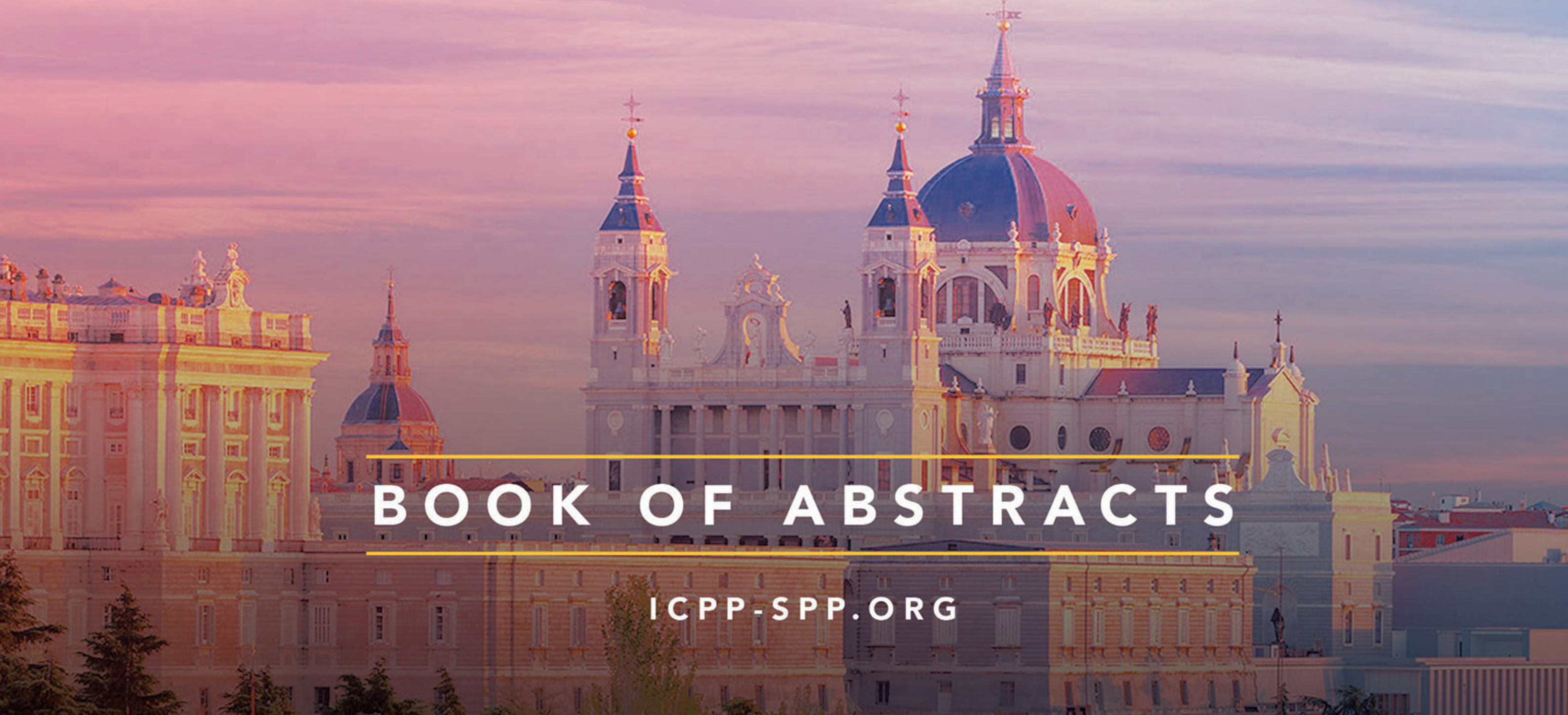
TWELFTH INTERNATIONAL CONFERENCE ON PORPHYRINS AND PHTHALOCYANINES

ICPP-12

10-15 JULY 2022 MADRID - SPAIN



BOOK OF ABSTRACTS

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Preface

In this book are gathered together all the abstracts of presentations given at the twelfth International Conference on Porphyrins and Phthalocyanines (ICPP-12) 10-15 July 2022 in Madrid, Spain as the first physical ICPP meeting since the pandemic.

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

Over 450 particpants from 37 different countries have contributed for a total of 481 abstracts, marking the desire for a comeback to ICPP physical meetings.

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 (8)
Oral Presentations (312)
Poster Presentations (161)

The papers associated with the abstracts are presented in 32 symposia organized by 74 symposium organizers.

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

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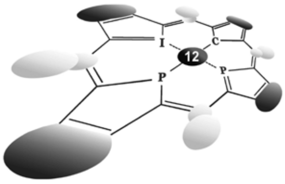

Development of Controlled Reactions using Phthalocyanine-based Materials

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Phthalocyanines (Pcs) and related macrocycles (azaporphyrinoids) are well-known artificial dyes in modern materials chemistry. To date, several strategies for the fine-tuning of their optical/electrochemical/aromatic properties have been proposed. Organic synthesis provides a wide array of organic molecules. The diversity of Pcs provides novel functionalities, which are the source of innovative science. Our group focuses on the chemical synthesis of Pcs, including "controlled reactions to produce novel Pcs" and "controlled reactions using Pcs". This lecture will discuss the recent achievements of controlled reactions in Pc chemistry.

The high electronegativity and high valence state of pentavalent phosphorus (P(V)) is expected to alter the spectroscopic properties of Pcs. We opened a synthetic strategy to prepare (aza)porphyrin P(V) complexes. These complexes featured unique physical properties owing to their combination with peripheral substituents [1]. Recentry, a synergistic effect between Si(IV) Pcs and their axial ligands has been also revealed. The near-infrared (NIR)-absorbing hydrophilic Si(IV) Pcs exhibited an efficient photodynamic activity under NIR light irradiation (810 nm) [2]. The chemoselective synthesis of Pcs is an important topic that has not received much attention. We proposed a novel Pb-mediated synthetic method, through which Pcs materials bearing electron-withdrawing groups were synthesized. These materials were shown to generate high levels of singlet oxygen and exhibited a high photostability [3–4]. In the process of investigating the Pc derivatives, we succeeded in synthesizing a novel ball-shaped metal complex that absorbs light in the NIR region. Various Pc precursors were utilized in the synthesis of symmetric and low-symmetry complexes. It was concluded that the position of the band and redox potentials could be tuned independently [5–6]. The Fine-tunability of Pcs allows for the development of a new transformation method employing far-red to NIR light. We developed several NIR catalysts for the transformation of organic molecules. The reactions further exhibited chemoselectivity with blue-to-green light-absorbing functional materials and high reaction activities even under shielded conditions [7–8].

In summary, our group has conducted extensive Pc-based research, including developing synthetic methods for Pcs production and their controlled reactions. These achievements create further opportunities for the flexible application of NIR light.

REFERENCES

1. Furuyama, T.; Kobayashi, N. *Phys. Chem. Chem. Phys.* **2017**, *19*, 15596-15612.
2. Furuyama, T.; Ishii, T.; Ieda, N.; Maeda, H.; Segi, M.; Uchiyama, M.; Nakagawa, H. *Chem. Commun.* **2019**, *55*, 7311-7314.
3. Furuyama, T.; Miyaji, Y.; Maeda, K.; Maeda, H.; Segi, M. *Chem. Eur. J.* **2019**, *25*, 1678-1682.
4. Furuyama, T.; Maeda, K.; Maeda, H.; Segi, M. *J. Org. Chem.* **2019**, *84*, 14306-14312.
5. Furuyama, T.; Shimasaki, F.; Saikawa, N.; Maeda, H.; Segi, M. *Sci. Rep.* **2019**, *9*, 16528.
6 Ishikawa, S.; Shimasaki, F.; Maeda, H.; Segi, M.; Furuyama, T. *Chem. Lett.* **2020**, *49*, 1394-1398.
7. Ishikawa, Y.; Kameyama, T.; Torimoto, T.; Maeda, H.; Segi, M.; Furuyama, T. *Chem. Commun.* **2021**, *57*, 13594-13597.
8. Katsurayama, Y.; Ikabata, Y.; Maeda, H.; Segi, M.; Nakai, H.; Furuyama, T. *Chem. Eur. J.* **2022**, *28*, e202103223.

Porphyrins, the Periodic Table, and Phototherapeutics

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I fell in love with porphyrins on my first day as a graduate student in Paul Gassman's laboratory at the University of Minnesota. I was mesmerized by the brilliant colors on the silica gel column as I chromatographed a sample of crude tetraphenylporphyrin. Over the next years, Gassman and subsequently my other mentors Jan Almlöf and Larry Que allowed me a free hand in charting my own course in research. I used the opportunity not only to deepen my knowledge of porphyrins, but also to develop skills across materials and surface science, synchrotron-based X-ray science, and quantum chemistry. From a chance meeting in 1990 with scientists at the local company Cray Research, Inc., I learned about a then-exotic theoretical method – density functional theory (DFT) – which I applied to porphyrins and other bioinorganic systems, ending up amazed at how well it worked. A CO tilting and bending potential for carbonmonoxyheme led to a new understanding of diatomic ligand discrimination by heme proteins [1] and in turn to a theoretical underpinning for the burgeoning field of heme-based sensors. Thanks to these successes, I gained a reputation – even as a postdoc – as one of the pioneers of the ab initio/DFT era of theoretical (bio)inorganic chemistry. Norwegian quantum chemist Odd Gropen, who visited Almlöf often, saw his chance and recruited me as an Associate Professor at his Department in the northern-Norwegian city of Tromsø. Through visits at synchrotrons, I kept up my interest in X-ray science. I discovered, for example, that X-ray photoelectron spectroscopy (XPS) can provide unique insight into the nature of hydrogen bonds. An XPS study of porphycenes prepared in Emanuel Vogel's laboratory established that short-strong hydrogen bonds, in spite of approaching geometrical symmetry, retain a substantial degree of charge asymmetry [2]. Years later, this line of work led to the isolation and crystallographic characterization of the long-sought *cis* tautomer of porphyrins [3].

In the new millenium, I wanted to explore the wide-open world of porphyrin analogues. I was intrigued by reports of surprisingly stable, high-valent metallocorroles – remarkable "bottleable" analogues of heme protein Compound I and II intermediates! We found that many first-row transition metal corroles are noninnocent (with significant $\text{corrole}^{\bullet 2-}$ character) and went on to develop comprehensive experimental and theoretical probes of the phenomenon [4], ultimately using state-of-the-art DMRG-CASPT2 studies to quantify metallocorroles according to their degree of noninnocence [5]. Second, we were able to map out a good chunk of the coordination chemistry of corroles [6], involving the lower half of the periodic table. We reported the first examples of ^{99}Tc, ReO, RuN, OsN, Pt, and Au corroles, inherently chiral Mo and W biscorroles, and multiple-bonded metallocorrole dimers [7]. In spite of the metal-ligand size mismatch inherent in their structures, the middle and late 5d metallocorroles by and large proved to be exceptionally stable. They were also found to exhibit NIR phosphorescence under ambient conditions and could be employed as photosensitizers in oxygen sensing, triplet-triplet annihilation upconversion, and *in vitro* photodynamic therapy (photocytotoxicity) experiments. Current research focuses on heavy element corroles as building blocks for next-generation cancer photo- and radiotherapeutics.

REFERENCES

1. Ghosh, A.; Bocian, D. F. *J. Phys. Chem*. **1996**, *100*, 6363.
2. Ghosh, A.; Moulder, J.; Bröring, M.; Vogel, E. *Angew. Chem. Int. Ed*. **2001**, *40*, 431.
3. Thomas, K. E.; McCormick, L. J.; Vazquez-Lima, H.; Ghosh, A. *Angew. Chem. Int. Ed.* **2017**, *56*, 10088.
4. Ganguly, S.; Ghosh, A. *Acc. Chem. Res.* **2019**, *52*, 2003.
5. Phung, Q. M.; Muchammad, Y.; Yanai, T.; Ghosh, A. *JACS Au* **2021**, *1*, 2303.
6. Ghosh, A. *Chem. Rev*. **2017**, *117*, 3798.
7. Alemayehu, A. B.; Thomas, K. E.; Einrem, R. F.; Ghosh, A. *Acc. Chem. Res*. **2021**, *54*, 3095.

Porphyrinoid-Based Charge and Photon Management

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At the heart of much of our research is the application of porphyrinoid molecules for ***Solar Energy Conversion*** schemes in terms of novel electron donor-acceptor ensembles and interfaces. Our expertise in time-resolved laser spectroscopic methods (i.e., femtosecond transient absorption spectroscopy, nanosecond transient absorption spectroscopy, flash-photolysis, time-correlated single photon counting), photochemistry, electrochemistry (i.e., spectroelectrochemistry and photoelectrochemistry) and photovoltaic device characterization gives assists in providing insight into fundamental aspects of ***Photon-*** and ***Charge-Management***. I will elude on how we leverage our ability to develop basic knowledge about processes that govern modular assemblies of nanoscale interfaces to reach macroscopic scales. To this end, I will highlight our interwoven work, which implements microscopic and ultrafast time-resolved spectroscopic investigations, and, which are perfectly complemented by device performance measurements and catalytic production of H_2/O_2 – all of them as analytical tools needed to analyze systems that convert solar energy into useful sources of power.

N-Confused Porphyrinoid-based Functional Near-infrared Dyes

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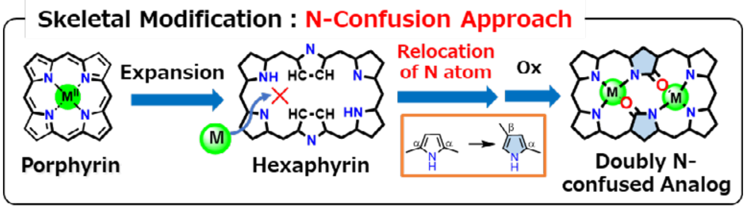
Porphyrins and their analogs can be potential near-infrared (NIR) chromophores offering new opportunities for optical materials used in the fields ranging from light-harvesting to sensing and therapeutic applications. Several skeletal modifications of the porphyrins, such as 1) core expansion, 2) peripheral fusion, and 3) chromophore array, have been used to downshift the light-responsive wavelength to the NIR window along with a high photo- and chemical stability. To date, our group has been devoted to the development of a series of π-conjugated "N-confused" porphyrin analogs embedded with inverted pyrrole rings as fundamental structures to furnish the unique metal coordination at the cavity (*cf.* Figure).[1] We thus proposed that metal complexation is the key to triggering the molecular orbital mixing/tuning of the N-confused porphyrinoids, enabling the remarkable NIR optical properties and the controlled excited-state dynamics.



For instance, a bis-Zn complex of doubly N-confused dioxohexaphyrin represents the distinct second NIR emissive and photoacoustic properties[2a]. Furthermore, the bis-Pd complex of doubly N-confused (nonoxo)hexaphyrin having a metal-carbon bond revealed the further low energy emission in the third NIR region.[2b] The bis-Pd complex of a contracted doubly N-confused dioxohexaphyrin was figured out to be a stable π radical. This molecule showed an immense two-photon absorption cross-section value upon second NIR pulse irradiation toward a nonlinear optical material.[2c] Similarly, the heteronuclear Au-Pd complex stabilized by an unsymmetrical N-confused oxohexaphyrin induced multiple metal-ligand charge-transfer transitions by d-π orbital interaction. The resulting molecular orbital feature led to the emergence of ultimate panchromatic dye (so-called black dye) with an efficient photothermal conversion ability.[2d] This presentation will provide detailed results and an overview of our achievements and future approach.

REFERENCES

1. (a) H. Furuta, T. Asano, T. Ogawa, *J. Am. Chem. Soc*. **1994**, *116*, 767; (b) P. J. Chmielewski, L. Latos-Grażyński, K. Rachlewicz, T. Głowiak, *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 779.
2. (a) K. Shimomura, H. Kai, Y. Nakamura, Y. Hong, S. Mori, K. Miki, K. Ohe, Y. Notsuka, Y. Yamaoka, M. Ishida, D. Kim, H. Furuta, *J. Am. Chem. Soc*. **2020**, *142*, 4429; (b) Y. Wang, K. Ogasahara, D. Tomihama, R. Mysliborski, M. Ishida, Y. Hong, Y. Notsuka, Y. Yamaoka, T. Murayama, A. Muranaka, M. Uchiyama, S. Mori, Y. Yasutake, S. Fukatsu, D. Kim, H. Furuta, *Angew. Chem. Int. Ed.* **2020**, *59*, 16161; (c) Y. Hisamune, K. Nishimura, K. Isakari, M. Ishida, S. Mori, S. Karasawa, T. Kato, S. Lee, D. Kim, H. Furuta, *Angew. Chem. Int. Ed.* **2015**, *54*, 7323; (d) Y. Wang H. Kai, M. Ishida, S. Gokulnath, S. Mori, T. Murayama, A. Muranaka, M. Uchiyama, Y. Yasutake, S. Fukatsu, Y. Notsuka, Y. Yamaoka, M. Hanafusa, M. Yoshizawa, G. Kim, D. Kim, H. Furuta, *J. Am. Chem. Soc*. **2020**, *142*, 6807.

Phthalocyanines and their analogues: Toward efficient fluorescence sensors and photosensitizers for PDT

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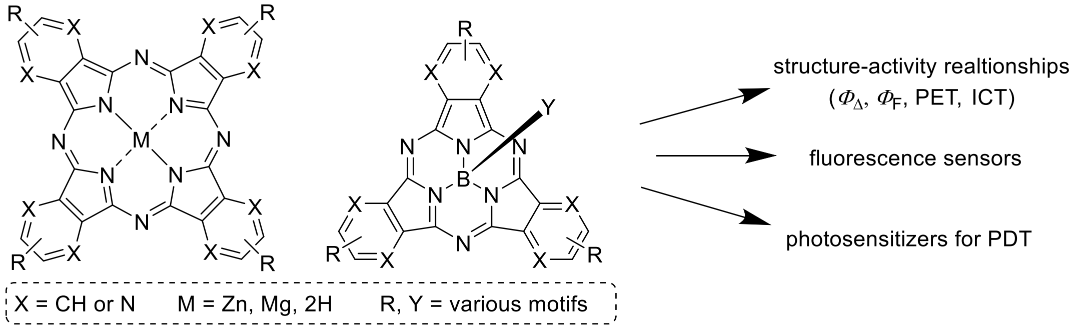
Phthalocyanines (Pcs) are well-known planar macrocycles with straightforward synthesis, interesting spectral and photophysical properties which can be easily tuned according to chosen structural motifs. Thanks to that, they are advantageously used in many different fields widely presented on ICPP conferences. My talk will give an overview of our research on phthalocyanines, subphthalocyanines and their aza-analogues (*i.e.*, tetrapyrazinoporphyrazines and pyrazino[2,3-b,g,l]subporphyrazines). First, our conclusions from study of structure-activity relationships including singlet oxygen production, fluorescence emission, photo-induced electron transfer (PET) and intramolecular charge transfer (ICT) will be discussed.[1] Second part of my talk will summarize our research in the field of red-emitting fluorescence sensors for pH (both acidic and basic)[2,3], various metal cations[4] and CO_2[5] working on principle of ICT. The last part of my talk will focus on our key findings in the area of photodynamic therapy[6,7], where our results enabled clear comparison of the role of type of the macrocycle as well as the role of peripheral substitution. Detail *in vitro* studies including monitoring of the progression of cell death provided the lead structures characterized by effective concentrations (EC_{50}) in nanomolar range, which ranks such derivatives among the best photosensitizers ever.



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REFERENCES

1. Novakova V, Donzello MP, Ercolani C, Zimcik P, Stuzhin PA, *Coord. Chem. Rev.*, **2018**, 361, 1-73.
2. Novakova V, Lásková M, Vavřičková H, Zimcik P, *Chem.- Eur. J.*, **2015**, 21 (41), 14382–14392.
3. Cidlina A, Miletin M, Fathi-Rasekh M, Nemykin V, Zimcik P, Novakova V, *Chem.- Eur. J.,* **2017**, 23, 8, 1795-1804.
4. Lochman, L.; Machacek, M.; Miletin, M.; Uhlirova, S.; Lang, K.; Kirakci, K.; Zimcik, P.; Novakova, V., *ACS Sens.* **2019,** 4, (6), 1552-1559
5. Lochman L, Zimcik P, Klimant I, Novakova V, Borisov SM, *Sens. Actuators, B,* **2017**, 246, 1100-1107.
6. Kollar J, Machacek M, Halaskova M, Lenco J, Kucera R, Demuth J, Rohlickova M, Hasonova K, Miletin M, Novakova V, Zimcik P, *J. Med. Chem.*, **2020**, 63, 7616-7632.
7. Demuth J, Gallego L, Kozlikova M, Machacek M, Kucera R, Torres T, Martinez-Diaz MV, Novakova V, *J. Med. Chem.*, **2021**, DOI: 10.1021/acs.jmedchem.1c01584.

