zwitterionic systems, remaining neutral, can form intermolecular interactions and spatially self-organize [3,4]. Non-covalent self-organization is a significant and widespread phenomenon that leads to the formation of ordered dimers and higher oligomers, sometimes extremely complex supramolecular systems [5]. The zwitterionic complexes may be of interest for the fabrication of electronic materials that use π-based interaction, such as semiconductors [6].

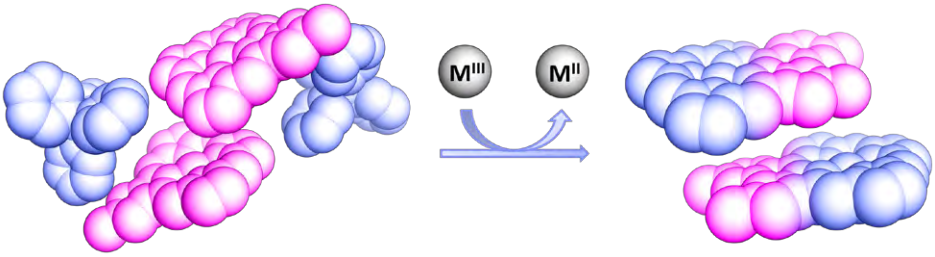

Figure 1. Formation and assembling of zwitterion complexes.

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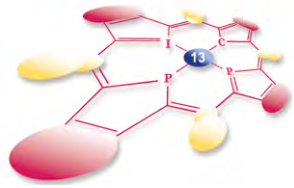

Subphthalocyanines as Donors in Multichromophore Energy-Transfer-Systems

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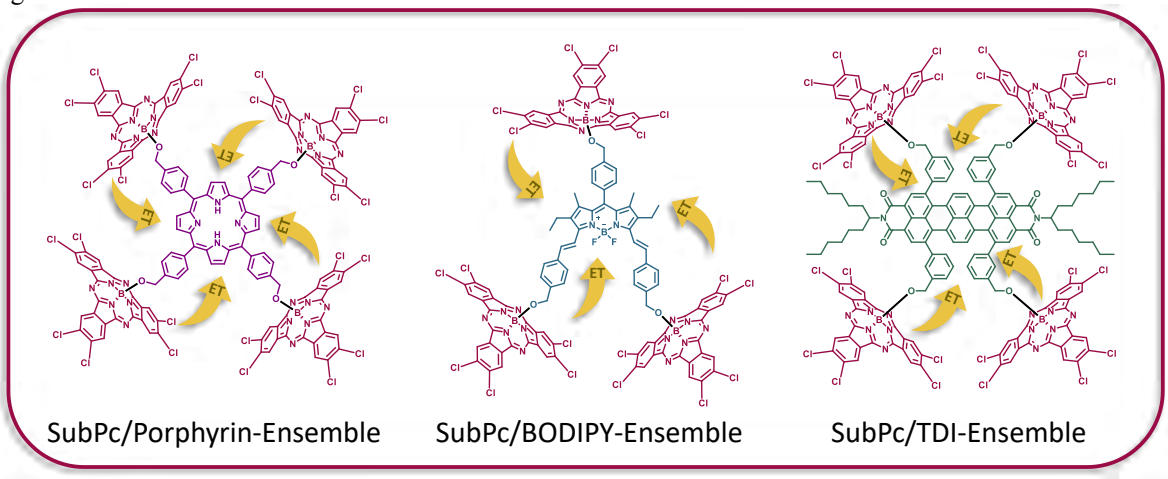
Photosynthesis is the most impressive example of the relevance and potential of photoinduced energy transfer systems.[1] Ongoing developments in the context of dye-sensitized solar cells (DSSCs) continue to produce prominent examples to capitalize on these concepts.[2] Efforts to provide efficient photosensitizers for DSSCs abound and inspire the design of innovative chromophore systems that are both intellectually intriguing and synthetically challenging. Our concept is based on the combination of covalently attached multiple chromophores that will maximize the efficiency of intramolecular light-induced interactions and, ideally, intermolecular electron transfer. We rely on subphthalocyanines (SubPcs) as the light-triggered energy donors and attach them as antenna dyes to different energy-accepting core molecules, such as modified porphyrin, BODIPY and rylene scaffolds (see figure below). Photophysical measurements confirm an energy transfer from the SubPc entities to the central scaffolds. We will report here the syntheses of a representative multichromophore ensemble along with the photophysics of its light-induced energy transfer processes, its electrochemical properties, and its potential for integration into DSSCs.



In further development, we modified selected ensembles by implementing a carboxylate-anchoring group to facilitate the binding of the multichromophore ensemble to the TiO_2 electrode of a DSSC.

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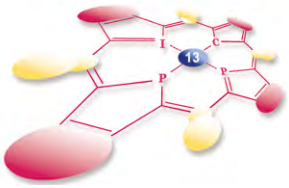

Photoinduced intramolecular electron transfer in chlorophyll-*a* derivatives directly bonding with quinone

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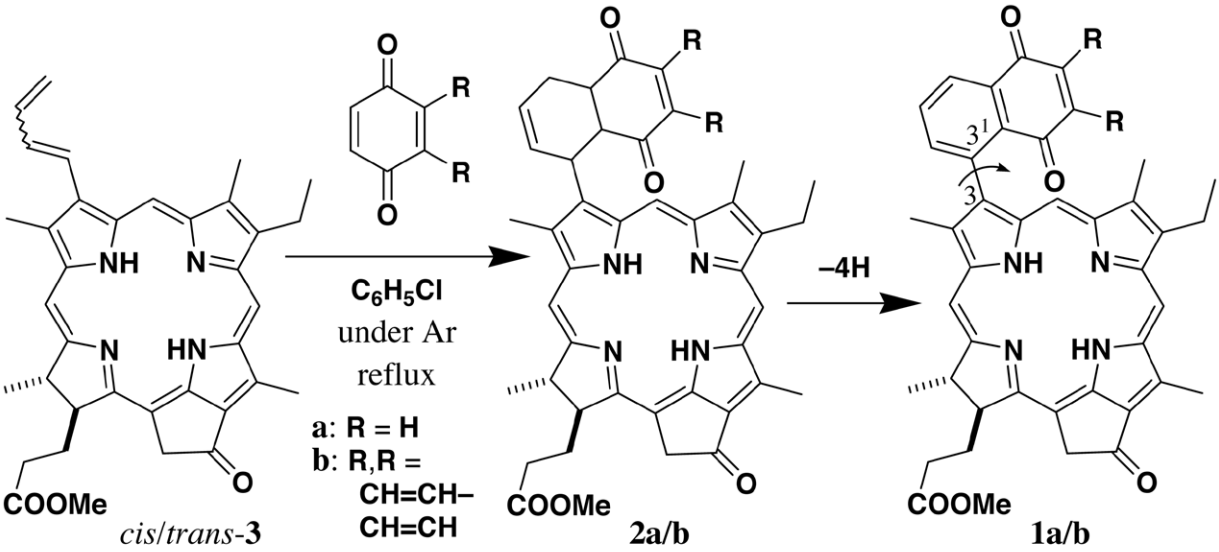
Methyl pyropheophorbides-*a* possessing a 1,4-naphthoquinon-5-yl **1a** or 9,10-anthraquinon-1-yl group **1b** at the 3-position were prepared by the Diels–Alder reaction [1] of 3-(1,3-butadienyl)chlorin **3** (*cis*/*trans* = 1/2) with benzoquinone or naphthoquinone and sequential twice dehydrogenative oxidation of the resulting adducts **2a**/**b** (Scheme 1). The synthetic chlorophyll-*a* derivatives directly bonded with the quinone were atropisomers (1 :1) around the C3–C3^1 bond [2], which were readily separated by HPLC. Since the quinone moiety was nearly perpendicular to the chlorin π-system, the distance and orientation between the chlorin and quinone chromophores were fixed in a molecule. The visible absorption spectra of the synthetic chlorin–quinone conjugates **1a**/**b** in a diluted acetonitrile solution were independent of the quinone part and the axial chirality. Their fluorescence emissions were almost completely quenched by intramolecular electron transfer from the photoexcited chlorin to the quinone, which resembled the charge-separating process in photosynthetic reaction centers.



Scheme 1. Synthesis of chlorophyll–quinone conjugates **1a**/**b**.

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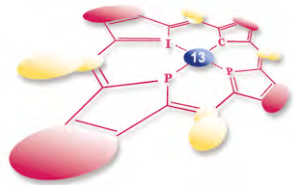

Chlorophyll-*a* derivatives fused by a π-conjugated E-ring with unique near-infrared absorption

Yamato Hashimoto, Kenshin Yamashita, Nobuyuki Hara, Mitsuaki Hirose and Hitoshi Tamiaki