Probing the intriguing world of heme enzymes with resonance Raman spectroscopy

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Heme enzymes are a large class of metalloproteins involved in an enormous variety of fundamental biological functions, widespread in all kingdoms. The active site architecture is unique for each enzyme and subtle differences within their catalytic center can alter substrate specificity and redox potential significantly with subsequent different functional properties. Their biochemical diversity and the understanding of their respective structure-function relationships are fundamental also for the development of different biotechnological applications.

The goal of my research has been to understand the role played by the key residues in the proximity of the heme cavity to decipher the structure-function relationship of heme-containing enzymes, using the UV-vis electronic absorption and resonance Raman (RR) spectroscopic techniques. For several enzymes, the comparative study of native and mutant enzymes, at different pH and temperatures, in the presence of various exogenous ligands, both in solution and single crystals, enabled us to define the role of the key residues in the heme cavity. The pioneering RR study of recombinant cytochrome c peroxidase demonstrated the power of the synergy of RR spectroscopy and site directed mutagenesis for elucidating subtle structural features important for protein stability and function. Moreover, RR and micro-RR techniques are able to provide a valuable complement to X-ray diffraction studies, from sample preparation to data collection and structural interpretation, yielding additional information, often beyond the resolution of the crystallographic experiment, on the dynamic and functional properties of heme enzymes in the crystalline state. For example, we have shown that the combination of RR spectroscopy on single crystals and solution samples of heme proteins is a sensitive tool to detect heme orientational disorder, even in the absence of structural data.

In the present report, the more exciting findings relevant to our understanding of the structure-function relationships of heme enzymes will be discussed. Moreover, our recent discoveries on the study of the biosynthesis of heme in Gram-positive bacteria of the Firmicutes and Actinobacteria phyla will be presented. The results allowed us to bring important contributions to our understanding of the survival mechanisms of Gram-positive bacteria, pathogens showing resistance to antibiotics.

2NH-Corrole Chemistry Based on the Development of *meso*-Free Corroles

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Corrole is a ring-contracted porphyrinoid possessing three methine carbons and one direct pyrrole-pyrrole linkage. The first synthesis of corrole was accomplished in 1965 by Johnson and Kay during their attempt to synthesize Vitamin B_{12}. A corrole usually has an inner *3NH*-type structure which can serve as a trivalent metal ligand. This property is contrasting to those of porphyrins that have an inner *2NH*-type structure. However, the synthetic chemistry of corroles had been far behind the porphyrin counterpart until effective syntheses of *meso*-triaryl-substituted corroles were developed in the early 2000s. Since I entered this field in 2013, a range of new corrole derivatives have been synthesized mainly based on the development of *meso*-unsubstituted corrole (*i.e., meso*-free corrole) which we reported in 2015.[1] In this lecture, I would like to present parts of my achievements as below.

1) *meso*-Heteroatom-substituted corroles and antiaromatic *meso*-oxoisocorroles
Effective *meso*-fabrication of 5,15-diarylcorroles has been achieved, including *meso*-nitration, *meso*-amination, and *meso*-oxygenation.[2] These studies revealed well-defined *meso*-substituent effects of corroles. Among them, *meso*-oxygenated corroles (*i.e.,* oxoisocorroles) were proved to show antiaromatic properties derived from the decent 16π conjugation circuit defined in a $C(\delta+)–O(\delta–)$ polarized resonance structure. The degree of paratropicity can be tuned by inner metal coordination and Lewis-acid coordination to the carbonyl moiety as well as photoexcitation in the case of the Pd(II) complex to generate its triplet state which shows Baird aromatic nature.

2) Redox-interconvertible corrole dimers
Two types of *meso-meso* linked corrole dimers (5-5’ linked and 10-10’ linked dimers) were synthesized via selective oxidation of *meso*-free corroles.[3] These dimers exhibited different optical properties depending on the linking position. Oxidation of these dimers resulted in the formation of doubly linked and triply linked corrole dimers with inner *2NH*-type structures as stable forms. The redox-interconversion between *2NH*-type and *3NH-t*ype forms were demonstrated, which revealed that the *2NH*-type dimers were closed-shell, non-aromatic species, while the *3NH*-type dimers were essentially aromatic, similar to fused porphyrin analogues.
Comparison with a previously reported case of 2-2’,18-18’ doubly linked corrole dimer that was shown to be an open-shell (singlet diradical) species,[4] fused corrole dimers having a *meso-meso* linkage tend to become closed-shell species because of the large spin-density at the *meso*-position. Another interesting case is the oxidation of *meso-to-meso* butadiyne-bridged corrole dimer to afford [5]cumulene-bridged *2NH*-type corrole dimer via radical homo-coupling.[5] These observations drove me to consider an active involvement of *2NH*-radical species during oxidative reactions of corroles. Finally, a *meso-meso* linked *2NH*-type corrole dimer diradical was isolated under air, which was found to be an intermediate into triply linked corrole dimer.[6]

REFERENCES

1. S. Ooi, T. Yoneda, T. Tanaka, A. Osuka, *Chem. Eur. J.* **2015**, *21*, 7772-7779.
2. T. Tanaka, K. Ueta, A. Osuka,, *Chem. Eur. J.* **2021**, 27, 15605-15615.
3. S. Ooi, K. Ueta, T. Tanaka, A. Osuka, *ChemPlusChem* **2019**, *84*, 578-588.
4. S. Hiroto, K. Furukawa, S. Shinokubo, A. Osuka, *J. Am. Chem. Soc.* **2006**, *128*, 12380-12381.
5. K. Ueta, K. Naoda, S. Ooi, T. Tanaka, A. Osuka, *Angew. Chem. Int. Ed.* **2017**, *56*, 7223-7226.
6. S. Ooi, B. Adinarayana, D. Shimizu, T. Tanaka, A. Osuka, *Angew. Chem. Int. Ed.* **2020**, *59*, 9423-9427.

Fundamental Excitations in Porphyrin Supermolecules

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Modulation of the nature and dynamics of fundamental excitations in highly conjugated structures is central to the design of the new materials for specialized emission, imaging, frequency doubling, optical limiting, photon upconversion, solar energy conversion, charge and spin transport, and quantum information science. Supermolecular chromophores – conjugated structures based on combinations of simple chromophoric building blocks that feature exceptionally strong electronic and excitonic interactions between these units – enable exquisite control over of the lifetimes, dynamics, delocalization, dephasing, and migration of excitons, polarons, and spins. This presentation will broadly cover the development of porphyrin-based supermolecules, and discuss how molecular design can be leveraged to control (i) the photophysics of these compositions, (ii) the natures and relative energies of their ground, electronically excited singlet, and electronically excited triplet states, and (iii) charge and spin transport, delocalization, and polarization in these systems.

REFERENCES

1. S. G. DiMagno, V. S.-Y. Lin, and M. J. Therien, *J. Am. Chem. Soc.* 1993, **115**, 2513.
2. S.-Y. Lin, S. G. DiMagno, and M. J. Therien, *Science (Washington, D. C.)* 1994, **264**, 1105.
3. P. J. F. de Rege, S. A. Williams, and M. J. Therien, *Science (Washington, D. C.)* 1995, **269**, 1409.
4. P. J. Angiolillo, V. S.-Y. Lin, J. M. Vanderkooi, and M. J. Therien, *J. Am. Chem. Soc.* 1995, **117**, 12514.
5. S. M. LeCours, H.-W. Guan, S. G. DiMagno, C. H. Wang, and M. J. Therien, *J. Am. Chem. Soc.*1996, **118**, 1497.
6. J. G. Goll, K. T. Moore, A. Ghosh, and M. J. Therien, *J. Am. Chem. Soc.* 1996, **118**, 8344.
7. A. G. Hyslop, M. A. Kellett, P. M. Iovine, and M. J. Therien, *J. Am. Chem. Soc.* 1998, **120**, 12676.
8. J. T. Fletcher and M. J. Therien, *J. Am. Chem. Soc.* 2002, **124**, 4298. DOI: 10.1021/ja012489h.
9. H. T. Uyeda, Y. Zhang, K. Wostyn, I. Asselberghs, K. Clays, A. Persoons, and M. J. Therien, *J. Am. Chem. Soc.* 2002, **124**, 13806.
10. P. P. Ghoroghchian, P. R. Frail, K. Susumu, D. Blessington, A. K. Brannan, F. S. Bates, B. Chance, D. A. Hammer, and M. J. Therien, *Proc. Natl. Acad. Sci. U.S.A.* 2005, **102**, 2922.
11. K. Susumu, P. R. Frail, P. J. Angiolillo, and M. J. Therien, *J. Am. Chem. Soc.* 2006, **128**, 8380.
12. T. V. Duncan, K. Susumu, L. E. Sinks, and M. J. Therien, *J. Am. Chem. Soc.* 2006, **128**, 9000.
13. T. Ishizuka, L. E. Sinks, K. Song, S.-T. Hung, A. Nayak, K. Clays, and M. J. Therien, *J. Am. Chem. Soc.* 2011, **133**, 2884.
14. J. Rawson, P. J. Angiolillo, and M. J. Therien, *Proc. Natl. Acad. Sci. U.S.A.* 2015, **112**, 13779.
15. T. Jiang, N. F. Polizzi, J. Rawson, and M. J. Therien, *J. Am. Chem. Soc.* 2017, **139**, 8412.
16. Y. Bai, J.-H. Olivier, H. Yoo, N. F. Polizzi, J. Park, J. Rawson, and M. J. Therien, *J. Am. Chem. Soc.* 2017, **139**, 16946.
17. N. F. Polizzi, T. Jiang, D. N. Beratan, and M. J. Therien, *Proc. Natl. Acad. Sci. U.S.A.* 2019, **116**, 14465.
18. G. Bullard, F. Tassinari, C.-H. Ko, A. Mondal, R. Wang, S. Mishra, R. Naaman, and M. J. Therien, *J. Am. Chem. Soc.* 2019, **141**, 14707.
19. T. Jiang, Y. Bai, P. Zhang, Q. Han, D. B. Mitzi, and M. J. Therien, *Proc. Natl. Acad. Sci. U.S.A.* 2020, **117**, 20430.
20. E. J. Viere, W. Qi, I. N. Stanton, P. Zhang, and M. J. Therien, *Chem. Sci.* 2020, **11**, 8095.2.

Chirality induction and self-assembly of metallo-porphyrins by chiral cyclohexanohemicucurbiturils

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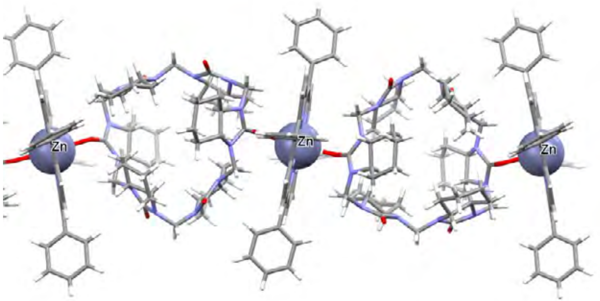
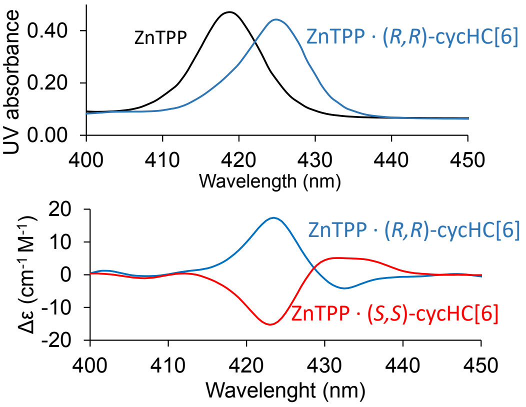
One of the intriguing phenomena in supramolecular chemistry is control over self-organisation of molecular entities. It requires availability of complementary interactions sites and size-compatibility of individual molecules. Porphyrins and cyclohexanohemicucurbiturils possess such features. For example, the size of the porphyrin ring is approximately 1 nm. It is known that cyclohexanohemicucurbit[*n*]urils (*n* = 6 and 8) are similarly sized [1, 2]. Additionally, these macrocycles bear complementary Lewis acid-base counterparts in their structures, making them well suitable for self-assembly with porphyrins [3].





Presentation will discuss synthesis and features of 6- and 8-membered homologues of cyclohexanohemicucurbiturils (cycHC[6] and cycHC[8]), their complexation with Zn- and Mg-porphyrins in solution and in solid phase. The fascinating chiroptical properties and structural characteristics of formed complexes and their application in sensing of chiral molecules.

REFERENCES

1. Aav, R. Shmatova, E. Reile, I. Borissova, M. Topić, F. Rissanen, K. *Org. Lett.*, **2013**, *15* 3786–3789.
2. Prigorchenko, E. Öeren, M. Kaabel, S. Fomitšenko, M. Reile, I. Järving, I. Tamm, T. Topić, F. Rissanen, K. Aav, R. *Chem. Commun.* **2015**, *51*, 10921–10924.
3. S. Kaabel, R. S. Stein, M. Fomitšenko, I. Järving, T. Friščić, R. Aav *Angew. Chem. Int. Ed.* **2019**, *58*, 6230-6234.
4. Ustrnul, L. Kaabel, S. Burankova, T. Martõnova, J. Adamson, J. Konrad, N. Burk, P. Borovkov, V. Aav, R. *Chem. Commun.* **2019**, *55*, 14434–1443.

Design Engineering of Phthalocyanine as Hole Selective Layers for Perovskites solar cells Fabrication

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Phthalocyanines as charge selective layers are viable alternatives to rival the use of classical Spiro-OMeTAD in perovskite solar cells (PSCs). The appealing tunable optoelectrical properties and chemical stability are their merits. However, low carrier concentration, transportability, and narrow bandgap limit their application, which can be overcome by the design engineering and choice of asymmetrically vs symmetrically substituted metal phthalocyanines, with different metals (MPcs, M = Zn or Cu). We investigated and established the correlation between electronic structures, charge carriers with the choice of core metal through an array of spectroscopic techniques. We further developed triple bonded π-conjugated zinc-phthalocyanine dimers through molecular engineering and evaluate their ability to extract holes in PSCs. The designed dimers promote the formation of uniform films, which is pinholes free a requirement for device fabrication. The fabricated PSC with our developed Pcs gave a competitive performance and showed notable long-term stability under stress conditions such as moisture and thermal. Additionally, they can work effectively without the use of any dopant, to boost reliability.

Replace Disinfection of wastewater in the mitigation of SARS-CoV-2 by photodynamic treatment

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Abstract The last few years have been marked by the SARS-CoV-2 pandemic. This virus is found in the intestinal tract reaching the wastewater system, and consequently the natural receiving water bodies. As such, inefficiently treated wastewater (WW) can be a means of contamination. The disinfection methods of WW currently used can lead to the formation of toxic compounds, be expensive, or inefficient. As such, new alternative approaches must be considered, namely microbial photodynamic inactivation (PDI). In this work, the phage ϕ6 was used as a model of the SARS-CoV-2. The phage viability was studied in WW under different environmental conditions of temperature, pH, salinity, solar and UV radiation. To assess the efficiency of virus inactivation, PDI assays were performed, both in phosphate-buffered saline (PBS) and in filtered WW, and toxicity tests of the resultant PDI-treated WW were performed on native marine microorganisms. Overall, the results showed that phage ϕ6 remains viable in different environments conditions for a considerable amount of time, with PDI being an efficient approach in the inactivation of the virus, and with the PDI-treated effluent showing no toxicity to native aquatic microorganisms under dilution realistic conditions, endorsing PDI as an efficient an safe WW tertiary disinfection method.

Acknowledgements : Thanks are due to University of Aveiro and FCT/MCTES for the financial support to CESAM (UIDP/50017/2020 + UIDB/50017/2020) and LAQV-REQUIMTE (UIDB/50006/2020) through national funds and, where applicable, co-financed by the FEDER, within the PT2020 Partnership Agreement, anced by FEDER through COMPETE 2020, POCI and PORL and FCT through PIDDAC). This work was financially supported by the project PREVINE (FCT-PTDC/ASP-PES/29576/2017), through national funds and when applicable co-financed by the FEDER, within the PT2020 Partnership Agreement and “Compete” 2020.

Computational Strategies for Designing Functional Molecular Switches from Expanded Porphyrins

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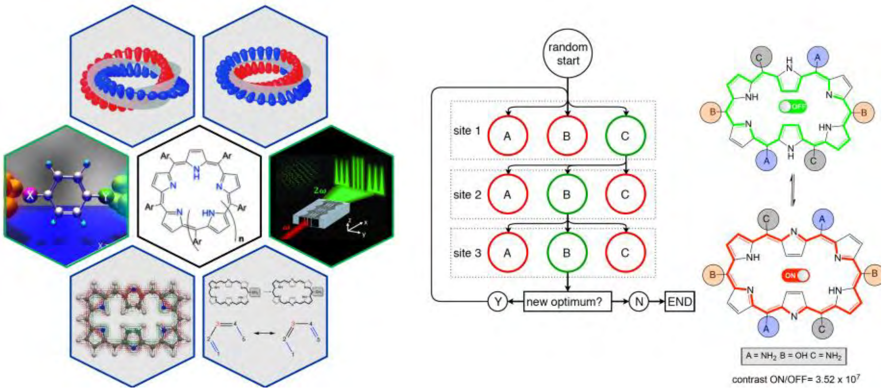
Expanded porphyrins are currently recognized as the ideal test bed to explore the correlation between molecular properties and (anti)aromaticity since they provide perfect aromatic and antiaromatic congener pairs with the same molecular framework but different number of π-electrons. These macrocycles are flexible enough to adopt different π-conjugation topologies, namely Hückel, Möbius and twisted-Hückel, allowing one to explore the concept of ground- and excited-state aromaticity in complex topologies. Nevertheless, the quantification of the aromaticity in expanded porphyrins is challenging due to the presence of multiple conjugation pathways and highly nonplanar geometries in certain topologies. In this talk, I will first introduce a multidimensional approach to quantify Hückel and Möbius aromaticity based on global and local descriptors rooted on the energetic, magnetic, reactivity, structural and electronic criteria [1,2]. Then, I will focus on the complex structure-property relationships between aromaticity, π-conjugation topology, photophysical and nonlinear optical properties [3]. It is noteworthy that the absorption spectra of certain antiaromatic Hückel structures are characterized by more intense absorption bands than its aromatic homologues, contrary to the general statement that antiaromatic porphyrinoids exhibit significantly attenuated absorption bands as compared to aromatic ones [3]. Our results pinpoint the importance of symmetry and topology on the first and second hyperpolarizability, while aromaticity has a not clear influence on these quantities. Overall, I will show how the concept of the reversal of aromaticity upon topology and redox interconversions can be exploited to create novel molecular electronic devices [3] and efficient nonlinear optical (NLO) switches [4]. Ultimately, innovative inverse design strategies can be applied to further explore the combinatorial chemical compound space of *meso*-substituted hexaphyrins in search of high-contrast NLO switches [5].



REFERENCES

1. M. Alonso, I. Fernandez, Quantifying aromaticity according to the energetic criterion. In *Aromaticity*, I. Fernandez, Ed. (Elsevier) **2021**, pp. 195-235.
2. I. Casademont-Reig, T. Woller, J. Contreras-García, M. Alonso, M. Torrent-Sucarrat, E. Matito, *Phys. Chem. Chem. Phys.* **2018**, *20*, 2787–2796.
3. T. Woller, P. Geerlings, F. De Proft, B. Champagne, M. Alonso, *J. Phys. Chem. C* **2019**, *123*, 7318-7335.
4. T. Stuyver, M. Perrin, P. Geerlings, F. De Proft, M. Alonso, *J. Am. Chem. Soc.* **2018**, *140*, 1313-1326.
5. E. Desmedt, T. Woller, J. L. Teunissen, F. De Vleeschouwer, M. Alonso, *Front. Chem.* **2021**, *9*, 786036.