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Methyl pheophorbide-*a* derivative **1a** (R^3 = CH=CH_2 in Fig. 1 middle) fused by a π-conjugated E-ring with the $C13^1$=$C13^2$ double bond was found as a synthetic example of the unique chlorophyll(Chl)-*a* derivatives [1–3], which showed split Soret absorption bands in the purple and ultraviolet-A regions and a broad absorption band at a near-infrared (NIR) region as its monomeric state (Fig. 1 left), but not its self-aggregated species. The 3-vinyl group of the Chl-*a* derivative **1a** was chemically transformed into ethyl, hydroxymethyl, dialkoxymethyl, and formyl groups **1b**–**e** [4]. All the resulting chlorins **1a**–**e** exhibited unique wide bands at a NIR region. The substitution effect on the peaks of their wide NIR bands was similar to that on the sharp redmost Qy maxima at a visible region of the corresponding pheophorbides with the $C13^1$–$C13^2$ single bond [5]. As shown in the right drawing of Fig. 1, proton signals at the C5-, C10-, and C20-positions (red) as well as of the peripheral C2-, C3-, C7-, and C8-substituents (blue) of **1** were upfield-shifted in ^{1}H NMR, compared with those of intact pheophorbides. The shifts were ascribed to the less ring current of the cyclic tetrapyrroles by π-conjugation of the E-ring. The non-fluorescent C3-substituted Chl-*a* derivatives **1a**–**e** could be useful as new materials absorbing NIR wavelength light.

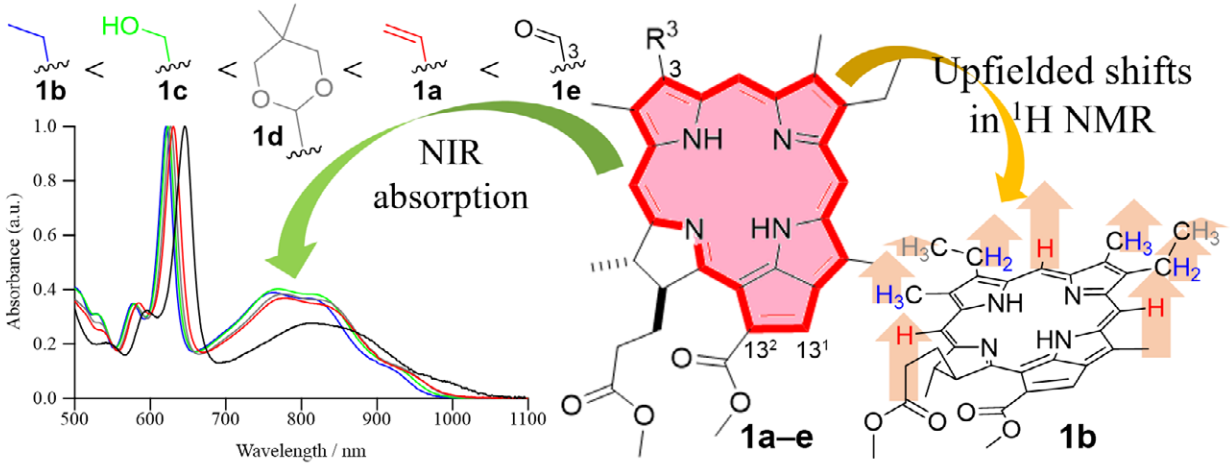

Fig. 1. Visible–NIR absorption spectra (left) of methyl 3-substituted 13^1,13^2-didehydro-13^1-deoxo-pheophorbides-*a* **1a**–**e** (middle) in THF and upfield shifts in ^{1}H NMR peaks of **1b** in $CDCl_3$ by π-conjugation at the E-ring (right).

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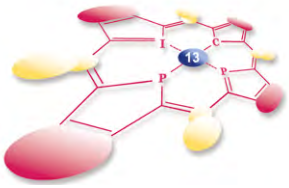

Skin Models for Probing the Penetration of Encapsulated Photosensitizers

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The combination of long-chain phospholipids (PLs) forming a bilayer and short-chain PLs forming the rim results in small disk-shaped particles referred to as bicelles. The hydrophobic interior of the bicelles provides a viable system for the delivery of hydrophobic drugs [1]. Our previous experiments have shown the possibility of encapsulating various photosensitizers (PSs) into bicelles with high encapsulation efficiency as was determined by quantitative NMR (Fig. 1A). Concentrations up to 5 mM and 2.5 mM of the PSs mTHPP and mTHPC, respectively, were completely encapsulated into 100 mM DHPC/DMPC bicelles. Using the Franz diffusion method followed either by extraction or skin embedding, it was possible to show PS penetration into the epidermis of porcine skin. Ongoing experiments are performed using different penetration enhancers to further increase the amount and depth of PS skin penetration. As an additional highly relevant and standardized model, artificial 3D skin is currently being developed. Two different models are considered for skin penetration experiments. In the first one, the artificial skin is made of a collagen scaffold containing Fibroblasts (FB) with Keratinocytes (KC) seeded on top of the scaffold. The crosstalk between FB and KC is necessary for the formation of optimal dermal-epidermal junction components [2]. For the second one, the scaffold is based on a 3D extracellular matrix (ECM), which is synthesized by the fibroblasts. Further endothelial cells (EC) are added to the FB and ECM to achieve vascularization of the artificial skin (Fig. 1B).