Synthesis and Redox Chemistry of Confused Isophlorins

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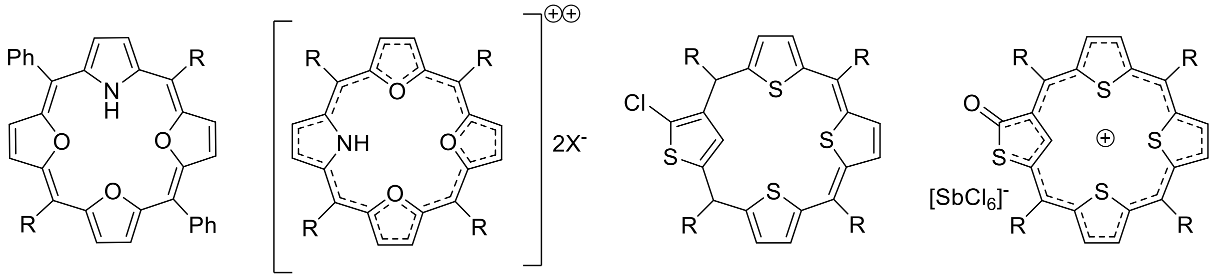
Isophlorin and its derivatives represent stable examples of anti-aromatic porphyrinoids [1]. To date, isophlorin derivatives have been synthesized with heterocyclic units such as furan, thiophene or selenophene. These 4nπ macrocycles tend to undergo reversible two-electron oxidation as substantiated by core-modified isophlorins [2, 3]. Altering the connectivity between the heterocyclic units can yield confused isophlorinoids as shown below. Confused isophlorins are structural isomers of the parent isophlorin, but with modified electronic and redox properties [4]. Particularly, a 20π S-confused isophlorin undergoes a two-electron irreversible oxidation to yield a short-lived 19π electron species which can be quickly oxidized to its 18π mono-catonic species. Their synthesis, structural, electronic and redox properties will be discussed in this presentation.



REFERENCES:

1. E. Vogel, *Pure Appl. Chem*. 1993, 65, 143.
2. B. K. Reddy, A. Basavarajappa, M. D. Ambhore and V. G. Anand. *Chem. Rev.* 2017, 117, 3420.
3. S. P. Panchal, S. C. Gadekar and V. G. Anand. Angew. *Chem. Int. Ed.,* 2016, 55, 7797.
4. S. Panchal and V. G. Anand. *Org. Lett.* 2017, 19, 4854.

Phthalocyanines as Functional Recognition Motif for Highly-Ordered Biobased Materials

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Supramolecular self-assembly of biomolecules provides a powerful bottom-up strategy to build functional nanostructures and materials. Among the different biomacromolecules, protein cages offer various advantages including uniform size, versatility, multi-modularity and high stability [1]. On the other hand, DNA-origami technology yields almost any arbitrary nanoscale shape with nanometer-scale accuracy. These structures are highly relevant for a broad array of applications such as drug delivery, imaging, and material science among others.

Herein, the electrostatic interaction between cationic phthalocyanines (Pcs) and protein cages (apoferritin and tobacco mosaic virus) proteins led to optically active crystals with different morphologies (Figure 1) [2]. Different approaches, such as thorough molecular design or supramolecular interactions were explored, in order to ensure the non-aggregating behavior of the Pcs in aqueous media. The same principles have been applied to basic DNA origami nanoforms, paving the way towards the use of DNA-based nanostructured photoactive materials [3].

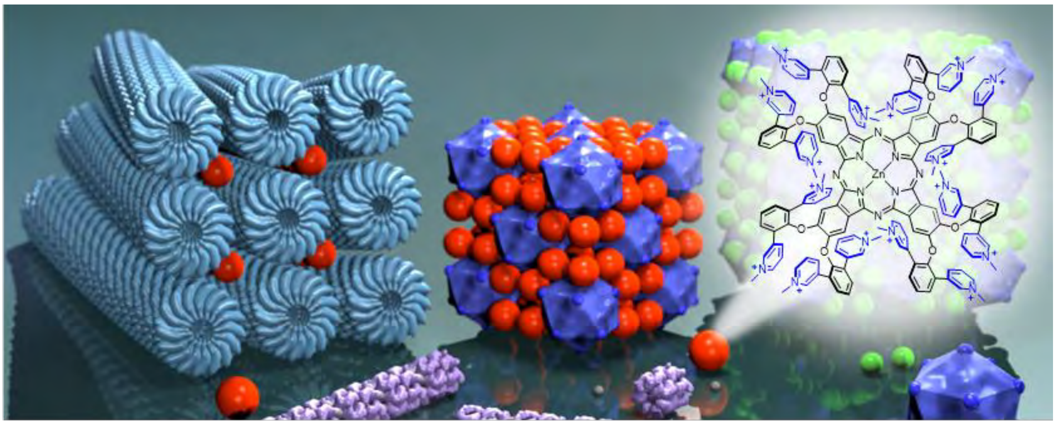
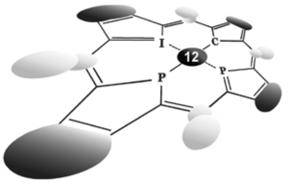


Figure 1. Schematic representation of the photoactive biohybrids

REFERENCES

1. A. Korpi, E. Anaya-Plaza, S. Välimäki, and M. Kostiainen, *Wiley Interdiscip Rev. Nanomed. Nanobiotechnol.*, **2020**, 12, e1578.
2. a) J. Mikkila, E. Anaya-Plaza, V. Liljeström, J. R. Caston, T. Torres, A. de la Escosura and M. Kostiainen, *ACS Nano*, **2016**, 10, 1565. b) E. Anaya-Plaza, A. Aljarilla, G. Beaune, Nonappa, J.V.I. Timonen, A. de la Escosura, T. Torres and M. Kostiainen, *Adv. Mater.*, **2019**, 31¸1902582.
3. a) A. Shaukat, E. Anaya-Plaza, S. Julin, V. Linko, T. Torres, A. de la Escosura, and M. A. Kostiainen, *Chem. Commun.*, **2020**, 56, 7341. b) A. Rahali, A. Shaukat, V. Almeida-Marrero, B. Jamoussi, A. de la Escosura, T. Torres, M. A. Kostiainen, and E. Anaya-Plaza, *Bioconjugate Chem.*, **2021**, 32, 1123.



Electronic Delocalization and Aromaticity in Covalent Porphyrin Nanostructures

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Template-directed synthesis can be used to create π-conjugated porphyrin rings that are as big as proteins.[1, 2] These systems mimic the light-harvesting behavior of photosynthetic chlorophyll arrays [3, 4] and they display global aromaticity in some oxidation states,[5-8] for example the 12-porphyrin nanoring template complex is globally aromatic in its 6+ oxidation state with a Hückel circuit of $4n + 2 = 162$ π electrons.[8] Recent work on these systems will be presented.

This presentation is dedicated in honour of Prof. Atsuhiro Osuka.

REFERENCES

1. P. S. Bols, H. L. Anderson, *Acc. Chem. Res.* **2018**, *51*, 2083–2092.
2. P. S. Bols, M. Rickhaus, L. Tejerina, H. Gotfredsen, K. Eriksen, M. Jirásek, H. L. Anderson, *J. Am. Chem. Soc.* **2020**, *142*, 13219–13226.
3. J. Pruchyathamkorn, W. J. Kendrick, A. T. Frawley, A. Mattioni, F. Caycedo-Soler, S. F. Huelga, M. B. Plenio, H. L. Anderson, *Angew. Chem. Int. Ed.* **2020**, *59*, 16455–16458.
4. G. Bressan, M. Jirásek, H. L. Anderson, I. A. Heisler, S. R. Meech, *J. Phys. Chem. C* **2020**, *124*, 18416–18425.
5. M. Jirásek, H. L. Anderson, M. D. Peeks, *Acc. Chem. Res.* **2021**, *54*, 3241–3251.
6. M. Jirásek, M. Rickhaus, L. Tejerina, H. L. Anderson, *J. Am. Chem. Soc.* **2021**, *143*, 2403–2412.
7. S. M. Kopp, H. Gotfredsen, J.-R. Deng, T. D. W. Claridge, H. L. Anderson, *J. Am. Chem. Soc.* **2020**, *142*, 19393–19401.
8. M. Rickhaus, M. Jirásek, L. Tejerina, H. Gotfredsen, M. D. Peeks, R. Haver, H. Jiang, T. D. W. Claridge, H. L. Anderson, *Nat. Chem.* **2020**, *12*, 236–241.

Cobalt Porphyrin Catalysts for Photocatalytic Generation of Solar Fuels and Commodity Chemicals

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This talk will describe two separate strategies to use Co-porphyrin catalyst to photocatalytically produce (i) CO from CO_2 [1] and (ii) polymer-grade ethylene from the acetylene contaminant of ethylene feed [2]. CO_2 reduction is accomplished in pure water with an unprecedented combination of performance parameters: turnover number (TON(CO)) >80,000, quantum yield (QY) >3% and selectivity >99%, using $CuInS_2$ colloidal quantum dots (QDs) as photosensitizer and a Co-porphyrin catalyst. The amine/ammonium-terminated ligand shells of the QDs are responsible for the exception performance of this system by establishing (i) an electrostatic assembly with Co-porphyrin, which allow the colocalization of protons, CO_2, and catalyst at the QD core that serves at the source of the electrons; (ii) a dynamic equilibrium between carbamic acid and free CO_2 that increases the local concentration of available CO_2; and (iii) "second-sphere" effects that improve the efficiency of the Co-porphyrin catalyst. Our room-temperature capture−conversion approach is possible because of the nanoconfined environment of the QD surface, which enables the particular reactivity of the carbamic acid as a labile sequestration agent [1]. In a separate system based on a Co-porphyrin catalyst, acetylene is reduced to ethylene, an intermediate in the production of ~50-60% of all plastics. The semi-hydrogenation of acetylene impurity to ethylene usually requires energy-intensive thermochemical routes. Our selective photocatalytic strategy is a major step toward the production of ethylene from acetylene with the lowest energy footprint possible. Our system reduces acetylene into ethylene with several advantages over the present hydrogenation technology, including (i) operation with near 100% conversion in an ethylene-rich gas feed and ≥99% selectivity under both non-competitive (no ethylene co-feed) and competitive (ethylene co-feed) conditions, the latter being industrially relevant; (ii) operation at room temperature using light and water in place of high temperature and an external H_2 feed, and (iii) use of earth-abundant cobalt in the catalyst, which works not only in combination with the benchmark photosensitizer $[Ru(bpy)_3]^{2+}$, but also with inexpensive and organic semiconductor (carbon nitride). These features offer substantial advantages over current hydrogenation technologies with respect to selectivity and sustainability [2].

REFERENCES

1. Arcudi F., Đorđević L., Nagasing B., Stupp S. I., Weiss E. A. "Quantum Dot-Sensitized Photoreduction of CO_2 in Water with Turnover Number > 80,000" *Journal of the American Chemical Society*, 143 (43), 18131–18138 (2021).
2. Arcudi F., Đorđević L., Schweitzer, N., Stupp. S. I., Weiss, E. A.. "Selective Catalytic Conversion of Acetylene to Ethylene Powered by Water and Visible Light." DOI: 10.21203/rs.3.rs-932017/v1 (2022)

Atropisomerism of porphyrin derivatives uncovers molecular motifs that promote cell uptake

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The intrinsic challenge of large molecules to cross the cell membrane and reach intracellular targets is a major obstacle for the development of new medicines. We report how the rotation along a single C–C bond between separable atropisomers of a drug in clinical trials [1] improves cell uptake and therapeutic efficacy. The atropisomers of redaporfin (a fluorinated sulfonamide bacteriochlorin photosensitizer of 1135 Da) [2] are separable and display orders of magnitude differences in photodynamic efficacy, which are directly related to their differential cellular uptake. We show that redaporfin atropisomer uptake is passive and only marginally affected by ATP depletion, plasma proteins or formulation in micelles. The α_4 atropisomer, where the sulfonamide substituents are on the same side of the tetrapyrrole macrocycle, exhibits the highest cellular uptake and phototoxicity. This is the most amphipathic atropisomer with a conformation that optimizes H-bonding with polar head groups of membrane phospholipids. Consequently, α_4 binds to the phospholipids on the surface of the membrane, flips into the membrane to adopt the orientation of a surfactant, diffuses and eventually flips to the interior of the cell (bind-flip-diffuse-flip mechanism). We observed increased α_4 internalization by cells of the tumor microenvironment *in vivo* and correlated this to the response of photodynamic therapy (PDT) [3] when tumor illumination is performed 24 h after α_4 administration. These results show that properly oriented aryl sulfonamide groups can be incorporated into drug design as efficient cell-penetrating motifs *in vivo* and unveil unexpected biological consequences of atropisomerism.

REFERENCES

1. Santos, L. L.; Oliveira, J.; Monteiro, E.; Santos, J.; Sarmento, C., Treatment of Head and Neck Cancer with Photodynamic Therapy with Redaporfin: A Clinical Case Report. *Case Rep Oncol* **2018,** *11* (3), 769-776.
2. Arnaut, L. G.; Pereira, M. M.; Dąbrowski, J. M.; Silva, E. F. F.; Schaberle, F. A.; Abreu, A. R.; Rocha, L. B.; Barsan, M. M.; Urbańska, K.; Stochel, G.; Brett, C. M. A., Photodynamic Therapy Efficacy Enhanced by Dynamics: The Role of Charge Transfer and Photostability in the Selection of Photosensitizers. *Chemistry – A European Journal* **2014,** *20* (18), 5346-5357
3. Donohoe, C.; Senge, M. O.; Arnaut, L. G.; Gomes-da-Silva, L. C., Cell death in photodynamic therapy: From oxidative stress to anti-tumor immunity. *Biochimica et Biophysica Acta (BBA) - Reviews on Cancer* **2019,** *1872* (2), 188308

Pyrrole containing systems for OAT and Water Splitting

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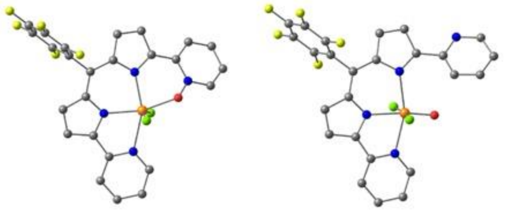
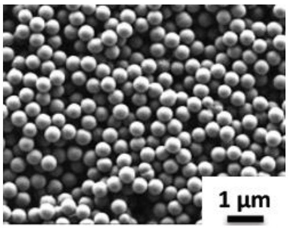
Oxygen Atom Transfer (OAT) reactions are important in chemical synthesis and biology where high valent metal-oxos are key catalytic species.[1] Bioinspired models have been investigated to replicate the reactivity and selectivity of hemic and non-hemic enzymes.[2] We developed a tetradentate dipyrrinpyridine ligand, a hybrid of hemic and non-hemic models. The catalytic activity of the iron(III) derivative was investigated in presence of iodosylbenzene. Unexpectedly, MS, EPR, Mössbauer, UV-Visible and FTIR spectroscopic signatures supported by DFT calculation provide convincing evidence for the involvment of a relevant Fe^{III}-O-N_{Py} active intermediate.[3] We have developed nanostructured conjugated polymers based on pyrrole (PPyr), that can act as photocatalysts to replicate the functions of Photosystem II. We found that when dispersed in water without the presence of any co-catalysts or any sacrificial agents, PPyr can photooxidize water to O_2. This study sets a new paradigm to rethink about the photosplitting of water.[4]



Fe^{III}-O-Pyridine Intermediate



Nano-PolyPyrrole for Water Splitting

REFERENCES

1. T. Corona, K. Ray, W. Nam, *ACS Cent. Sci.* **2019**, *5*, 13-28.
2. a) J. T. Groves, R. C. Haushalter, M. Nakamura, T. E. Nemo, B. J. Evans, *J. Am. Chem. Soc.* **1981**, *103*, 2884-2886; b) A. R. McDonald, L. Que, Jr., *Coord. Chem. Rev.* **2013**, *257*, 414-428;
3. Nhat-Tam Vo et al. *Chem.Comm.,* **2021**, 57, 12836-12839.
4. *in submission*

Ring-Opening and Ring-Closing Reactions of Porphyrins on Surfaces

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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 supports [1]. In particular on-surface metalation and covalent polymerization reactions in an ultrahigh vacuum (UHV) environment have provided elegant routes to tetrapyrrole complexes, polymers, and hybrid structures with distinct chemical, physical, and structural properties [2-4].

Here, I will review some our recent activities employing temperature-induced ring-opening and ring-closing reactions on coinage metal supports in UHV, affording specific porphyrin derivatives and nanostructures. Specifically, the examples cover the surface-mediated formation of a tripyrrin derivative from conformationally distorted free-base tetraphenylporphyrin (2H-TPP) [5] and the synthesis of square-like porphyrin tetramers from unsubstituted Zn- and free-base porphines (see Fig.). Low-temperature scanning tunnelling microscopy (STM), spectroscopy (STS), and bond-resolved atomic force microscopy (AFM) supported by complementary theoretical modelling were used to comprehensively characterize precursors, intermediates and reaction products with sub-molecular resolution. The formation of the planar tripyrrin derivative occurs by cleaving off one pyrrole units from 2H-TPP in an "inverted" precursor conformation on Cu(111) and thus involves a ring-opening reaction. The tetramer is achieved by dehydrogenative homocoupling of porphines on Ag(100), involving intermolecular ring-closure. The resulting product affords a central, planar cyclooctatetraene (COT) moiety, which can promote antiaromatic behaviour. These results open routes to study intriguing tetrapyrrole derivatives on surfaces.

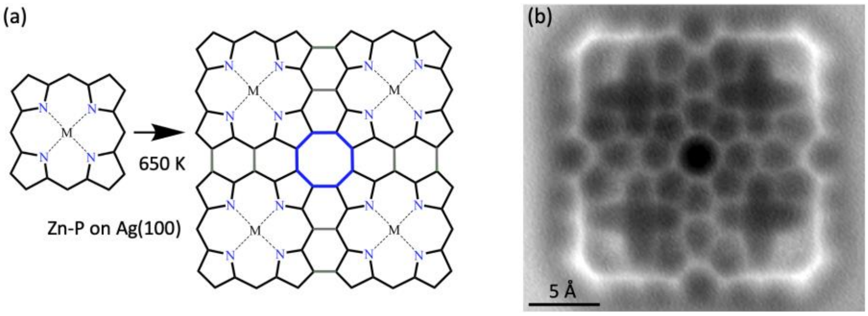

Figure. (a) Scheme of dehydrogenative porphine coupling to square-like tetramer with a central COT moiety (in blue). (b) AFM image of Zn-tetramer on Ag(100).

REFERENCES

1. W. Auwärter *et al.*, Nature Chem. 7, 105 (2015)
2. K. Diller *et al.*, Chem. Soc. Rev. 45, 1629 (2016)
3. L. Grill *et al.*, Nature Chem. 12, 115 (2020)
4. L.M. Mateo *et al.*, Chem. Sci. 12, 247 (2020)
5. F. Bischoff *et al.*, J. Am. Chem. Soc. 143, 15131 (2021)

Phthalocyanine-Based Electric Double Layer Transistors and Photoelectric Conversion

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In recent years, organic electronics using the electric double layer (EDL) at the electrode-electrolyte interface has attracted much attention, but many organic semiconductors are soluble in electrolytes such as ionic liquids (ILs), which causes problems with device stability. Phthalocyanine analogues are organic semiconductors that have been studied for a long time, and their advantages include the ability to fabricate high-quality thin films and chemical stability, which is expected to lead to the development of organic electronics combined with ionic liquids.

In our previous work [1, 2], we examined EDL organic thin-film field-effect transistors (OTFTs) with ionic liquids as gate dielectrics and with PbPc and TiOPc thin films as semiconductors. PbPc and TiOPc are known to exhibit bipolar electrical conduction. By testing ten different ILs, we found that the threshold gate voltages for hole and electron injection were proportional to the rest potentials of the ILs. This dependence suggested that the hole and electron injection occur at the HOMO and LUMO levels of the bipolar organic semiconductors from the electrode potential in IL. We also examined the EDL-OTFTs of PtPc, with various LiCl-PEG (polyethylene glycol) solutions of different concentrations as gate electrolytes. The threshold voltages linealy followed the concentration dependence of the rest potentials the LiCl-PEG solutions [3].

We have been also studying photoelectric conversion using polarization currents, using a [metal(M)|Insulator(I)|Semiconductor(S)|Metal(M)] (MISM) structure, in which the S layer efficiently causes photoelectric charge separation, while the polarization in the I layer helps the charge separation in the S layer, and the synergistic effect of the two produces a huge transient photocurrent [4]. However, in such a MISM photocell, it is sufficient to increase the capacitance of the I layer in order to increase the intensity of the transient photocurrent, but the response speed decreases. To overcome this trade-off between intensity and speed, we proposed an asymmetric MISIM photocell by combining a high-κ IL and a low-κ organic polymer insulator as the I layers. Actually, a MISIM cell, fabricated using an IL and an organic polymer insulator as the I layers, and SnNPc with near-infrared absorption as the S layer, realized 300 MHz bandwidth photoelectric conversion with 850 nm laser excitation. [5].

REFERENCES

1. For review, see T. Fujimoto, K. Awaga, *Phys. Chem. Chem. Phys.* **15**, 8983 (2013).
2. T. Fujimoto, M.M. Matsushita, K. Awaga, *J. Phys. Chem. C*, **117**, 5552 (2013).
3. C. Nanjo, D. Yokogawa, M.M. K. Awaga, *Phys. Chem. Chem. Phys.*, **22**, 12395 (2020).
4. L. Hu, X. Liu, S. Dalgleish, M.M. Matsushita, H. Yoshikawa, K. Awaga, *J. Mater. Chem. C*, **3**, 5122 (2015).
5. L. Reissig, S. Dalgleish, K. Awaga, *Sci. Reports*, **8**, 15415 (2018)

Corrole insights in pericyclic and Mannich type reactions

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The research developed in the last decades shows that the structural features of corroles conferred by the low symmetry, ring trivalent coordination core and tautomeric isomerism can have important implications not only on their chemistry but also on their applications [1, 2]. The promising achievements already obtained with these contracted macrocycles in different fields like sensing, catalysis, and photodynamic therapies among others can justify the strong activity on synthetic approaches to afford key derivatives with adequate features for a specific application [1, 2]. Among the different synthetic approaches to obtain new corroles the functionalization/post-functionalization of β-pyrrolic positions via cycloadditions reactions are really promising procedures [1].

In this communication, it will be presented how simple cycloaddition reactions in the presence of azomethine ylides lead to corroles with unusual and unexpected structures. It will also be discussed the derivatization of these macrocycles through Mannich type reactions.

Experimental procedures, mechanistic considerations and spectroscopic data of the same macrocycles will be presented and discussed.

Acknowledgements Thanks are due to University of Aveiro and FCT/MCTES for the financial support to CESAM UIDP/50017/2020 + UIDB/50017/2020 + LA/P/0094/2020 and the LAQV-REQUIMTE (UIDB/50006/2020) through national funds and, where applicable, co-financed by the FEDER, within the PT2020 Partnership Agreement, and to the Portuguese NMR Network, which partially support the NMR spectrometers by Infrastructure Project Nº 022161 (co-financed by FEDER through COMPETE 2020, POCI and PORL and FCT through PIDDAC). This work was financially supported by the project Corlutna (POCI-01-0145-FEDER-031523) funded by FEDER, through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI), and by national funds (OE), through FCT/MCTES.

REFERENCES

1. J.F.B. Barata, M.G.P.M.S. Neves, M.A.F. Faustino, A.C. Tomé, J.A.S. Cavaleiro, *Chem. Rev.* **2017**, *117*, 3192.
2. C.D. Natale, C.P. Gros, R. Paolesse, *Chem. Soc. Rev.*, **2022**, DOI:10.1039/d1cs00662b, *in press*

Light Harvesting, Charge Separation and Charge Transport in Covalent Organic Frameworks

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Photoactive molecular building blocks such as porphyrins and phthalocyanines can be spatially integrated into the crystalline lattice of covalent organic frameworks (COFs), allowing us to create models for organic bulk heterojunctions, chemical sensors and porous electrodes for photoelectrochemical systems. In this presentation, we will address means of controlling the morphology and packing order of COFs in thin films [1] and with spatially locked-in building blocks.[2]

We will discuss different strategies aimed at creating electroactive networks capable of light-induced charge transfer. For example, we have developed a COF containing stacked thienothiophene-based building blocks acting as electron donors with a 3 nm open pore system, which show light-induced charge transfer to an intercalated fullerene acceptor phase.[3] 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.[4] Additional synthetic efforts have led to several COFs integrating extended chromophores capable of efficient harvesting of visible and near infrared light, for example [5].

Extending newly developed 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.[6] The detailed mechanism of excited state dynamics in light-harvesting conjugated COFs has been revealed by means of transient absorption spectroscopy.[7] 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.[8] Finally, COF films can also act as ultrafast solvatochromic chemical sensors [9] and show very efficient electrochromic response.[10] The great structural diversity and morphological precision that can be achieved with COFs make these materials intriguing model systems for organic optoelectronic materials.

REFERENCES

1. Medina et al., *J. Am. Chem. Soc*. 2015, *137*, 1016.
2. Ascherl et al., *Nature Chem*. 2016, *8*, 310.
3. Dogru et al., *Angew. Chem*. Int. Ed. 2013, *52*, 2920.
4. Calik et al., *J. Am. Chem. Soc*. 2014, *136*, 17802.
5. Keller et al., *J. Am. Chem. Soc*. 2017, *139*, 8194.
6. Sick et al., *J. Am. Chem. Soc*. 2018, *140*, 2085.
7. Jakowetz et al., *J. Am. Chem. Soc*. 2019, *141*, 11565.
8. Rotter et al., *Chem. Sci*. 2020, *11*, 12843.
9. Ascherl et al., *Nature Commun*. 2018, *9*, 3802.
10. Bessinger et al., *J. Am. Chem. Soc.* 2021, *143*, 7351.

Aryl- and Heteroaryl-substituted Thioalkyl-Porphyrazines for Optoelectronic Applications

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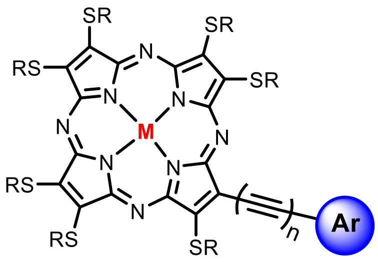
Tetrapyrroles are among the most widely employed molecular scaffolds for optoelectronic applications, i.e. organic photovoltaic (OPV), non-linear optics (NLO), and liquid crystals (LC). However, the large majority of these applications concern porphyrin and phthalocyanine macrocycles, while alkyl porphyrazines are much less investigated in this field. On the contrary, the latter display interesting optical and electronic properties which makes them promising constituents of optoelectronic materials. Moreover, particularly interesting are thioalkyl-porphyrazines, because the sulfur atoms at the periphery allows these molecules to display discotic columnar mesophases [1] and impart peculiar spectroscopic and electrochemical properties. Their UV-visible spectrum shows, in fact, very broad and intense absorption bands in correspondence to main the solar emission spectrum, and their HOMO-LUMO bandgap results suitable for OPV. Taking advantage of an original asymmetrization procedure [2], we obtained several non-symmetrical mono-aryl and ethynylaryl thioalkyl-porphyrazines where the aryl choice allowed to tune the electronic, spectroscopic, and self-aggregation properties [3]. Moreover, these aryl substituted derivatives provides unconventional "push-pull" systems displaying NLO properties [3b], constituting efficient light acceptors for OPV dye-sensitized (DSSC) solar cells[3b] and dyes for the construction of photoactive nanohybrids with nanocarbons (i.e. carbon nanotubes and graphene) [4]. Looking for further improvement of the optoelectronic performances of these compounds, novel mono aryl- and heteroaryl-substituted thioalkyl porphyrazines have been synthesized with the aim to optimize both the optical response and the anchoring properties on TiO_2, essential feature for application in DSSC cells. In this communication these novel achievements will be described.



M = H_2, Ni, Pd; **Ar** = aryl, heteroaryl
R = alkyl; n = 0,1

REFERENCES

1. Belviso, S.; Ricciardi, G.; Lelj, F. *J. Mater. Chem*. **2000**, *10*, 297.
2. Belviso, S.; Ricciardi, G.; Lelj, F.; Monsù Scolaro, L.; Bencini, A.; Carbonera, C. *J. Chem. Soc., Dalton Trans.*, **2001**, 1143.
3. (a) Belviso, S.; Amati, M.; Rossano, R.; Crispini, A.; Lelj, F. *Dalton Trans*. **2015**, *44*, 2191. (b) Belviso, S.; Tessore, F.; Santoro, E.; Righetto, S.; Penconi, M. *J. Phys. Chem. C* **2019**, *123*, 13074.
4. Belviso, S.; Capasso, S.; Santoro, E.; Najafi, L; Lelj, F.; Superchi, S.; Casarini, D.; Villani, C.; Spirito, D.; Bellani, S.; Del Rio Castillo, A. E.; Bonaccorso, F. *Adv. Funct. Mater.* **2018**, 1705418.

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

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For some time, our group has been focused on the molecular design, synthesis and application of boron subphthalocyanines (BsubPcs) and subnaphthalocyanines (BsubNcs), which are macrocycles with a chelated central boron atom [1]. Our focal point has been and continues to be equally balanced between the basic and applied chemistry and their application in organic photovoltaics (OPVs)/organic solar cells (OSCs)[2a] and organic light emitting diodes (OLEDs) [2b]; electrochemical [2c] and photophysical properties being critical to these applications.

For this presentation, I will focus on our progress on 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 has been shown to be 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 recently 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. As this was in parallel with the separation method development, the computational data is also comparable to the electrochemical data.

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 accelerated development of BsubNcs, BsubPcs and the hybrids whereby their molecular design and synthesis was first been justified through a computational model.

REFERENCES

1. (a) Claessens, C. G.; *et al. Chem. Rev.* **2014**, *114* (4), 2192-2277.
2. (a) Morse, G. E.; Bender, T. P., *ACS Appl. Mater. Interfaces* **2012**, *4* (10), 5055-5068. (b) Plint, T. G.; *et al.*, *Opt. Mater.* **2018**, *75*, 710-718. (c) Grant, T. M.; *et al.*, *Chem. Rec.* **2019**, *19* (6), 1093-1112. (c) Sampson, K. L.; *et al. J. Phys. Chem. A* **2018**, *122* (18), 4414-4424.
3. (a) Dang, J. D.; *et al. J. Mat. Chem. A* **2016**, *4* (24), 9566-9577. (b) Jones, S.T.E.; *et al.*; *ChemRxiv*. **2020**, https://doi.org/10.26434/chemrxiv.13366190.v1.
4. (a) Holst, D.; *et al.*; *New J. Chem.*, **2021**, 45, 5791-5807. (b) Holst, D.; *et al.*; *New J. Chem.*, **2021**, 45, 21082-21091.

Insights on the usefulness and challenges in application of chiral and achiral bis-metalloporphyrin hosts for determining the absolute configuration of chiral guests

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During the past few decades, the application of porphyirn-based sensors for the search of molecular and supramolecular chirality has undergone a fast development in organic, bioorganic, theoretical and material sciences (1-3). The progress has shown a positive impact of broader spectroscopic and advanced theoretical analysis that can better tackle the conformational diversity. The latter has proven to be one of the most difficult aspects in the structural analysis of porphyrin host-guest complexes, in particular, when the search of absolute configuration of chiral guest is the main goal.

We will discuss a few examples of bidentate complexations of chiral guests to achiral flexible porphyrin tweezer-hosts, and also when both, the tweezer-host and guest, are chiral. Interestingly, the host-guest complexes that are involved in either enantio-or diastereoselective interactions reveal significant differences in their conformational diversity. It became clear the latter is the prime challenge for the analysis of diagnostic exciton-split CD and chiral sensing towards the guest AC (4-7). Therefore, the selection of suitable tweezer-host does represent one of the most critical aspects when the main goal is ~~a~~ determination of the guest's AC. For this purpose, we carried-out Molecular Dynamics (MD) simulations, *ab initio* geometry optimization and calculations of electronic CD (ECD) by TD-DFT along with 1H-NMR experimental analysis to facilitate the interpretations and better understanding the potential application of both types, achiral and chiral, tweezers (8).

REFERENCES

1. Pescitelli, G.; Di Bari, L; Berova, N. *Chem. Soc. Rev*. 2014, 43, 5211.
2. Berova, N.; Pescitelli, G.; Petrovic, A. G.; Proni, G. *Chem. Comm.*. 2009, 40, 5958;
3. Ozcelik, A.; Pereira-Cameselle, R.; Ulrih, N.P.; Petrovic, A.G.; Alonso-Gómez, J.L *Censors*, 2020, 974
4. Petrovic, A. G.; Vantomme, G.; Negrón-Abril, Y. L.; Lubian, E.; Saielli, G.; Menegazzo, I.;Cordero, R.; Proni, G.; Nakanishi, K.; Carofiglio, T.; Berova, N. *Chirality,* 2011, 23, 808;
5. Saha, B; Ikbal, S. A.; Petrovic, A. G.; Berova, N.; Rath, S. P. *Inorg Chem* .2017, 56. 3849;
6. Saha, B; Petrovic, A. G.;Dhamija, A; Berova, N.; Rath, S. P. *Inorg Chem* .2019, 58, 1142
7. Saha, B; Ikbal, S. A.; Rath, S. P. *Inorg Chem* .2020, 59, 7795-7809
8. Petrovic, A. G.; Berova, N.; Rath, S. P. *unpublished results*

Thin films of chiro-optically active porphyrin-based supramolecular adducts: Design and preliminary applications

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Porphyrins (Pp) represent ideal compounds for the design and the optimization of thin layers for different applications, due to their unique optical and redox properties [1,2]. Furthermore, Pp are ideal building blocks for the formation of supramolecular complexes driven by non-covalent approaches [3]. In this context, supramolecular chirality plays a key role in the functioning of supramolecular chiral adducts with intriguing potential in the field of applied science and technology [4]. Thus, in this contribution, different supramolecular adducts based on achiral or chiral Pp derivatives (non-water soluble) and water-soluble silica nanohelices (Figure 1) differently functionalized (i.e. $-NH_2$, -OH) have been obtained and simultaneously transferred onto solid supports by means of self-assembly humid approaches, as Langmuir Schaefer and Layer-by-Layer. The chosen methods ensure high control of the deposition parameters and reproducibility, which are both key factors for preserving Pp peculiar physical-chemical properties [1]. The hybrid films have been extensively characterized through different methods, Atomic Force Microscopy, UV-Vis Absorption and Fluorescence Spectroscopy, Ellipsometry, Raman, Circular Dichroism. Preliminary and fundamental evidence of possible applications as active layers for chiral discrimination have been finally achieved.

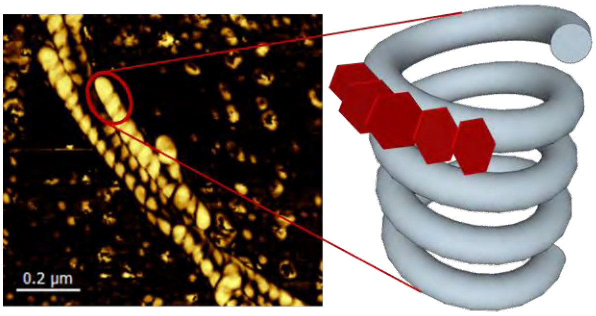

Figure 1. AFM image and a schematization of porphyrin-decorated silica nanohelice adducts deposited by LS approach.

REFERENCES

1. Simona Bettini, Ludovico Valli, Gabriele Giancane; *Molecules* **2020**, *25*(16), 3742.
2. Simona Bettini, Nitika Grover, Michela Ottolini, Cornelia Mattern, Ludovico Valli, Mathias O. Senge, Gabriele Giancane; *Langmuir* **2021**, *37*(47), 13882–13889.
3. Massimiliano Gaeta, Ivan Pietro Oliveri, Maria Elena Fragala`, Salvatore Failla, Alessandro D'Urso, Santo Di Bella, Roberto Purrello; *Chem. Commun.* **2016**, *52*, 8518.
4. Victor Borovkov; *Symmetry* **2014**, *6*, 256-294.

A Functional Myoglobin Model with Increased O_2/CO Binding Selectivity in Aqueous Solution

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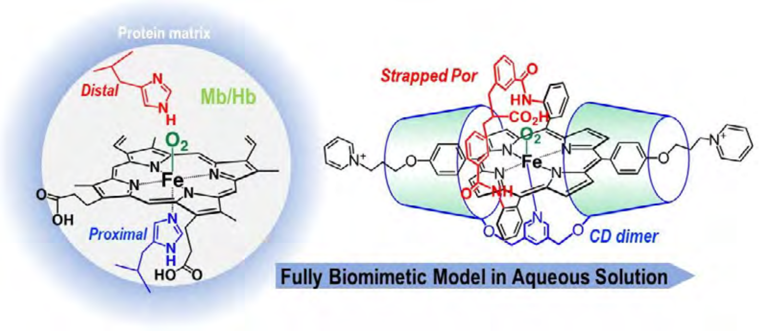
Myoglobin (Mb) and hemoglobin (Hb) are responsible for storage and transportation of molecular oxygen (O_2) in mammals [1,2]. In both Mb and Hb, heme is bound by a proximal histidine (His) and surrounded by polar amino acid residues including a distal His.



In the present report [3], a water-soluble strapped iron(III)tetraaryl-porphyrin (**Fe^{III}Por-1**) bearing two propyl pyridinium groups at the meso positions and an overhanging carboxylic acid group at the apical position of the strap was synthesized to mimic the function of myoglobin with the distal polar functionality in aqueous solution. As a result, **Fe^{III}Por-1** forms a stable 1:1 inclusion complex with a per-*O*-methylated β-cyclodextrin dimer delivering a pyridine linker (**Py3OCD**), and providing both a hydrophobic environment and a proximal fifth ligand to stabilize the O_2-complex. The ferrous complex (**Fe^{II}PorCD-1**) binds both O_2 and CO in aqueous solution. The O_2 and CO binding affinities ($P_{1/2}^{O2}$ and $P_{1/2}^{CO}$) and half-life time ($t_{1/2}$) of the O_2 complex of **Fe^{II}PorCD-1** are 6.3 and 0.021 Torr, and 7 h, respectively, at pH 7 and 25°C.

The O_2 and CO kinetics indicate that the strapped structure in **Fe^{II}PorCD-1** inhibits the entrance of these gaseous ligands into the iron(II) center, as evidenced by lower k_{on}^{O2} and k_{on}^{CO} values.

Therefore, this 1:1 supramolecular complex **Fe^{II}PorCD-1** functions as a water-soluble Mb functional model with both a proximal ligand to iron(II) and distal polar functionality. It is remarkable that the distal COOH group directed to the iron(II) center located at the hydrophobic cavity of the CD dimer induces a “kick off” effect with respect to coordinated CO, while it has the reverse effect of stabilization of coordinated O_2. Therefore, the distal overhanging COOH group in the present model system leads to the best O_2/CO selectivity among the aqueous Mb biomimetics reported so far.

REFERENCES

1. Perutz, M. F. *Annu. Rev. Physiol.* **1990**, *52*, 1–25.
2. Jameson, G. B.; Ibers, J. A. In *Bioinorganic Chemistry*; Bertini, I., Gray, H. B., Lippard, S. J., Valentine, J. S., Eds.; University Science Books: Mill Valley, CA, **1994**; pp 167–251.
3. Mao, Q.; Das, P. K.; Gac, S. L.; Boitrel, B.; Dorcet, V.; Koji Oohora; Hayashi, T.; Kitagishi, H., *Inorg. Chem.* **2021,** 60, 12392-12404.