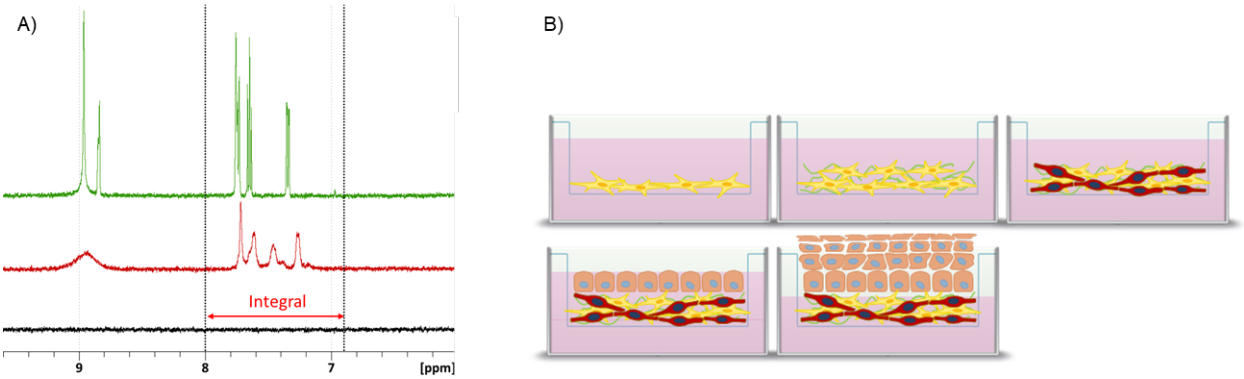

Figure 1. A: NMR spectra of mTHPP in D2O (black), in 100mM DMPC/DHPC Bicelles (red), and in Acetone D6 (green). B: Step-by-step preparation of the vascularized artificial 3D skin. The yellow cells represent the Fibroblasts (FB), the red ones represent the endothelial cells (EC) and the orange ones the Keratinocytes (KC). As soon as the KC is added, the medium (pink) is reduced as visible on the changed medium levels.

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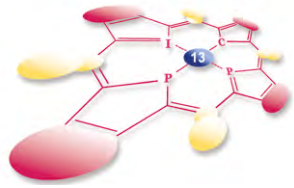

Axially coordinated supramolecular assemblies formed between zinc porphyrins or phthalocyanines and 2-pyridone-bodipys as non-fullerene acceptors

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To investigate the supramolecular donor-acceptor assemblies in light-harvesting systems, we have characterized several electron-deficient BODIPYs (acceptor) that were axially coordinated to zinc porphyrins and phthalocyanines (Figure 1). Conjugated electron-deficient 2-pyridone-BODIPYs with terminal pyridine or imidazole fragments were used to investigate how electron-withdrawing functional groups affect the formation, stability, and relaxation dynamics of the charge-separated (CS) states. The binding affinity of the porphyrinoids and the BODIPY ligand's nucleophilicity toward axial coordination in the supramolecular assembly were analyzed using UV-Vis, fluorescence, NMR, HRMS, spectroelectrochemical, and time-resolved spectra. The expected complexation of 1 : 1 via axial coordination of the nitrogen atom of the pyridine group with the central zinc atom of porphyrinoid is confirmed by ^{1}H NMR and HRMS. The binding constants for imidazole-containing BODIPYs are significantly higher than those containing pyridine.

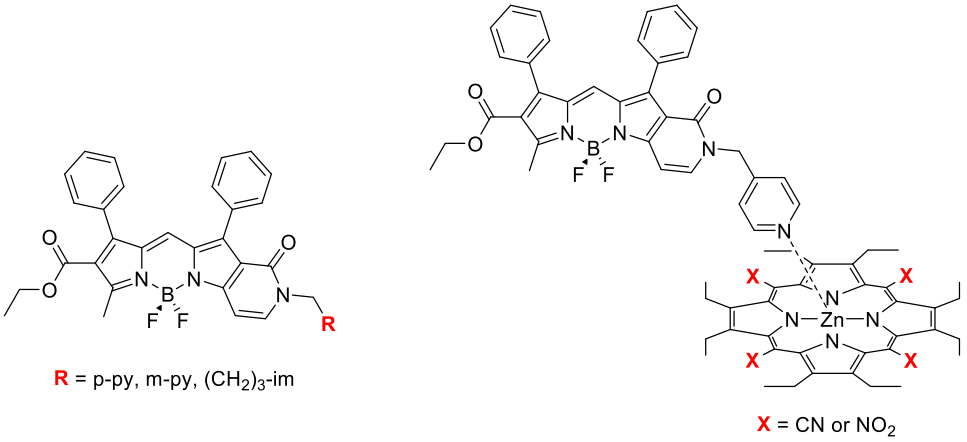

Figure 1. Structures of 2-pyridone-BODIPYs and example of axial coordination to functionalized ZnOEP.