O-annulation of porphyrin scaffoldings: Synthesis and optoelectronic properties

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In this oral contribution, I will focus on the synthetic strategies to prepare novel π-extended O-embedded porphyrins and study the effect of the O-dopant on the molecular optoelectronic properties. Four generations of O-fused porphyrins peripherally annulated with pyrano rings will be reported. In the first part, we will discuss the synthetic developments to obtain mono- and di-pyranoporphyrins through CuO-mediated pyran annulation reaction. In a second instance, we will discuss the synthesis of tetra- and octa-pyranoporphyrins. It was found that the increase in the number of O-bridges led to the slight bathochromic shift of absorption maxima, thus indicating a weak conjugation between the porphyrin core and the co-planarized meso-aryl substituents. Consequently, the insignificant changes of the optical bandgap along with the series of mono- and di- pyranoporphyrins were detected. On the other hand, the cyclic voltammograms of O-embedded porphyrins showed the pronounced shrinking of the electrochemical HOMO-LUMO bandgap. Spectroelectrochemical investigations suggested that these molecules could also use as electrochromic-active units, and their integrations into first electrochromic devices discussed. Together with the in-solution studies, O-annulations were also performed on surfaces and their results discussed herein.

Optical Sensing of Temperature and Oxygen with Dually Emitting Metalloporphyrins

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Complexes of porphyrins with platinum group metals represent one of the most important group of indicators for optical oxygen sensing [1]. Temperature-sensitive response of oxygen sensors makes measurement of this parameter essential for precise oxygen monitoring. Optical temperature probes [2] offer advantage of measuring temperature in exactly the same way the oxygen measurement is performed. However, so far combination of two probes has been unavoidable that significantly increases the complexity of the system and is associated with the risk of undesirable effects such as FRET between the probes, leaching etc. Design of new generation of indicators that would enable simultaneous sensing of oxygen and temperature is therefore of highest interest.

Thermally activated delayed fluorescence (TADF) represents a process where fluorescence is emitted after thermal activation of the molecule that was previously promoted to the excited triplet state. Such emitters have been primary used in OLED technology but rarely for sensing. Although TADF emission is also known for porphyrins, it is often too weak to be practically useful for sensing. Recently reported benzoporphyrin dyes show strong TADF at elevated temperatures along with phosphorescence [3] and thus have high potential for sensing of temperature. However, the dynamic range of these systems was not optimal for majority of applications that are realized at ambient temperatures and physiological conditions. In this work we report new metalloporphyrins with decreased singlet-triplet energy gap that show viable TADF already at low temperatures combined with attractive spectral properties (Fig. 1). When embedded into virtually oxygen-impermeable polymer matrices they build a new family of molecular thermometers that utilize self-referenced ratiometric read-out with spectrally separated dual emission. Immobilization into oxygen-permeable matrices results in dual oxygen/temperature sensors that combine ratiometric read-out of temperature with the decay time-based oxygen read-out.

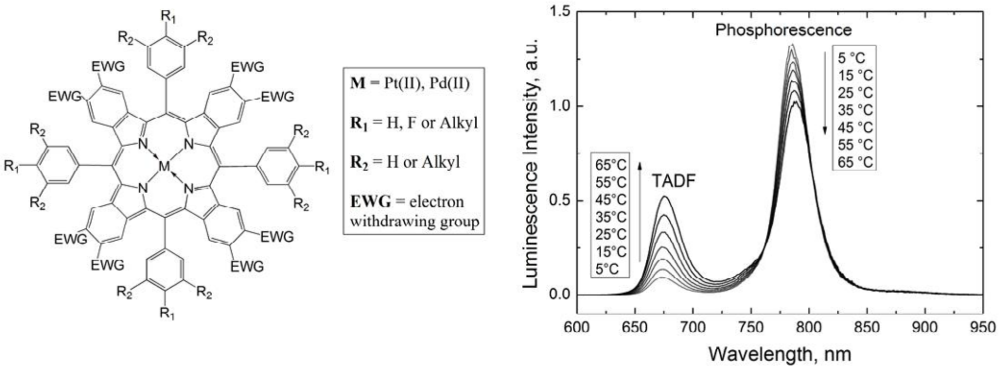
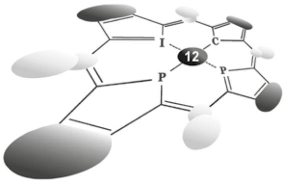


Figure 1: General chemical structure of the new emitters and temperature dependency of the luminescence spectra of a Pt(II) complex embedded into polystyrene.

REFERENCES

1. X. D. Wang and O. S. Wolfbeis, *Chem. Soc. Rev.* **2014**, 43, 3666-3761.
2. X. D. Wang, O. S. Wolfbeis, R. J. Meier, *Chem. Soc. Rev.* **2013**, 42, 7834-7869.
3. P. Zach et al., *ACS Appl. Mater. Interfaces*, **2017**, 9, 38008-38023.



Supramolecular chirogenesis in porphyrin chemistry: Recent developments and further prospects

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Chirality is one of the most fundamental issues of Nature and plays a profound role in many natural and various artificial systems making it of paramount importance not only for fundamental science but also for different practical applications including pharmaceuticals, agriculture, fragrances, cosmetics, food and bio additives, catalysis, functional materials, nonlinear optics, etc. Therefore, the process of chirality sensing is of prime interest of modern research endeavors. Amongst known methods the supramolecular chirogenic approach to detect chirality is the most challenging and prospective. Porphyrinoid based supramolecular chirogenic structures so far have attracted much attention for chirality-sensing purposes, owing to their appropriate chemical, physico-chemical, and spectral properties, easy handling and versatile modification, direct relation to many biological processes, and wide applicability. This prompted us to apply porphyrinoid-based supramolecular systems for design and development of smart chirality sensors.

Several years ago, we have discovered that a simple ethane-bridged bis-porphyrin and bis-chlorin structural motifs can be effectively served for different application purposes owing to the specific molecular and supramolecular functionalities. In particular, the unique functional property of this bis-porphyrin host is based upon the structural semi-flexibility of covalent linkage between two porphyrin units resulting in the environmentally assisted syn-anti conformational switching and tweezer formation depending upon the guest structure, which can be effectively detected by various spectroscopic methods and employed in different sensing areas, such as chirogenic probes, chiral recognitions, and chemical sensors [1-6].

Further developments and prospects toward new chirality sensors on the basis of porphyrin structures for new classes of organic compounds including chiral pollutants and corresponding theoretical evaluation of chirogenic systems will be discussed [7-12].

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REFERENCES

1. Borovkov V. *Symmetry* **2014**, *6*, 256-294.
2. Borovkov V. *Symmetry* **2010**, *2*, 184-200.
3. Borovkov V., Inoue Y. *Eur. J. Org. Chem.* **2009**, 189-197.
4. Hembury G.A., Borovkov V. V., Inoue, Y. *Chem. Rev.* **2008**, *108*, 1-73.
5. Borovkov V.V., Inoue Y. *Top. Curr. Chem.* **2006**, *265*, 89-146.
6. Borovkov V.V., Hembury G.A., Inoue Y. *Acc. Chem. Res.* **2004**, *37*, 449-459.
7. Ustrnul L., Kaabel S., Burankova T., Martõnova J., Adamson J., Konrad N., Burk P., Borovkov V., Aav R. *Chem. Commun*., **2019**, *55*, 14434-14437.
8. Konrad N., Meniailava D., Osadchuk I., Adamson J., Hasan M., Clot E., Aav R., Borovkov V., Kananovich D. *J. Porphyrins Phthalocyanines*, **2020**, *24*, 840-849.
9. Osadchuk I., Borovkov V., Aav R., Clot E. *Phys. Chem. Chem. Phys.*, **2020**, *22*, 11025-11037.
10. Osadchuk I., Konrad N., Truong K.-N., Rissanen K., Clot E., Aav R., Kananovich D., Borovkov V. *Symmetry*, **2021**, *13*, 275.
11. Osadchuk I., Aav R., Borovkov V., Clot E. *ChemPhysChem*, **2021**, *22*, 1817-1833.
12. Konrad N., Horetski M., Sihtmäe M., Truong K.-N., Osadchuk I., Burankova T., Kielmann M., Adamson J., Kahru A., Rissanen K., Senge M.O., Borovkov V., Aav R., Kananovich D. *Chemosensors*, **2021**, *9*, 278.

Porphycenes networks, 2D and 3D thin film with intriguing properties suitable for *in situ* sensing

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Among the various chemical detection systems, optical sensors play a fundamental role thanks to their easy working operation and transduction mechanism and the wide range of applications (e.g. vapor sensors for acids or volatile compounds) as miniaturized devices in *point-of-care* medicine, environmental analysis, explosive tracing... Leading research is focusing in exploring novel active and stable materials which can be processed by different techniques, hence enabling for the realization of a broad range of sensing setups.

Porphycene (H_2Po), a tetrapyrrolic 18π electrons chromophore (inset Fig.1a), is a constitutional isomer of the porphyrin family and differs from them in the pattern of connection of the four pyrrole rings.[1] The different size of the inner core and the reduced symmetry of the molecule, compared to porphyrins, endow H_2Po with unique stability and optical features suitable for the exploitation as ultrafast responsive material. Herein we report the first studies on **H_2Po** continuous and ***compact 2D/3D vacuum deposited thin films***. The films are studied by means 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* (Fig.1b-d) when the film is exposed to acid and we verified the fast reversibility of the process.

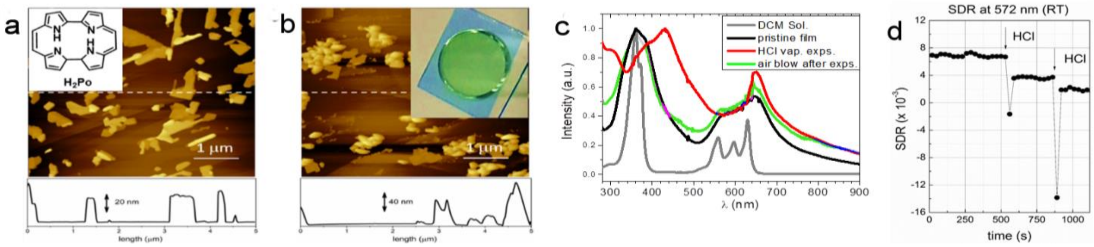

Figure 1 : a) topography of pristine H2Po film; b) topography after the exposure to HCl vapors and recovery of the SDR signal (*inset*, green area, film exposed to acid vapors; blue one, unexposed film; c) comparative UV-Vis spectra of H_2Po, solution and thin film w/wo exposure to HCl; d) SDR signals modulation towards HCl vapors.

REFERENCES

1. E. Vogel, M. Köcher, H. Schmickler, J. Lex, *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 257.
2. A. Bossi, J. Waluk, R. Yivlialin, M. Penconi, M. Campione, G. Bussetti, *ChemPhotoChem*, **2020**, *4*, 5264
3. M. Penconi, L. Ferraro, J. Waluk, L. Duò, F. Ciccacci, A. Bossi, M. Campione, G. Bussetti, *Proceedings* **2020**, *56(1)*, 44.

Bottom-up Fabrication and Atomic-scale Characterization of Porphyrin-based Nanostructures

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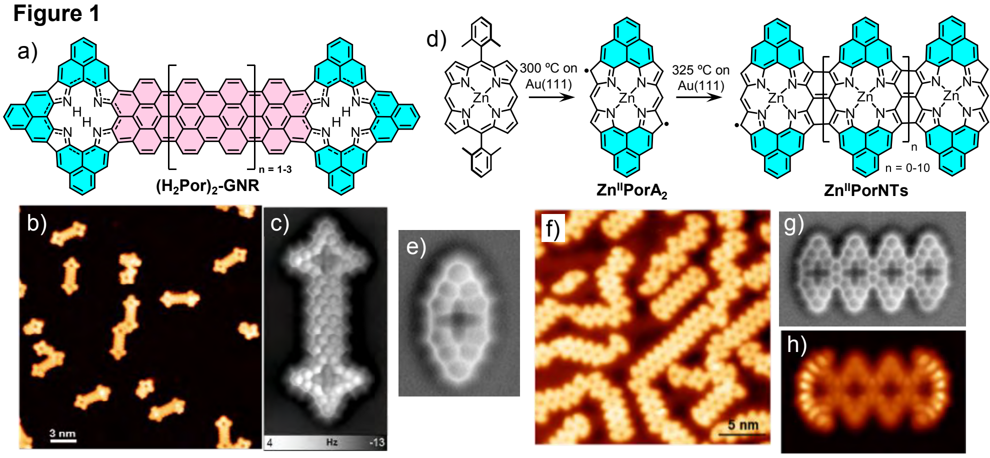
During the last decade, on-surface synthesis has emerged as a powerful tool for the construction of large, planar, π-conjugated structures that are not accessible through standard solution chemistry.[1] Among the building blocks used for the fabrication of such surface-supported nanoarchitectures, porphyrins (Pors) are of particular interest thanks to their planar structure with an aromatic core of 18 π-electrons, remarkable thermal stability, tunable redox properties, and intense optical features.[2] We report here the on-surface fabrication, and structural and electronic characterization of novel Por-graphene nanoribbon (GNR) hybrids (**(H_2Por_2)-GNR** in Figure 1a-c)[3a,c], as well as π-extended Pors (**$Zn^{II}PorA_2$** in Figure 2d,e)[3b] and Por nanotapes (NTs) (**$Zn^{II}PorNTs$** in Figure 2d,f-h)[3d] showing open-shell character.

Figure 1



REFERENCES

1. S. Clair, D. G. de Oteyza, *Chem. Rev.* **2019**, *119*, 4717.
2. K. M. Kadish, K. M. Smith, R. Guilard, The Porphyrin Handbook, Vol. 1-10, Academic Press, Burlington, 2000.
3. a) L. M. Mateo, Q. Sun, S.-X. Liu, J. J. Bergkamp, K. Eimre, C. A. Pignedoli, P. Ruffieux, S. Decurtins, G. Bottari, R. Fasel, T. Torres, *Angew. Chem. Int. Ed.* **2020**, *59*, 1334; b) Q. Sun, L. M. Mateo, R. Robles, P. Ruffieux, N. Lorente, G. Bottari, T. Torres, R. Fasel, *J. Am. Chem. Soc.* **2020**, *142*, 18109; c) L. M. Mateo, Q. Sun, K. Eimre, C. A. Pignedoli, T. Torres, R. Fasel, G. Bottari, *Chem. Sci.* **2021**, *12*, 247; d) Q. Sun, L. M. Mateo, R. Robles, N. Lorente, P. Ruffieux, G. Bottari, T. Torres, R. Fasel, *Angew. Chem. Int. Ed.* **2021**, *60*, 16208.

Polyporphine/phthalocyanine-based heterojunctions for gas sensing

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Owing to high interfacial conductivity, organic heterostructures hold great promises to augment the electrical performances of electronic devices [1,2]. In this endeavor, our research strategy focusses on developing bilayer heterostructures by combining polyporphines (pMP) and phthalocyanine (MPc) for redox gases sensor application. Because of the variable reactivity of the meso- and β-hydrogen in the metal porphine (MP), it can be electropolymerized through either meso-meso C-C coupling or additional β- β C-C coupling, resulting in "Type-1" or "Type-2" pMP (Fig. 1). However, the electrical conductivity is very different for the two polymers. In pMP-1, because of only meso-linkages of the monomer units, each unit is oriented orthogonally to its neighboring units, restricting the delocalization of the π-electrons and thus forming a low-conducting polymer film. On the contrary, because of the fusion of the monomer units in the 2D plane in pMP-2, there is an extension of the π-conjugation, resulting in the formation of a high-conducting polymer films. We have performed such electropolymerizations directly on the sensor electrodes and have further deposited a high conducting lutetium bis-phthalocyanine (LuPc2) to obtain the organic heterojunction sensors. Our study reveals that sensors based on pMP-1 materials are highly sensitive to redox gases such ammonia and promise to detect NH3 below the environmental guidelines, at room temperature. This work also highlights the high potentiality of porphine and phthalocyanine based heterostructures in the development of gas sensors, which application in this field remains in infancy currently.

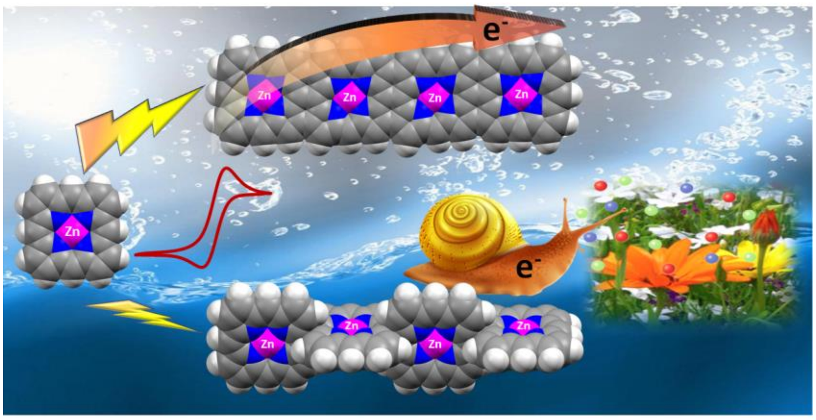

Figure 1: Scheme of electropolymerization of zinc porphine into pZnP-1 and pZnP-2.

REFERENCES

1. A. Kumar, R. Meunier-Prest, M. Bouvet, Sensors, 20, 4700, **2020**.
2. Z. Şahin, R. Meunier-Prest, F. Dumoulin, A. Kumar, Ü. Isçi, M. Bouvet, Sens. Actuators B, 332, 129505, **2021**.
3. A. Kumar, N. Alami Mejjati, R. Meunier-Prest, A. Krystianiak, O. Heintz, E. Lesniewska, C. H. Devillers, M. Bouvet, Chem. Eng. J., 429, 132453, **2022**.

Cytochrome Catalysts for Artificial Photosynthesis

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The synthesis of fuels in light-driven reactions is a vital approach to providing alternatives to fossil fuels. Two such reactions are the reduction of aqueous protons to dihydrogen (H_2) and the reduction of CO_2 to CO, a component of synthesis gas. In this work, we employ engineered biomolecular catalysts for proton reduction and CO_2 reduction. The use of biomolecular catalysts facilitates working in water and yields catalysts with defined active-site microenvironments that may be tuned to enhance activity and selectivity.

Two catalysts will be presented. One is cobalt microperoxidase-11 (CoMP11-Ac), consisting of cobalt protoporphyrin IX covalently bound to an 11-mer peptide.[1] The second is a synthetic cobalt "mimochrome," (CoMC6*a), a synthetic mini-protein binding a cobalt deuteroporphyrin.[2] Both mini-proteins function as electrocatalysts for hydrogen production from water and for CO_2 reduction to CO. Investigation of the dependence of electrocatalytic current and potential on pH and buffer provides insights into mechanism and factors that impact product selectivity.[3, 4] In CoMP11-Ac, the rate-determining step of the H_2 production reaction depends on buffer pK_a,[3] while in CoMC6*a, the order in which electrons and protons are assembled into H_2 is affected by buffer pK_a, while the reaction rate depends strongly on buffer structure.[4] The influence of the buffer as proton donor on selectivity for CO_2 reduction vs. proton reduction also will be discussed.

Both CoMP11-Ac and CoMC6*a are robust components of systems for visible light-driven hydrogen production. Upon pairing these catalysts with $[Ru(bpy)_3]^{2+}$ as a photosensitizer and ascorbate as a sacrificial electron donor, irradiation with blue or green light yields H_2 and, under a CO_2 atmosphere, CO. Analysis of the effect of reaction components on activity reveals that system lifetime is limited by degradation of $[Ru(bpy)_3]^{2+}$, while the catalysts remain active. Both systems are unusual for showing optimal activity near pH 7, which differs from most systems for photochemical H_2 using $[Ru(bpy)_3]^{2+}$ and ascorbic acid, which typically function best at acidic pH values.[5] Furthermore, the use of organic dye sensitizers is successful in these systems, yielding heavy metal-free systems for photochemical fuel production. Progress toward developing systems for selective CO production and the implementation of more robust photosensitizers will be presented.

REFERENCES

1. Kleingardner, J. G.; Kandemir, B.; Bren, K. L. *J. Am. Chem. Soc.* **2014**, *136*, 4-7.
2. Firpo˒ V.; Le, J. M.; Pavone, V.; Lombardi, L.; Bren, K. L. *Chem. Sci.,* **2018**, *9*, 8582-8589.
3. Alvarez-Hernandez, J. L.; Sopchak, A. E.; Bren, K. L. *Inorg. Chem.,* **2020,** *59*, 8061-8069.
4. Le, J. M. ;Alachouzos, G.; Marco Chino, M. ;Frontier, A. J. ; Lombardi, A.; Bren, K. L. *Biochemistry,* **2020**, 59, 1289-1297.
5. Edwards, E. H, ; Jelušić, J. ; Chakraborty, S.; Bren, K. L. *J. Inorg. Biochem.,* **2021**, 217, 111384

Tetrahedral Pegs in Square Holes: Diboron Phthalocyanines and Porphyrazines

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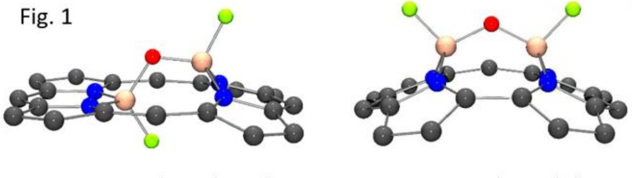
Porphyrins and phthalocyanines stand out as ligands which can coordinate an extraordinary number of elements of the periodic table, except for the very electronegative and radioactive elements. Most adopt the conventional coordination mode in which the element resides in the N_4 hole of the ligand, but boron is unusual in that it gives rise to binuclear tetrapyrrole macrocycle complexes.[1] This reflects both the small size of boron and its preference for tetrahedral coordination, which is not compatible with the square planar coordination environment and size mismatch afforded by these macrocycles. Diboron tetrapyrrole complexes afford a unique opportunity to examine the stereochemistry of the tetrapyrrole ligand environment that transcends the traditional approaches of varying the sizes of the macrocycle core and/or the normally single coordinating element.

Many of the diboron tetrapyrrole complexes contain a B_2OX_2 core (X=F, OH, Ph), in which each boron is coordinated by a pair of adjacent nitrogens, and the stereochemistry of the B_2OX_2 moiety varies depending on the particular macrocycle. Figure 1 illustrates *transoid*-B_2OF_2(porphyrin) and *cisoid*-B_2OF_2(corrole) in which each stereochemical type also induces different structural distortions, with doming (*cisoid*) or ruffling (*transoid*) of the ligand as well as marked tetragonal elongation. Our initial studies on porphyrin and corrole [1] have been extended to include calixphyrin [2], porphyrazine and phthalocyanine, and find that different isomers can be observed for the same ligand, and in some cases their interconversion [3]. We have supported these observations with a detailed DFT study in which we looked at the stereochemical preferences for B_2OF_2 complexes of 12 different terapyrrole macrocycles. The results accord well with our experimental observations and give unique new insights into factors influencing the stereochemical preferences for coordination complexes of tetrapyrrole macrocycles.

Fig. 1



B_2OF_2(porphyrin) B_2OF_2(corrole)

REFERENCES

1. (a) P. J. Brothers, *Chem. Commun*. **2008**, 2090–2102; (b) P. J. Brothers, *Inorg. Chem.* **2011**, *50*, 12374–12386.
2. A. C. Y. Tay, B. J. Frogley, D. C. Ware, P. J. Brothers, *Dalton Trans.* **2018**, *47*, 3388–3399.
3. A. C. Y. Tay, B. J. Frogley, D. C. Ware, J. Conradie, A. Ghosh, P, J. Brothers, *Angew. Chem. Int. Ed.* **2019**, *58*, 3057-3061.

Converting pyrroles in porphyrins to non-pyrrolic moieties: Going once, going twice, going trice!

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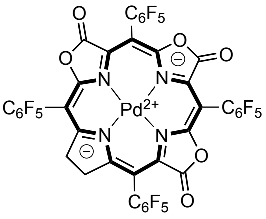
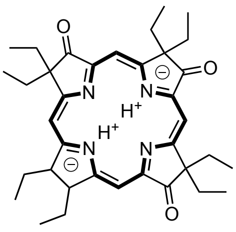
Over the years, we developed synthetic strategies to convert one or two pyrrolic building blocks in (hydro)porphyrins into a variety of non-pyrrolic heterocycles, forming so-called 'pyrrole-modified porphyrins' [1]. Many mono-substituted systems mimic classic chlorins, while many bis-modified systems mimic tetrahydroporphyrins (bacteriochlorins and isobacteriochlorins). Frequently, shifts of their hydroporphyrin-type spectra can be traced back to conformational effects [2]. Because of a profound electronic influence of β-oxo-substituents on the porphyrinic chromophore [3], mono- and bis-modified systems containing β-oxo-substituents (including the porpholactones) always deviate significantly from their archetype hydroporphyrins. The properties of the porpholactones are an excellent example for this [4].

Irrespective of the known electronic influence, we were nonetheless surprised to find that tris-modified systems, such as trilactones **1** [5], and the related (known) octaethylpyrrocorphine triketones **2** [6] could be readily prepared. Moreover, all regioisomers of these tris-β-oxo-chromophores possess unique electronic properties, including broadly varying degrees of diatropicity. Their proposed aromatic structures were probed using ^{1}H NMR spectroscopy, X-ray diffractrometry, chemical modifications, and were computationally verified.

The work further highlights the electronic influence of the β-oxo-substituents and conceptually expands the understanding of tris-modified hydroporphyrinoid analogues.



1
+ 3 other regiosiomers



2
+ 3 other regiosiomers

REFERENCES

1. Brückner, C., *Acc. Chem. Res.* **2016,** *49* (6), 1080–1092.
2. (a) Guberman-Pfeffer, M. J.; Greco, J. A.; Samankumara, L. P.; Zeller, M.; Birge, R. R.; Gascón, J. A.; Brückner, C., *J. Am. Chem. Soc.* **2017,** *139* (1), 548–560. (b) Luciano, M. P.; Atoyebi, A. O.; Tardie, W.; Zeller, M.; Brückner, C., *J. Org. Chem.* **2020,** *85* (23), 15273–15286.
3. Liu, M.; Chen, C.-Y.; Hood, D.; Taniguchi, M.; Diers, J. R.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *New J. Chem.* **2017**, *41*, 3732–3744.
4. (a) Hewage, N.; Daddario, P.; Lau, K. S. F.; Guberman-Pfeffer, M. J.; Gascón, J. A.; Zeller, M.; Lee, C. O.; Khalil, G. E.; Gouterman, M.; Brückner, C., *J. Org. Chem.* **2019,** *84* (1), 239–256. (b) Ning, Y.; Jin, G.-Q.; Zhang, J.-L., *Acc. Chem. Res.* **2019,** *52* (9), 2620-2633.
5. Hewage, N.; Guberman-Pfeffer, M. J.; Chaudhri, N.; Gascón, J. A.; Zeller, M.; Brückner, C., unpublished.
6. (a) Inhoffen, H. H.; Nolte, W. *Justus Liebigs Ann. Chem.* 1969, *725*, 167–176. (b) Chaudhri, N.; Guberman-Pfeffer, M. J.; Li, R.; Zeller, M.; Brückner, C. *Chem. Sci.* **2021**, *12*, 12292–12301.

PorphyStruct: Quick conformational analysis for Corroles and other Porphyrinoids

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Macrocyclic conformations have been proven to be of great influence on metal porphyrin electronic structure and reactivity. The importance of the non-planar modes was shown in the past to be particularly evident for biometal complexes (esp. iron porphyrins) and for porphyrinoid ligands in protein scaffolds. A tool for conformational analysis was published by Shelnutt et al. in 1997 [1] and largely eased the discussions, bringing important correlations between non-planar distortions and reactivity pattern to the porphyrin chemists' attention.[2]

PorphyStruct{ }
Structural Analysis of Porphyrinoids

For porphyrinoids with lower symmetry through differing connectivities like the corroles, porphyrin isomers, nor- and heterocorroles, and the like, the 1997 tool is not applicable, and a detailed analysis of the reactivity and structure based on non-planar distortion modes is as yet difficult to assess. We have now designed a new digital tool "PorphyStruct"[3] by which the conformational realities of many porphyrinoids can be investigated, and present here results from first analyses.

REFERENCES

1. Jentzen W, Song X-Z, Shelnutt JA, *J. Phys. Chem. B* 1997; **101**: 1684–1699; Jentzen W, Ma J-G, Shelnutt JA, *Biophys. J.* 1998; **74**: 753–763; C. J. Kingsbury, M. O. Senge, *Coord. Chem. Rev.* **2020**, *431*, 213760.
2. Senge MO, MacGowan MA, O'Brien JM, *Chem. Commun.* 2015; **51**: 17031–17063; Al-Karadaghi S, Franco R, Hansson M, Shelnutt JA, Isaya G, Ferreira GC, *Trends Biochem. Sci.* 2006; **31**: 135–142; Takeda J, Ohya T, Sato M, *Inorg. Chem.* 1992; **31**: 2877–2880.
3. J. Krumsieck, M. Bröring, *Chem. Eur. J.* **2021**, *27*, 11580-11588.

Electron-Triggered Spin State Switching in a Viologen-Substituted Nickel Porphyrin

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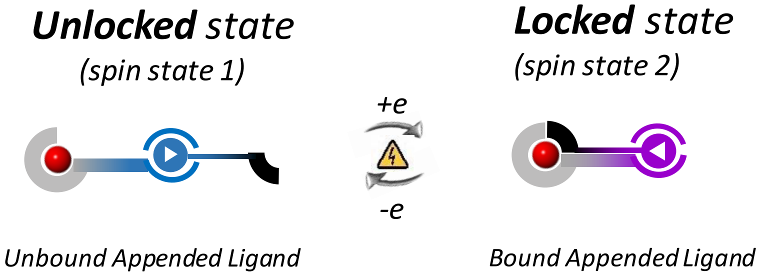
In recent years, controlling molecular motions has emerged as a promising approach for the development of molecules exhibiting switchable magnetic states, the underlying idea being that modifying the structure of a molecular system could induce drastic modifications of its magnetic properties. From a practical standpoint, these ambitious objectives have so far mainly been addressed with coordination complexes using light as an input signal [1, 2] In contrast, far less progress has been made in these directions with electron-responsive systems even though electrochemistry stands as a particularly attractive trigger in the perspective of applications in solid-state devices or to avoid risks of bleaching associated to high energy light irradiations. In this context, our recent efforts have focused on the development of molecular systems for which large amplitude movements actuated by electron transfer can be used to control the magnetic state of magnetically active metalloporphyrin centers.

Following our previous works on porphyrin-based redox-responsive mechanoreactive (supra)molecular architectures [3-5], we will detail in this presentation one recent strategy wherein the local environment and the electronic configuration (High Spin versus Low Spin states) of a nickel porphyrin can be determined with an electric trigger enabling to control the nature and number of coordinated ligands. In more specific terms, we will show, on the ground of electrochemical, spectro-electrochemical and magnetic measurements supported by DFT data, that a coordination induced spin state switching process can be actuated in solution by the mechanical folding and unfolding of isolated molecules triggered by application of suitable potential values [6].



REFERENCES

1. Doistau, B.; Benda, L.; Hasenknopf, B.; Marvaud, V.; Vives, G., *Magnetochemistry* **2018**, 4 (1), 5.
2. Dommaschk, M.; Peters, M.; Gutzeit, F.; Schütt, C.; Näther, C.; Sönnichsen, F. D.; Tiwari, S.; Riedel, C.; Boretius, S.; Herges, R., *J. Am. Chem. Soc*. **2015**, 137 (24), 7552.
3. Iordache, A.; Retegan, M.; Thomas, F.; Royal, G.; Saint-Aman, E.; Bucher, C., *Chem. Eur*. J. 2012, 18, 7648
4. Kahlfuss, C.; Denis-Quanquin, S.; Calin, N.; Dumont, E.; Garavelli, M.; Royal, G.; Cobo, S.; Saint-Aman, E.; Bucher, C., *J. Am. Chem. Soc*. **2016**, 138, 15234
5. Chowdhury, S.; Nassar, Y.; Guy, L.; Frath, D.; Chevallier, F.; Dumont, E.; Ramos, A. P.; Demets, G. J.-F.; Bucher, C., *Electrochim. Acta* **2019**, 316, 79.
6. Bucher et al. *Submitted for publication*.

Out-Of-Plane Metal Coordination for a True Bottom-Up Building with Porphyrin Bricks

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The desirable self-assembly (SA) of repeated 2D stacked layers requires a "holistic analysis" of three interconnected components: the electrode, the interface, and the molecular component; among them, the contact interface bears the largest burden responsibilities. Epitaxial growth (EG) of coherent (2D + n) stacked heterojunction by solvent-free deposition holds great promise, although the feasibility has never been demonstrated given multiple drawbacks (*e.g.*, surface-ligand effect, SLE) [1,2].

Here, it is demonstrated how a coherent (2D + n), being n = 4, layered heterorganic film is grown on an archetypal Fe metal electrode [3]. The ground-breaking achievement is the result of the in-vacuum integration of:

chemical decoupling of the basal organic layer (a Zn-tetraphenylporphyrine, ZnTPP) from the electrode,

2D-ordering of the ZnTPP commensurate to the substrate,

rigid, stoichiometric, orthogonally arranged, molecule-to-molecule coupling between ZnTPP and a di-topic linear bridging ligand (*i.e.*, DPNDI) guided by SA coordination chemistry, and sharp (chemical) termination of the layered film.

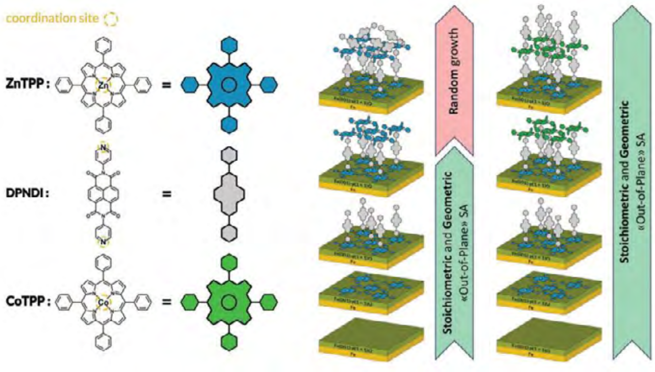

Figure 3. Left, molecular structures of ZnTPP and DPNDI and CoTPP together with their simplified drawings. The circles indicate the coordination sites for clarity; right, proposed molecular construction designed in this work.

REFERENCES

1. J. M. Gottfried, Surface chemistry of porphyrins and phtalocyanines, *Surf. Sci. Rep*. **70** (2015) 259-379.
2. F. Haag *et al*., The Flexible On-Surface Self-Assembly of a Low-Symmetry Mabiq Ligand: An Unconventional Metal-Assisted Phase Transformation on Ag(111), *J. Phys. Chem. C* **125** (2021) 23178-23191.
3. A. Orbelli Biroli *et al*., Out-Of-Plane Metal Coordination for a True Solvent-Free Building with Molecular Bricks: Dodging the Surface Ligand Effect for On-Surface Vacuum Self-Assembly, *Adv. Funct. Mater.* **31** (2021) 2011008.

Stepwise synthesis of a new family of porphyrinoid hybrids

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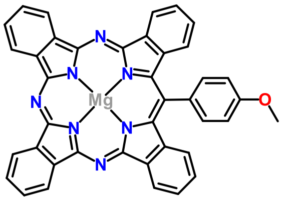
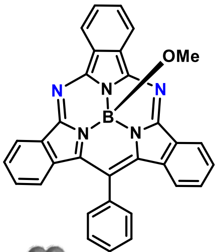
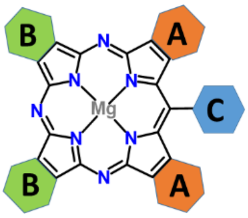
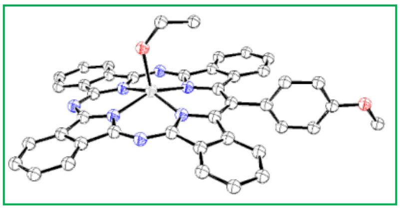
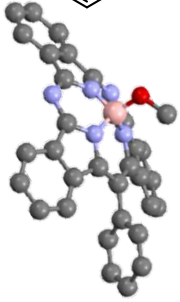
Previous work from our group has developed syntheses of hybrids between porphyrin and phthalocyanine/sub phthalocyanine cores. Most recently we disclosed a modified procedure that selectively yields symmetrical 2:2 meso-aryl triazatetrabenzoporphyrins (TBTAPs) bearing different benzo units in an ABBA arrangement.

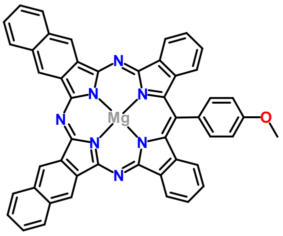




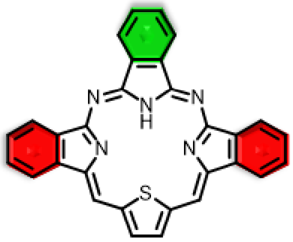








In this presentation we reveal further insight on the formation of ABBA-C hybrids through synthesis and reaction of key intermediates, and further describe the stepwise synthesis of new TBDAP (diaza-) porphyrinoid hybrids.



REFERENCES

1. A. Diaz-Moscoso, G. J. Tizzard, S. J. Coles and A. N. Cammidge, Angew. Chem. Int. Ed. 52, 10784-10787, 2013.
2. S. Remiro-Buenamanana, A. Diaz-Moscoso, D. L. Hughes, M. Bochmann, G. J. Tizzard, S. J. Coles and A. N. Cammidge, Angew. Chem. Int. Ed. Engl. 54, 7510-7514, 2015.
3. F. Alkorbi, A. Diaz-Moscoso, J. Gretton, I. Chambrier, G. J. Tizzard, S. J. Coles, D. L. Hughes, and A. N. Cammidge, Angew. Chem. Int. Ed. Engl. 60, 7632-7636, 2021.

Synthesis, Characterization and Derivatization of *meso*-Perfluoro-alkyl Corroles

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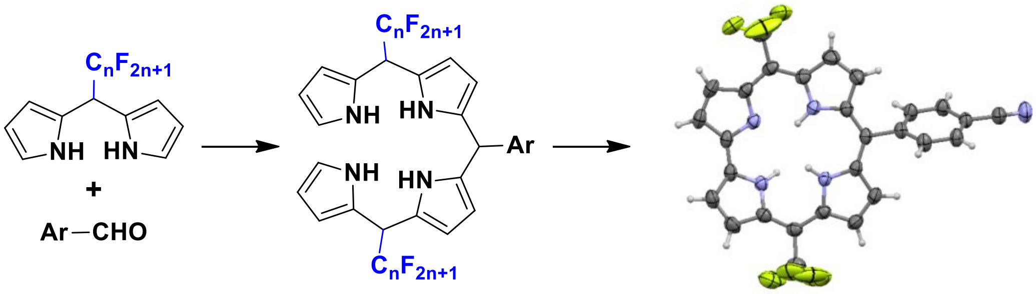
Several synthetic pathways leading to *meso*-substituted corroles have been developed during the last two decades as well as strategies introducing functional groups on corrole or on metallocorroles [1]. On the contrary, if *meso*-alkyl corroles are considered, very rare examples of such macrocycles were described, [2] probably because of the low stability of corrole bearing electron-donating groups. One way to circumvent this issue is to introduce *meso*-perfluoroalkyl chains that would keep a strong-electron-withdrawing character. This presentation will describe how the condensation of a *meso*-perfluoroalkyl dipyrromethane [3] on various benzaldehyde derivatives were used, after the isolation of the intermediate corresponding bilane, to prepare corroles bearing two perfluoroalkyl groups on the 5 and 15 *meso* positions. The impact of these substituents on the physicochemical properties of the macrocycles will be described by the study of their electrochemical and photophysical properties. A part of this presentation will focus on the preparation of ABC corroles produced by the controlled hydrolysis of one of the electron-withdrawing alkyl chains leading to unprecedented *meso*-keto-corroles.