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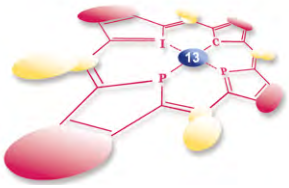

Fluorine Substituted Subphthalocyanines for Photodynamic Therapy

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Boron subphthalocyanines (BSubPcs) have garnered attention due to their optical properties, showing promise for applications in organic photovoltaics and organic light-emitting diodes [1]. Despite this potential, BSubPcs have been underutilized in biomedical research, particularly as photosensitizers for photodynamic therapy. In this work, we explore the photodynamic effectiveness of three distinct substituted BSubPcs, examining the impact of fluorine substitution, either as peripheral ligands or in a phenoxy axial substituent. *In vitro,* fluorescence imaging confirmed the successful internalization of phenoxy- and fluorophenoxy- substituted BSubPc derivatives, leading to intense fluorescence within tumor cells. Furthermore, upon irradiation with 525nm light after incubation with cancer cells, a significant increase in cytotoxicity was observed compared to the unirradiated group. This work underscores the potential of boron subphthalocyanines for fluorescence imaging-guided photodynamic therapy application.

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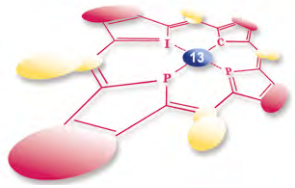

SubPc-Pyridone-Dyads for Storage and Delayed Release of Singlet Oxygen

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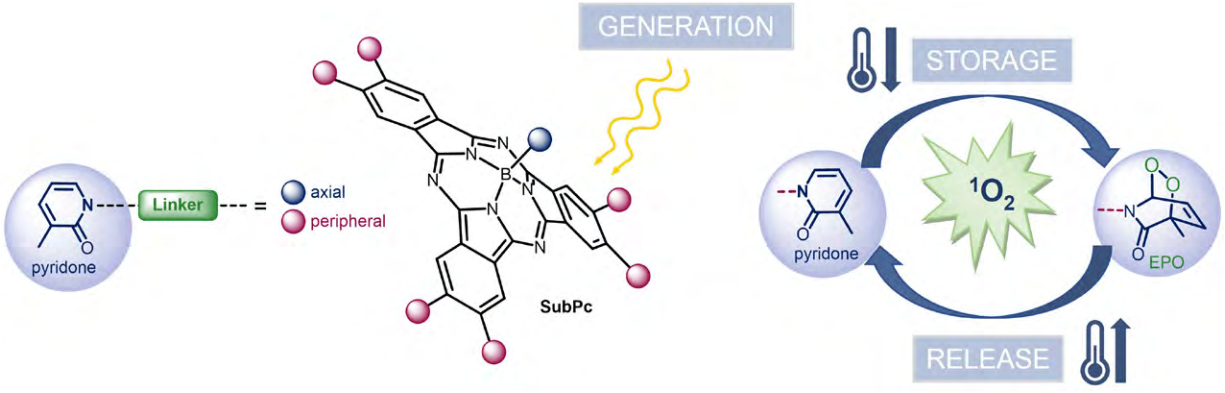
The cycloaddition of singlet oxygen ($^1O_2$) by pyridones leads to the formation of endoperoxides (EPOs), and hence to the storage and provision of $^1O_2$ with a thermally triggered delay under a cycloreversion process.[1] Therefore, in the context of photomedical treatments, EPOs are considered an alternative $^1O_2$ source to conventional photosensitizers, as they can overcome the limiting factor of strong tumor hypoxia.[2,3] The release of $^1O_2$ by EPOs takes place with the recovery of the parent compound so that the storage process is reversible and repeatable.[1-3] In this context, dyadic systems consisting of pyridones with photosensitizers such as porphyrin and BODIPY have already been investigated.[2-4] This work focuses on the combination of subphthalocyanines (SubPcs) and pyridones. We present here several dyadic systems consisting of chloro- and iodo-SubPcs as photosensitizers that were functionalized with axially or peripherally attached pyridones as EPO-forming units. We show that the dyads are active $^1O_2$ photosensitizers in the wavelength range of their absorption maxima and store SubPc-sensitized $^1O_2$ as pyridone-centered EPOs. We have investigated the reversibility of this process by photophysical, photochemical and NMR-spectroscopic means and present these results along with the latest synthetic developments.