REFERENCES

1. a) R. Orłowski, D. Gryko, D. T. Gryko, *Chem. Rev.*, **2017**, 117, 3102. b) J. F. B. Barata, M. G. M. S. Neves, M. A. F. Faustino, A. C. Tomé, J. A. S. Cavaleiro, *Chem. Rev.*, **2017**, 117, 3192.
2. a) M. K. Tse, Z. Zhang, T. C. W. Mak, K. S. Chan, *Chem. Commun.*, **1998**, 1199. b) R. Goldschmidt, I. Goldberg, Y. Balazs, Z. Gross, *J. Porphyrins Phthalocyanines*, **2006**, 10, 76. c) Q. -C. Chen, M. Soll, A. Mizrahi, I. Saltsman, N. Fridman, M. Saphier, Z. Gross, *Angew. Chem. Int. Ed.,* **2018**, 57, 1006.
3. a) P. –G. Julliard, S. Pascal, O. Siri, D. Cortés-Arriagada, L. Sanhueza, G. Canard, *Comptes Rendus Chimie*, **2021**, 24, 27.

Identifying Intermediates in Electrocatalytic Water Oxidation with a Manganese Corrole Complex

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Water nucleophilic attack (WNA) on high-valent terminal Mn-oxo species is proposed for O−O bond formation in natural and artificial water oxidation. Different mechanisms have been proposed for the O−O bond formation in the OEC, including water nucleophilic attack (WNA) on a $Mn^{V}(O)$ moiety or coupling of two high-valent Mn-oxo moieties [1-2]. WNA on $Mn^{V}(O)$ is also proposed for catalytic water oxidation with synthetic Mn complexes, but the proposed mechanism has rarely been supported experimentally [3-5]. Herein, we report an electrocatalytic water oxidation reaction with Mn^{III} tris(pentafluorophenyl)corrole (**1**) in propylene carbonate (PC) [6]. O_2 was generated at the $Mn^{V/IV}$ potential with hydroxide, but a more anodic potential was required to evolve O_2 with only water. With a synthetic $Mn^{V}(O)$ complex of **1**, a second-order rate constant, $k_2(OH^-)$, of 7.4×10^3 M^{-1} s^{-1} was determined in the reaction of the $Mn^{V}(O)$ complex of **1** with hydroxide, whereas its reaction with water occurred much more slowly with a $k_2(H_2O)$ value of 4.4×10^{-3} M^{-1} s^{-1}. This large reactivity difference of $Mn^{V}(O)$ with hydroxide and water is consistent with different electrocatalytic behaviors of **1** with these two substrates. Significantly, during the electrolysis of **1** with water, a Mn^{IV}-peroxo species was identified with various spectroscopic methods, including UV-vis, electron paramagnetic resonance, and infrared spectroscopy. Isotope-labeling experiments confirmed that both O atoms of this peroxo species are derived from water, suggesting the involvement of the WNA mechanism in water oxidation by a Mn complex. Density functional theory calculations suggested that the nucleophilic attack of hydroxide on $Mn^{V}(O)$ and also WNA to $1e^-$-oxidized $Mn^{V}(O)$ are feasibly involved in the catalytic cycles but that direct WNA to $Mn^{V}(O)$ is not likely to be the main O−O bond formation pathway in the electrocatalytic water oxidation by **1**.

REFERENCES

1. Britt, R. D.; Marchiori, D. A. Photosystem II, Poised for O_2 Formation. *Science* **2019**, *366*, 305-306.
2. Zhang, X.-P.; Chandra, A.; Lee, Y.-M.; Cao, R.; Ray, K.; Nam, W. Transition Metal-Mediated O-O Bond Formation and Activation in Chemistry and Biology. *Chem. Soc. Rev.* **2021**, *50*, 4804-4811.
3. Larson, V. A.; Battistella, B.; Ray, K.; Lehnert, N.; Nam, W. Iron and Manganese Oxo Complexes, Oxo Wall and Beyond. *Nat. Rev. Chem.* **2020**, *4*, 404-419.
4. Kim, S. H.; Park, H.; Seo, M. S.; Kubo, M.; Ogura, T.; Klajn, J.; Gryko, D. T.; Valentine, J. S.; Nam, W. Reversible O-O Bond Cleavage and Formation between Mn(IV)-Peroxo and Mn(V)-Oxo Corroles. *J. Am. Chem. Soc.* **2010**, *132*, 14030-14032.
5. Gao, Y.; Åkermark, T.; Liu, J.; Sun, L.; Åkermark, B. Nucleophilic Attack of Hydroxide on a Mn^{V} Oxo Complex: A Model of the O-O Bond Formation in the Oxygen Evolving Complex of Photosystem II. *J. Am. Chem. Soc.* **2009**, *131*, 8726-8727.
6. Li, X.; Zhang, X.-P.; Guo, M.; Lv, B.; Guo, K.; Jin, X.; Zhang, W.; Lee, Y.-M.; Fukuzumi, S.; Nam, W.; Cao, R. Identifying Intermediates in Electrocatalytic Water Oxidation with a Manganese Corrole Complex. *J. Am. Chem. Soc.* **2021**, *143*, 14613-14621.

Insights into chiral porphyrin J-aggregates

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Under acidic conditions and/or in the presence of various cationic species, the anionic water soluble tetrakis(4-sulfonatophenyl) porphyrin (TPPS) self-assembles into nanostructures that can exhibit chirality as consequence of spontaneous symmetry breaking (1,2) or by transfer induced with external chiral species.(3,4) Counter-anions (5,6) and mixing protocols (7) can largely affect the kinetics of aggregation and the final observed dissymmetry g factor.

In this contribution, we report on the impact of organic and inorganic counter-anions on the kinetics and thermodynamics of the J-aggregate nanotubes formation, discussing the observed trends in terms of the Hofmeister series and the hydrogen-bond making and breaking ability of the anions. Some experiments of seeding will be presented and discussed in the frame of the mechanistic pathway to the formation of nanotubes.

REFERENCES

1. Arteaga, O.; El-Hachemi, Z.; Canillas, A.; Crusats, J.; Rovirac, M.; Ribo´, J.M. Chem. Commun., 2016, 52, 10874.
2. Romeo, A.; Castriciano, M. A.; Occhiuto, I.; Zagami, R.; Pasternack, R. F.; Scolaro, L. M. J. Am. Chem. Soc. 2014, 136, 40.
3. Castriciano, M. A.; Romeo, A.; Zagami, R.; Micali, N.; Scolaro, L. M. Chem. Commun. 2012, 48, 4872.
4. Castriciano, M. A.; Romeo, A.; De Luca, G; Villari, V.; Scolaro, L. M.; Micali, N. J. Am. Chem. Soc. 2011, 133, 765.
5. Occhiuto, I.G.; Zagami, R.; Trapani, M.; Bolzonello, L.; Romeo, A.; Castriciano, M.A.; Collini, E. Scolaro, L.M. Chem. Commun. 2016, 52, 11520.
6. Zagami, R.; Romeo, A.; Castriciano, M.A.; Scolaro, L.M. J. Mol. Liq. 2021, 332, 115801.
7. Castriciano, M.A.; Cardillo, S.; Zagami, R.; Trapani, M.; Romeo, A.; Scolaro, L.M. Int. J. Mol. Sci. 2021, 22, 797.

Complexes of 2-Aza-21-carbaporphyrin as Ligands

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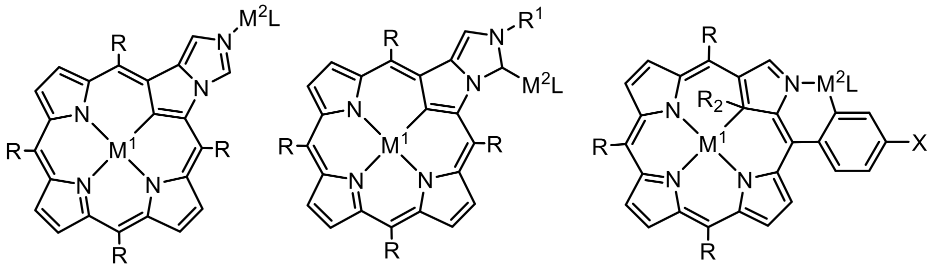
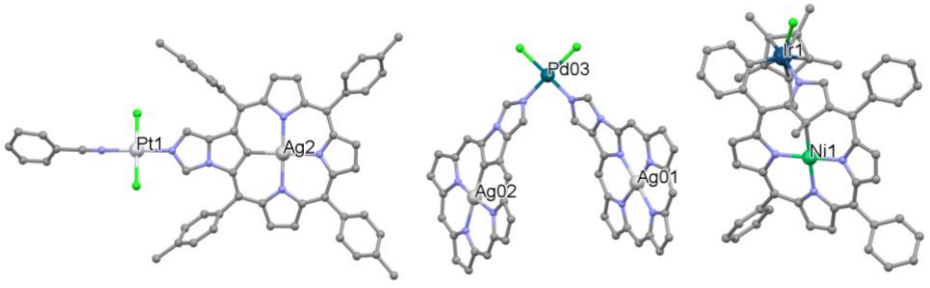
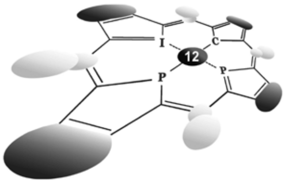
Owing to its unique structure, 2-aza-21-carbaporphyrin, a.k.a. N-confused porphyrin (NCP) is a hybrid ligand as it possesses two distinct donor sets. One of them is defined by internal NNNC coordination core of macrocyclic character, and the other is localized on the perimeter of the porphyrinoid ring. A distinct reactivity of the *confused* pyrrole facilitates regioselective modifications of both donor sets altering their coordination properties by substituents with supplementary donor groups. Our recent studies resulted in preparation of several NCP derivatives [1] of this type which were consecutively applied in synthesis of complexes consisting of different transition metal ions. Synthesis, structural characterization, spectroscopic, catalytic, and redox properties, as well as chirality of these hybrid ligands and their monomeric and oligomeric complexes will be subjects of this presentation.





REFERENCES

1. Ren, D., Liu, B., Li, X., Koniarz, S., Pawlicki, M., Chmielewski, P.J. *Org. Chem. Front.*, **2019**, *6*, 908-919; Ren D., Koniarz S., Li X., Chmielewski P.J., *Chem. Commun.*, **2020**, *56*, 4836.



Fucoidan-based Theranostic Nanogel for Enhancing Imaging and Photodynamic Therapy

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My laboratory has been developing various types of activatable and dual-targeted photosensitizing agents as smart theranostics for selective near-infrared fluorescence imaging and photodynamic therapy (PDT) of cancers and inflammatory diseases. Recently a fucoidan-based theranostic nanogel (CFN-gel) consisting of a fucoidan backbone, redox-responsive cleavable linker, and photosensitizer was developed to achieve activatable near-infrared fluorescence imaging of tumor sites and an enhanced PDT to induce the complete death of cancer cells. A CFN-gel has nanomolar affinity for P-selectin and VEGF. Moreover, a CFN-gel is non-fluorescent and non-phototoxic upon its systemic administration due to the aggregation induced self-quenching in its fluorescence and singlet oxygen generation. After internalization into cancer cells and tumor neovascular endothelial cells, its photoactivity is recovered in response to the intracellular redox potential, thereby enabling selective near-infrared fluorescence imaging and an enhanced PDT of tumors. It also provides a significant antitumor effect in the absence of light treatment *in vivo*. Our study indicates that a fucoidan-based theranostic nanogel is a new theranostic material for imaging and treating cancer with high efficacy and specificity.

REFERENCES

1. MH Cho et al., Nano-Micro Lett. (2020) 12:47.
2. H Kang et al., Nano Today (2018) 23:59-75
3. Y Choi et al., Cancer Res. (2006) 66(14):7225-7229.

High performing CF_3–containing phosphorus corroles

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Main group containing corroles continue to be targets of intense research interest; various derivatives are studied by research groups worldwide for a variety of applications. In some earlier cases, such compounds have helped supply examples of diamagnetic corroles. As far as the *synthesis* of new corrole derivatives is concerned, the preparation of novel systems is generally less focused at the core and more at the periphery (beta positions) of the macrocyclic system. The central atom/ion is in some cases smaller and more snugly arranged in the pocket; different combinations of beta position substitution is expected to unlock novel systems with impressive electronics and even structural features. Moreover, we can study how both the centre and periphery can work together in one molecule. While there are numerous possible designs and classes, we wanted to convey some emphasis on phosphorus corroles and –CF_3 containing species which involves analogues as well as isomers. Comparisons to systems such as porphyrins etc. are also constructive. We hope to expand the known landscape of new and atomically precise derivatives in corrole chemistry; much has been achieved in the past 5 years through a collaboration with the laboratories of Z. Gross (IIT Technion). The synthetic corrole research was performed at IIT unless otherwise mentioned.

REFERENCES

1. Zhan, X.; Lee, W.; Sudhakar, K.; Kim, D.; Mahammed, A.; Churchill, D. G.; Gross, Z. Solvent Effects on the Phosphorescence of Gold(III) Complexes Chelated by beta–Multisubstituted Corroles *Inorg. Chem.*, **2021**, *60*, 12, 8442–8446. 10.1021/acs.inorgchem.1c00906.
2. Lee, W.; Zhan, X.; Palma, J.; Vestfrid, J.; Gross, Z.; Churchill, D. G. Minding our P–block and Q–bands: paving inroads into main group corrole research to help instil broader potential, *Chem. Commun.* **2021**, *57*, 38, 4605–4641., 10.1039/d1cc00105a.
3. Zhan, X.; Kolanu, S.; Fite, S.; Chen, Q. C.; Lee, W.; Churchill, D. G.; Gross, Z.; Clean Ar–Me conversion to Ar–aldehyde with the aid of carefully designed metallocorrole photocatalysts *Photochem. Photobiol. Sci.*, **2020**, *19*, 8, 996–1000. 10.1039/d0pp00218f.
4. Zhan, X.; Zini, Y.; Fridman, N.; Chen, Q.–C.; Churchill, D. G.; Gross, Z.; "Hetero–Multifunctionalization" of Gallium Corroles: Facile Synthesis, Phosphorescence, Redox Tuning, and Photooxidative Catalytic Improvement Chempluschem, **2020**, *85*, 1, 163–168. 10.1002/cplu.201900667.
5. Zhan, X.; Yadav, P.; Diskin–Posner, Y.; Fridman, N.; Sundararajan, M.; Ullah, Z.; Chen, Q.–C.; Shimon, L. J. W.; Mahammed, A.; Churchill, D. G.; Baik, M. H.; Gross, Z. Positive shift in corrole redox potentials leveraged by modest beta–CF3–substitution helps achieve efficient photocatalytic C–H bond functionalization by group 13 complexes Dalton Trans, **2019**, *48*, 32, 12279–12286. 10.1039/c9dt02150g.
6. Zhan, X.; Teplitzky, P.; Diskin–Posner, Y.; Sundararajan, M.; Ullah, Z.; Chen, Q.–C.; Shimon, L. J. W.; Saltsman, I.; Mahammed, A.; Kosa, M.; Baik, M. H.; Churchill, D. G.; Gross, Z. Maximizing Property Tuning of Phosphorus Corrole Photocatalysts through a Trifluoromethylation Approach, **2019**, *58*, 9, 6184–6198. 10.1021/acs.inorgchem.9b00436.

Enhancing magnetic hysteresis in single-molecule magnets based on Lanthanide-Phtalocyanine complexes

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The possibility of constructing single-molecule magnets (SMMs) based on mononuclear lanthanide complexes was first demonstrated in 2003 by Ishikawa on double-decker lanthanide(III) phthalocyanine complexes. Since then, this topic has become one of the hot topics in molecular magnetism [1] and significant breakthroughs have been recently reported, such as the discovery of mononuclear SMMs exhibiting magnetic hysteresis at temperatures as high as 80 K [2]. The origin of such unusual behaviour is associated with the combination of a strong uniaxial magnetic anisotropy and a molecular rigidity. In this context, (molecular and lattice) vibrations, can prevent pathways for memory loss, thus enhancing the spin relaxation. Here we show a novel approach to enhance the performance of these magnetic molecules, which involves an engineering of the molecular vibrations. It consists of preparing dinuclear lanthanide complexes keeping the double-decker structure thanks to the fusion of two phtalocyanine molecules through a chemical bond. The larger rigidity of this structure shifts the vibrations responsible for spin relaxation towards higher energies and, thus, the electron-vibration coupling also decreases. This results in the observation of hysteretic effects at temperature as high as 50 K, a temperature that is much higher than that observed for the mononuclear analogue.

REFERENCES

1. E. Coronado *Nat. Rev. Mater.* 5, 87-104 (2020).
2. F.S. Guo, B.M. Day, Y.C. Chen, M.L. Tong, A. Mansikkamäki, R.A. Layfield, *Science* 362, 1400-1403 (2018)

Self-assembly of dipeptide-chromophore hybrids and applications

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The principal processes in natural photosynthesis, namely solar harvesting and conversion is achieved via self-assembly of chromophores. The scientific community is inspired to develop molecules with self-assembling ability aiming to the construction of materials with improved properties [1]. Self-assembled architectures that mimic chlorophylls and bacteriochlorophylls are of great interest for light harvesting applications [2]. Various chromophores such as porphyrins, and bodipy have been covalently attached to peptides resulting in hybrids that retained their self-assembling ability [3]. Herein, we examined the self-assembly ability of different chromophores which are covalently linked to aliphatic dipeptides. Altering various parameters such as the protecting group, the different solvent as well as the ratio of the solvent mixture the formation of dissimilar nanostructures was observed. Interestingly, in the case of a peptide-porphyrin hybrid the formation of hydrogel in HFIP-H_2O solvent mixture was obtained. This is of great importance since hydrogels that contain porphyrin chromophores can be used for hydrogen production, water oxidation, photodynamic therapy and photocurrent generation [4]. However, in all the above-mentioned hydrogel systems the chromophore was not covalently attached to the peptide gelator molecule. As illustrated in **Figure 1**, we have prepared eight different dipeptide-chromophore hybrids utilizing porphyrin and bodipy dyes, isoleucine and alanine peptides and four different protecting groups.

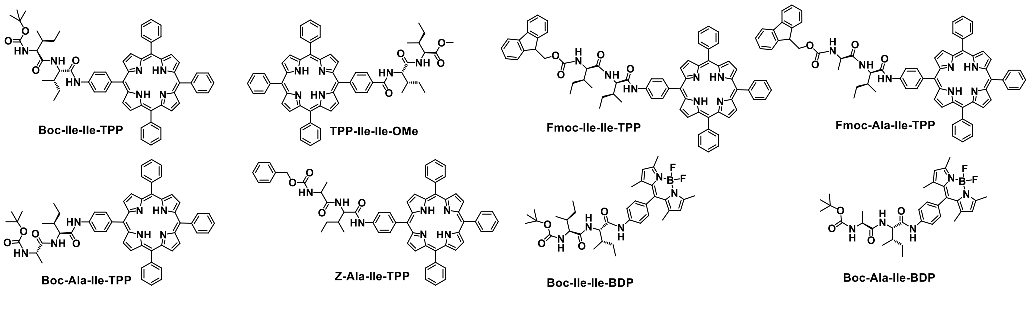

Figure 1: Chemical structures of all dipeptide-chromophore hybrids.

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1. T.S. Balaban, et al.; *Angew. Chem. Int. Ed*, 2003, **42**, 2140,
2. K.J. Channon, et al.; *J. Am. Chem. Soc.*, 2009, **131**, 12520,
3. Nikoloudakis E et al.; Chem. Commun., 2019, 55, 14103.
4. P. Liao, et al.; *J. Mater. Chem. A*, **2018**, 6, 3195.

Helicene-porphyrin conjugates

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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] Recently, we demonstrated that we can take advantage of the Exciton Coupling Chirality to design new efficient π-extended helicene architectures with original chiral absorption and emission responses,[2] achieving a remarkable enhancement of the chiroptical activities at the ground and excited states.[3] In this work, we report 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 $\Delta\varepsilon$ 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. Other examples combining helicenes and porphyrins will be presented.