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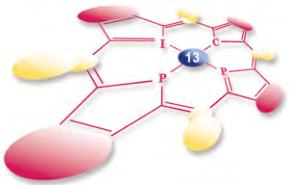

Direct Macrocyclization Synthesis and Metal Complexation of Thiazole Containing Calix[3]pyrrole analogues

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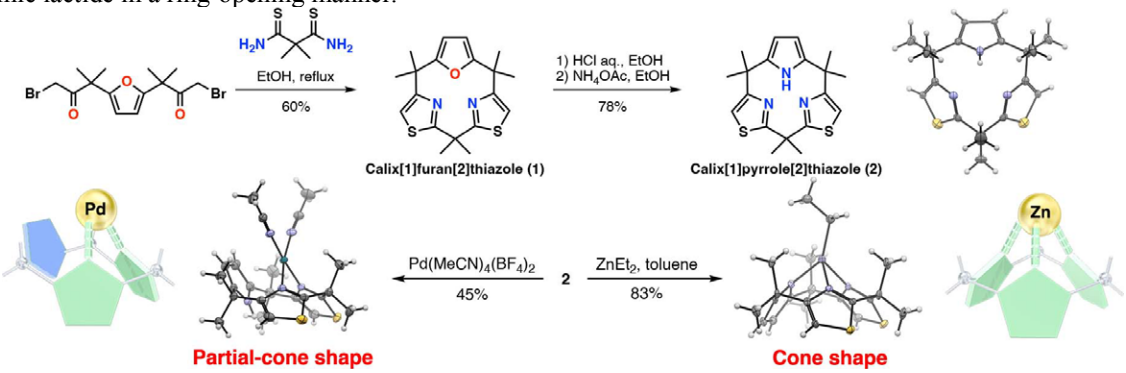
Over the past two decades, after reconstruction and anion binding properties of calix[4]pyrrole were first determined in 1996 by J. L. Sessler, many transformations and modifications have been made to modify the binding affinity of calix[4]pyrrole and its higher analogues [1]. Unfortunately, the chemistry of calix[n]pyrrole ring contraction and metal coordination has not been nearly explored yet. Calix[3]pyrrole is a novel tripyrrole macrocycle that our group has recently reported. Because of the strained structure of the internal NH sites, it rapidly cleaves the ring in acidic conditions, making it impossible to obtain by acidic condensation of pyrrole and carbonyl compounds. Rather, it was created by macrocyclization and pyrrole ring formation from linear pretreatment of hexaketones, requiring numerous steps and low yields. But since it lacks boron, it is a tripyrrole macrocycle from which a boron complex could be formed [2].
In this instance, we report a thiazoles contain calix[3]pyrrole analogue (**1**), obtained directly from linear precursor with 60% yield via Hantszch thiazole formation. Since Compound 1 lacks an inner NH site, it demonstrated excellent stability in acidic conditions. Alternatively, the related pyrrole compound calix[1]pyrrole[2]thiazole (**2**) was produced by the acid-catalyzed hydrolysis of the furan ring and the Paal-Knorr pyrrole ring formation of 1. With two imine N sites and one pyrrole NH site, compound 3 suggests that compound **2** can function as either a monoanionic tridentate ligand or a neutral bidentate ligand. Due to their bidentate coordination, the complexes exhibited a partial-cone conformation when complexed with Ag(1) or Pd(Ⅱ) using their tetrafluoroborate salts. Furthermore, the solid-state structures of these complexes demonstrated the emergence of self-assembly and weak anion-binding characteristics. Due to its tridentate coordination, the complex exhibited a cone-shaped conformation upon complexation with Zn(II) using diethylzinc, this complex might catalyze the polymerization of racemic lactide in a ring-opening manner.



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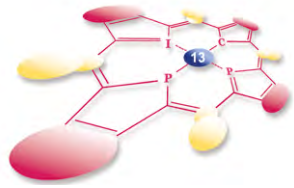

Shaping the Second Coordination Sphere for Electrocatalytic Energy Conversion

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Energy conversion plays an important role in our daily lives and the advancement of technology. At its core, energy conversion encompasses the transformation of one form of energy into another, driving processes essential for sustaining life and powering various applications. One crucial aspect is the activation of small molecules, a fundamental process to gain valuable chemicals. Furthermore, energy conversion enables the efficient storage and utilization of energy, vital for addressing pressing global challenges such as climate change and the transition to sustainable energy sources. Since the activation of small molecules requires a lot of energy, some heterogeneous and homogeneous molecular catalysts have been developed in recent years to lower the energy requirements. Among them, metallo-porphyrins have shown high activity and selectivity in catalytic electroreduction.

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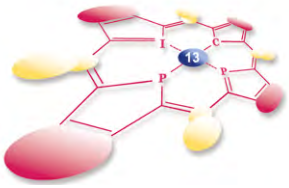

Taking advantage of a remote template effect to synthesize bipyridine-strapped porphyrins

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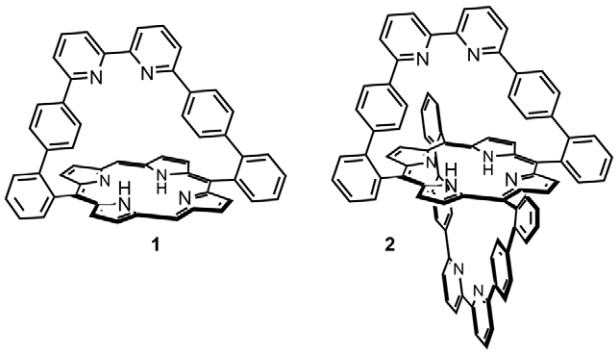
The use of metal templates to control allosteric properties or spatial orientation of remote substituents has been widely used for molecular architectures containing 2,2'-bipyridine moieties. [1] A remote metal template has now been used to synthesize two bipyridine-strapped porphyrins **1** and **2** that could not be obtained by classical methods. [2] The binding of zinc(II) to a bipyridine incorporated within a strap bearing two aldehyde groups orients the aldehydes correctly for condensation with dipyrrylmethane or pyrrole. The presence of the metal template enhanced the yield 10-fold for the single-strapped porphyrin **1** and allowed the formation of a double-strapped porphyrin **2** that had been previously impossible to prepare. These strapped porphyrins provide binding sites for two or three distinct metal centers and the resulting homo- or heterometallic structures are of interest as multispin scaffolds or as a scaffold for double-stranded rotaxanes. In addition, the flexibility of the bipyridine strap of porphyrin **1** may lead to interesting properties of an iron(II)-copper(I) derivative of this compound as a cytochrome *c* oxidase mimic.



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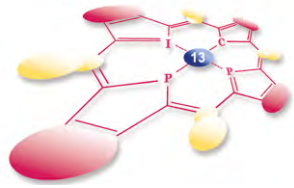

Symmetry Breaking Charge Transfer Leading to Charge Separation in a Far-Red Absorbing Bisstyryl-BODIPY Dimer

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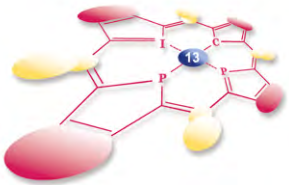
Symmetry breaking charge transfer is one of the important photo-events occurring in photosynthetic reaction centers that is responsible for initiating electron transfer leading to a long-lived charge-separated state and has been successfully employed in light-to-electricity converting optoelectronic devices. In the present study, we report a newly synthesized, far-red absorbing and emitting BODIPY-dimer to undergo symmetry-breaking charge transfer leading to charge-separated states of appreciable lifetimes in polar solvents. Compared to its monomer analog, both steady-state and time-resolved fluorescence originating from the S_1 state of the dimer revealed quenching which increased with an increase in solvent polarity. The electrostatic potential map from DFT calculations suggested the existence of a quadrupolar type charge transfer state in polar solvents, and the electrochemically determined redox gap to be smaller than the energy of the S_1 state supporting thermodynamic feasibility of the envisioned symmetry-breaking charge transfer and separation. The spectrum of the charge-separated state arrived from spectroelectrochemical studies, revealing diagnostic peaks helpful for transient spectral interpretation. Finally, ultrafast transient pump-probe spectroscopy provided decisive evidence of charge separation in polar solvents by far-red pulsed laser light irradiation. The measured lifetime of the final charge-separated states was found to be 165 ps in dichlorobenzene, 140 ps in benzonitrile and 43 ps in dimethyl sulfoxide, revealing their significance in light energy harvesting, especially from the less-explored far-red region.



Post-synthetic Modification of Bis-iron(III)-μ-oxo-porphyrin Prisms to Enhance Oxygen Reduction Electrocatalysis

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Coordination-driven self-assembly allows for the facile and high-yielding synthesis of redox-active polynuclear metalloporphyrin-based catalysts for the Oxygen Reduction Reaction (ORR)[1-5]. Over the past few years, we have demonstrated that catalysts can be tuned based on geometry, rigidity, electronegativity, metal-metal distance, and metal ion identity[6, 7]. The dinuclear cobalt porphyrin catalysts that have been developed throughout these studies are among the most selective and active molecular catalysts for ORR. The iron active site of the cytochrome c oxidase inspires us to apply our structural platform to iron porphyrins for further ORR catalysis reactivity and mechanistic studies. Herein, we use rhodium-based molecular clips for the post-synthetic modification of μ-oxo iron(III) porphyrin dimers, instead of as self-assembly building blocks. Although the cofacial geometry is inherent to the μ-oxo core, under ORR catalysis conditions, the μ-oxo dimer is rapidly cleaved, resulting in reactivity differences between traditional unclipped bis-iron(III)-μ-oxo porphyrins and our post-synthetically tethered architectures. The geometries of these dinuclear iron porphyrins were established by ^{1}H NMR, ESI-MS, and molecular modeling methods. Catalytic reactivity was explored electrochemically using cyclic voltammetry and rotating electrode measurements. The H_2O versus H_2O_2 selectivity of these iron catalysts for ORR is sensitive to the molecular clip tethering the two porphyrin sites together and differs significantly from untethered μ-oxo structures. A reaction mechanism was proposed based on spectroelectrochemistry data**.**

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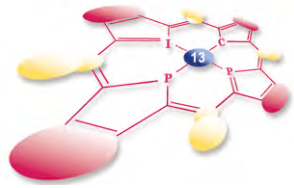

Antibody induction in mice by cobalt porphyrin-phospholipid liposome-displayed recombinant enterotoxigenic *Escherichia coli* colonization antigens

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Enterotoxigenic *Escherichia coli* (ETEC) strains cause infectious diarrhea and colonize host intestine epithelia via surface-expressed colonization factors. Colonization factor antigen I (CFA/I), a prevalent ETEC colonization factor, is a vaccine target since antibodies directed to this fimbria can block ETEC adherence and prevent diarrhea. Two recombinant antigens derived from CFA/I were investigated with a vaccine adjuvant system that displays soluble antigens on the surface of immunogenic liposomes. The first antigen, CfaEB, is a chimeric fusion protein comprising the minor (CfaE) and major (CfaB) subunits of CFA/I. The second, CfaEad, is the adhesin domain of CfaE. Owing to their His-tag, recombinant CfaEB and CfaEad, spontaneously bound upon admixture with nanoliposomes containing cobalt-porphyrin phospholipid (CoPoP), as well as a synthetic monophosphoryl lipid A (PHAD) adjuvant. Intramuscular immunization of mice with sub-microgram doses of CfaEB or CfaEad admixed with CoPoP/PHAD liposomes elicited serum IgG and intestinal IgA antibodies. The smaller CfaEad antigen benefitted more from liposome display. Serum and intestine antibodies from mice immunized with liposome-displayed CfaEB or CfaEad recognized native CFA/I fimbria as evidenced by immunofluorescence and hemagglutination inhibition assays using the CFA/I-expressing H10407 ETEC strain. These data show that colonization factor-derived recombinant ETEC antigens exhibit immunogenicity when delivered in immunogenic particle-based formulations.

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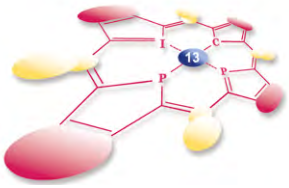

Lu bisphthalocyanine-centered poly(*ε*-caprolactone) star polymers with different chain amounts and lengths

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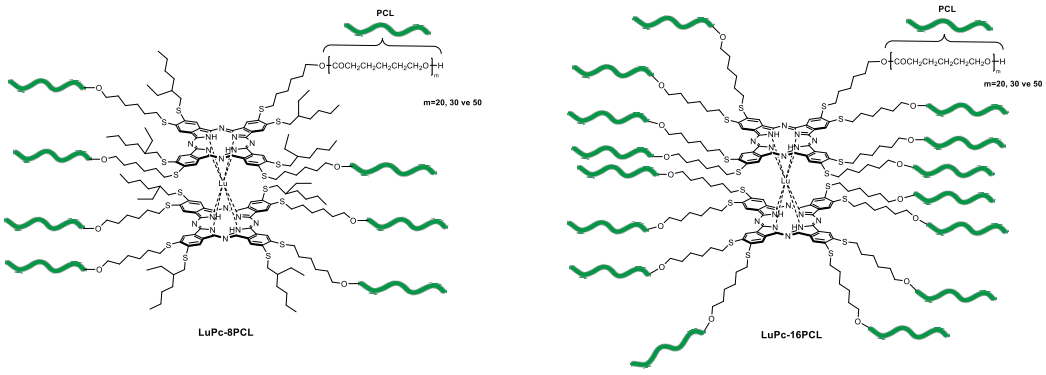
Lanthanide bisphthalocyanine complexes are known to be optical redox sensors and as such have been used for example for the sensing of NADH.[1] However they difficult to functionalized and only a handful of this type of complexes are reported.[2] On the other hand, poly(***ε***-caprolactone) (PCL) polymers are known to be excellent to form biocompatible materials.[3] A few phthalocyanine-centered PCL star polymers are reported.[4]

In order to obtain biocompatible Lu bisphthalocyanine centered PCL star polymers, octa and hexadeca hydroxylated Lu phthalocyanines have been prepared and sued as initiator for the ring-opening polymerization (ROP) of ε-caprolactone. The different polymers that have been obtained have been characterized.



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