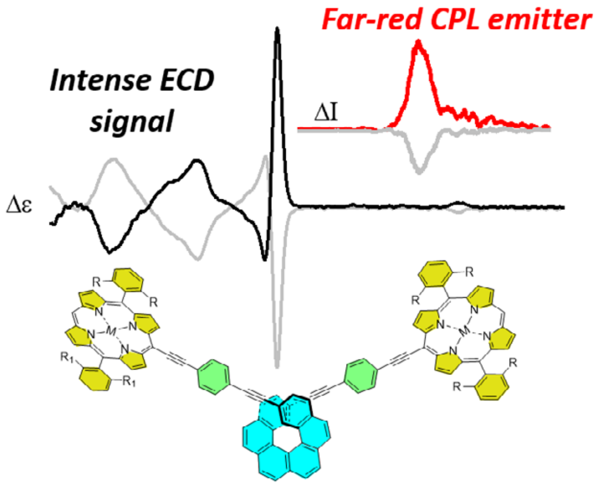

Figure 1: Chemical structure and Chiroptical (ECD and CPL) activities of helicene-porphyrin derivatives

REFERENCES

1. a) J. R. Brandt et al., *Nat. Rev. Chem.,* **2017**, *1*, 0045; b) J. Crassous et al., *Chem. Rev*., **2019**, *119*, 8846.
2. a) K. Dhbaibi et al., *Chem. Sci*., **2018**, *9*, 735; b) K. Dhbaibi et al., *Front. Chem*., **2020**, *8*, 237.
3. a) K. Dhbaibi et al., *Chem. Sci.,* **2020**, *11*, 567; b) K. Dhbaibi et al., *Chem. Sci*., **2021**, *12*, 5533.
4. K. Dhbaibi, P. Matozzo, L. Abella, M. Jean, N. Vanthuyne, J. Autschbach, L. Favereau, J. Crassous, *Chem. Comm.* **2021**, *57*, 10743.

Excited Charge Transfer in Porphyrin and BODIPY Connected TCBD-Ferrocene Conjugates

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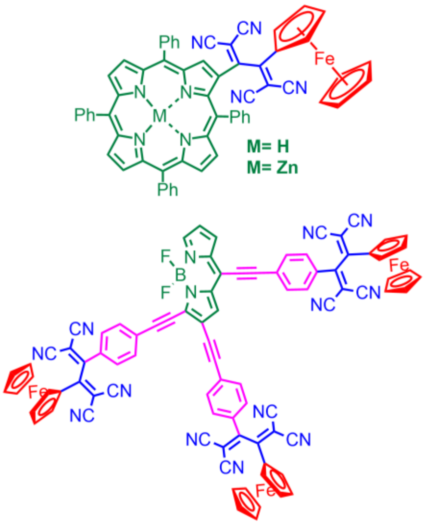
Light-induced electron transfer is a key step in solar energy conversion, and a process with myriad relevance in the fields of artificial photosynthesis, photocatalysis, photoconductivity, and molecular photovoltaics. In a donor-acceptor, D-A system, light absorption by a chromophore results in the formation of an excited state species, followed by a charge transfer between an electron donor (D) and an electron acceptor (A) leading to a charge-separated $D^{\cdot+}$-$A^{\cdot-}$ species. The optimization of these processes and comprehending their mutual interplay to ultimately achieve charge-separated species is of paramount importance for the development of efficient systems in solar light conversion schemes.

As part of our continued effort in this field of research[1-3], using a combination of cycloaddition-retroelectrocyclization reaction, porphyrins (H_2P and ZnP) and BODIPYs are decorated at their various macrocycle positions with strong charge-transfer complexes, viz., tetracyanobuta-1,3-diene (TCBD)-Ferrocene as a novel class of push-pull systems [4,5]. The physicochemical properties of these compounds have been investigated using a range of electrochemical, spectroelectrochemical, DFT as well as steady-state and time-resolved spectroscopic techniques. Charge transfer interactions between singlet excited porphyrin/BODIPY and the electron-withdrawing TCBD directly attached to the macrocycle π-system extended the absorption well into the near-infrared region. The occurrence of photoinduced charge transfer and separation has been established by complementary transient absorption spectral studies followed by global and target data analyses. The role of central metal in the porphyrin cavity and the location of the BODIPY ring substitution effect in governing these photo events will be discussed.



REFERENCES

1. F. Khan, Y. Jang, Y. Patil, R. Misra, and F. D'Souza, , *Angew. Chem. Int. Ed.* **2021**, *60*, 20518–20527.
2. I. S. Yadav, A. Z. Alsaleh, R. Misra and F. D'Souza, '*Chem. Sci*. **2021**, *12*, 1109-1120.
3. D. Pinjari, A. Z. Alsaleh, Y. Patil, R. Misra and F. D'Souza, *Angew. Chem. Int. Ed*. **2020**, *59*, 23697-23705.
4. B. Sekaran, A. Dawson, Y. Jang, K. V. MohanSingh, R. Misra and F. D'Souza, *Chem. Eur. J.* **2021**, *27*, 14335-14344.
5. J. Sindhe, M. B. Thomas, M. Poddar, R. Misra, F. D'Souza, *J. Phys. Chem. C*. **2021**, *125*, 23911-23921.

“From-Imprinted-to-Template”: The Supramolecular Role of Porphyrin Hetero-Aggregates

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In 2007 we demonstrated that exploiting the kinetic inertness of porphyrin hetero-aggregates it is possible to switch on-off the induced chirality in the absence of chiral template.[1] Indeed, supramolecular assembly of oppositely charged porphyrins yields to kinetic inert hetero-aggregates able to memorize the chiral information imprinted by the chiral template in aqueous solution. [2] Hence, in the attempt to asymmetrically drive the oxidation of L-DOPA to melanin-like polymers, we employed a “from-Imprinted-to-Template” approach by exploiting the well-known inertia of porphyrin hetero-aggregates. However, although detailed studies on L-DOPA polymerization mechanism have been carried out, scant knowledge on the intrinsic chiroptical features of melanin polymers are reported to date. The unique proof was the demonstration of atropisomerism caused by slow rotation about interunit bonds from DHICA oligomers [3].

Herein, we demonstrate that, in phosphate-buffered saline solution, porphyrin hetero-aggregates made up of 5,10,15,20-tetrakis(4-N-methylpyridyl)porphyrin, H_2T4, and copper(II) 5,10,15,20-tetrakis(4-sulfonatophenyl) porphyrin, CuTPPS, chirally guide the oxidation of L-DOPA with the surprising generation of asymmetric melaninic structures. Notably, complete spectroscopic investigations (UV/Vis and Circular Dichroism) revealed that chiral information is first induced to hetero-aggregates by monomeric L-DOPA acting as chiral inducer. Afterwards, owing to a close-range contact between chiral template and porphyrin hetero-aggregates, the stored chiral information is transferred, in turn, during the melanin synthesis despite the disruption of porphyrin hetero-aggregates in such a process. Meanwhile, the original chiral information from DOPA was completely consumed generating asymmetric melanin oligomers [4].

These promising results illustrate a rare example of temporary chiral mediation which pave the way to new perspectives concerning the organization of melanin pigments with unexpected biological and technological applications.

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REFERENCES

1. Mammana A., D’Urso A., Lauceri R. and Purrello R., *J. Am. Chem. Soc.*, **2007**, *129*, 8062–8063
2. Gaeta, M., Oliveri I. P., Fragalà M. E., Failla S., D’Urso A., Di Bella S. and Purrello R., *Chem. Commun.* **2016**, *52*, 8518–8521.
3. Pezzella A., Vogna D. and Prota G., *Tetrahedron Asymmetry*, **2003**, *14*, 1133–1140.
4. Gaeta M., Randazzo R., Villari V., Micali N., Pezzella A., Purrello R., d’Ischia M. and D'Urso A., *Frontiers in Chemistry*, **2020**, *8*, 1188.

8-Membered ring synthesis via carbene radicals

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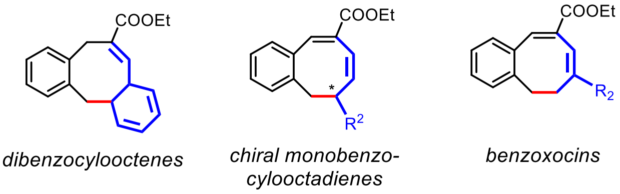
Activation of carbene precursors by planar, low-spin cobalt(II) complexes leads to formation of carbene radical intermediates [1]. These are intrinsically reactive metal-bound carbon radicals, useful for catalytic synthesis of a variety of ring compounds and other useful organic building blocks and undergo several selective transformations [2-3].

We recently discovered that carbene radicals are useful for the catalytic synthesis of 8-membered ring compounds.

One-pot catalytic procedures are developed producing dibenzo-cyclooctenes [5], mono-benzo-cyclooctadienes, and benzoxocins (Scheme 1). This presentation is focused on the mechanisms and applicability of these unusual metalloradical reactions for the synthesis of medium-sized ring compounds and describes our first attempts to prepare chiral monobenzocyclooctadienes in an enantioselective manner.



Scheme 1. Synthesis of 8-membered rings.

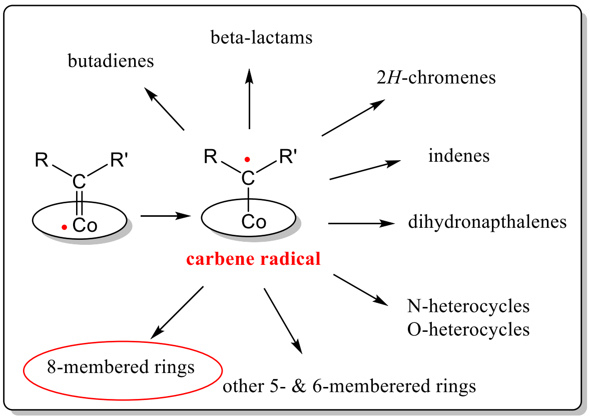


Figure 1. Recently explored scope of reactions.

REFERENCES

1. Dzik, W.I.; Zhang, X.P.; de Bruin, B., *Inorg. Chem.* **2011**, *50*, 9896.
2. Paul, N.D.; Mandal, S. Otte, M. Cui. X. Zhang, X.P.; de Bruin, B., *J. Am. Chem. Soc.* **2014**, *136*, 1090.
3. Das, B.G.; Chirila, A.; Tromp, M.; Reek, J.N.H; de Bruin, B., *J. Am. Chem. Soc.* **2016**, *138*, 8968.
4. te Grotenhuis, C.; van den Heuvel, N.; van der Vlugt, J. I.; de Bruin, B. *Angew. Chem. Int. Ed.* **2018**, *57*, 140.
5. Zhou, M.; Lankelma, M.; van der Vlugt, J.I.; de Bruin, B. *Angew. Chem. Int. Ed.* **2020**, *59*, 11073.
6. Zhou, M.; Wolzak, L.A. Li, Z.; de Zwart, F.J. Mathew, S.; de Bruin, B. *J. Am. Chem. Soc.* **2021**, 143, 20501.

Tailoring Metalloporphyrins (M= Zn(II), Ni(II), Cu(II), Au(III)) for binary and ternary Organic Solar Cells with high V_{oc} and PCE

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Although the pioneering use of porphyrins in organic solar cells (OSCs) was disappointing, as reported efficiencies were very low; the situation has changed over the last five years as Zn-porphyrins with ABAB structures linked to acceptor units have been applied as donors resulting in efficiencies of up to 12% in binary OSCs and 15% in ternary OSCs.

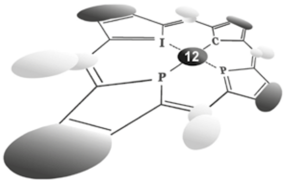
The optical and electrochemical properties of porphyrins can be adjusted by molecular design and functionalization on the β or meso positions of the porphyrin ring as well as by introduction of different central metal ions. Due to the high HOMO level of Zn-Porphyrin derivatives, the Voc of OSCs using this family of compounds are lower than 0.9 V limiting the PCE of devices.

However, the choice of the centrally bounded metal cation within the porphyrin core plays an important role in the electronic properties allowing the modulation of the frontier orbital levels and thereby use the porphyrin-based molecule as donor or acceptor component of the device.

Here, I´ll present our recent work in design, synthesis, and application of porphyrin-based small molecules with different central metal for highly efficient OSCs.

REFERENCES

1. V. Cuesta, M. Vartanian, P. de la Cruz, R. Singhal, G. D. Sharma and F. Langa. *J. Mater. Chem. A*, **2017**, 5, 1057.
2. S. Arrechea, A. Aljarilla, P. de la Cruz, M. K. Singh, G. D. Sharma and F. Langa. *J. Mater. Chem. C*, **2017**, 5, 4742.
3. M. Vartanian, R. Singhal, P. de la Cruz, S. Biswas, G.D. Sharma, F. Langa. *ACS Appl. Energy, Mater.*, **2018**, 1, 1304.
4. M. Vartanian, P. de la Cruz, F. Langa, S. Biswas and G. D. Sharma. *Nanoscale*, **2018**, 10, 12100.
5. M. Vartanian, R. Singhal, P. de la Cruz, G. D. Sharma and F. Langa. *Chem. Commun.,* **2018**, 54, 14144.
6. V. Cuesta, R. Singhal, P. de la Cruz, G. D. Sharma and F. Langa. *ACS Appl. Mater. Interfaces*, **2019**, 11, 7216.
7. Cuesta, R. Singhal, P. de la Cruz, G. D. Sharma and F. Langa, *ChemSusChem*, **2021**, 14, 3439.
8. H. Dahiya, V. Cuesta, P. de la Cruz, F. Langa and G. D. Sharma *ACS Appl. Energy Mater.*, **2021**, 4, 4498.



Biohybrid Strategies for Delivery and Targeting with Third-Generation Photosensitizers

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Tomás Torres and Santiago Guisán Ceinos

Organic Chemistry Department / Institute for Advanced Research in Chemistry (IAdChem), Universidad Autónoma de Madrid, Cantoblanco (Madrid), Spain

Phthalocyanines (Pc) are an important class of non-natural organic pigments. Due to their extended conjugation, these 18 π-electron macrocyclic aromatic systems absorb intensely at the near-IR spectral region. The energy of the resulting photoinduced excited state can be utilized for different biomedical applications.[1, 2] To this end, the incorporation of Pc into biological nanostructures is highly desirable, because it provides them with better photosensitizing features, and with the capacity to travel and be delivered within biological tissues. In this presentation we will show supramolecular approaches toward Pc-based biohybrid materials.[3, 4]

For example, we will discuss a straightforward non-covalent strategy to encapsulate silicon (IV) phthalocyanine (SiPc) photosensitizers (PS) in biocompatible and biodegradable polymeric micelles. Importantly, the encapsulated PS derivatives are amphiphilic, with the SiPc unit contributing to the hydrophobic core, while lipophilicity increases along the series, making possible to correlate the loading efficacy in micelles with the hydrophobic/hydrophilic balance of the PS structure. This has led to a new kind of third-generation nano-PS that efficiently photogenerates $^1O_2$, while preliminary *in vitro* experiments demonstrate an excellent cellular uptake and a promising PDT activity.[5]

In a second line, a biohybrid approach to tackle the issues that normally prevent a good photodynamic efficacy of Pc against cancer (e.g., high aggregation, low solubility and biocompatibility, etc.) will be described, based on zinc (II) Pc (ZnPc) derivatives with dendritic arms containing the well-known carbohydrate N-acetylneuraminic acid, also called sialic acid, which ensures water-solubility, biocompatibility and cell internalization.[6] Importantly, these dendritic PS have been encapsulated in liposome nanocarriers and used for a tailored multivalent targeting of siglecs (sialic acid-binding immunoglobulin-like lectins), which display diverse biological functions in interactions with pathogens, autoimmune diseases, neurodegeneration, brain disorders and tumoral processes.[7]

Finally, we will explore strategies for smart photoinduced PS delivery through biohybrid gels composed on nucleobase-containing low molecular weight hydrogelators.

REFERENCES

1. van de Winckle *et al.*, *Chem. Eur. J.* **2015**, *21*, 18551.
2. van de Winckle *et al.*, *Adv. Funct. Mater.* **2018**, 1705938.
3. Almeida-Marrero *et al.*, *Chem. Soc. Rev.* **2018**, *47*, 7369.
4. Anaya-Plaza *et al.*, *Adv. Mater.* **2019**, *31*, 1902582.
5. Setaro *et al.*, *J. Mat. Chem. B* **2020**, *8*, 282.
6. Almeida-Marrero *et al.*, *Chem. Eur. J.* **2021**, *27*, 9634.
7. Almeida-Marrero *et al.*, Submitted.

Phthalocyanine and subphthalocyanine cages: molecular flasks for chemical reactions over fullerenes

Gema de la Torre, **Marta Moreno Simoni, Sunit Kumar and Tomás Torres**

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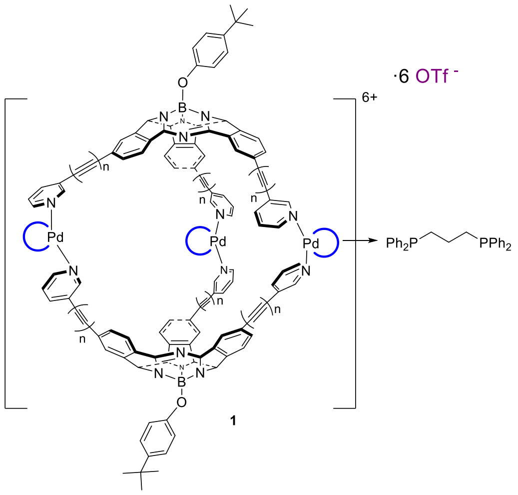
Metallo-organic ensembles built with aromatic panels are challenging targets since they provide cavities for the encapsulation of guest molecules through π-π interactions. Capsules based on porphyrins [1] or phthalocyanines [2] offer large defined spaces for the encapsulation of large organic guests such as fullerenes. Beyond the mere recognition of fullerenes by these metallo-organic cages, some authors have taken advantage of the shape complementarity and space confinement in the host:guest complexes to carry out organic transformations that do not proceed outside the cage[3]. Here, we describe phthalocyanine-based metallo-organic assemblies able to form host:guest complexes with different aromatic species. In particular, we have applied subphthalocyanine-based capsules **1** formed by Pd-directed dimerization of two C_3-symmetry subphthalocyanines[4] as molecular flasks to induce photoredox reaction with guest fullerenes, triggered by the subphthalocyanine excited state. Also, cycloaddition reactions over fullerenes in water media are reported, where the subphthalocyanine capsules behave as hydrophobic pockets. Confinement of the fullerene in the void space of the SubPc capsule proves essential to effectively perform these transformations.



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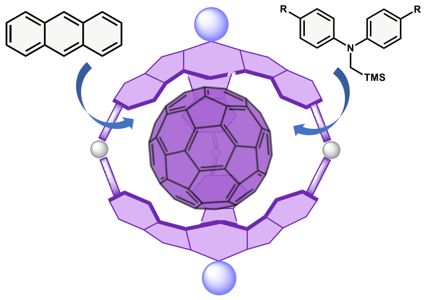

REFERENCES

1. C. Fuertes-Espinosa, C. García-Simón, E. Castro, M. Costas, L. Echegoyen, X. Ribas, X. Chang, S. Lin, G. Wang, C. Shang, Z. Wang, K. Liu, Y. Fang, P. J. Stang, *J. Am. Chem. Soc*. **2020**, *142*, 15950–15960.
2. E. Fazio, C. J. E. Haynes, G. de la Torre, J. R. Nitschke, T. Torres, *Chem. Commun*. **2018**, *54*, 2651–2654.
3. T. K. Ronson, B. S. Pilgrim, J. R. Nitschke, *J. Am. Chem. Soc*. **2016**, *138*, 10417–10420.
4. I. Sánchez-Molina, B. Grimm, R. M. Krick Calderon, C. G. Claessens, D. M. Guldi, T. Torres, *J. Am. Chem. Soc*. **2013**, *135*, 10503–10511.

Redox reactivity of porphyrins: from π-extension to *meso*/β functionalization and material electrosynthesis

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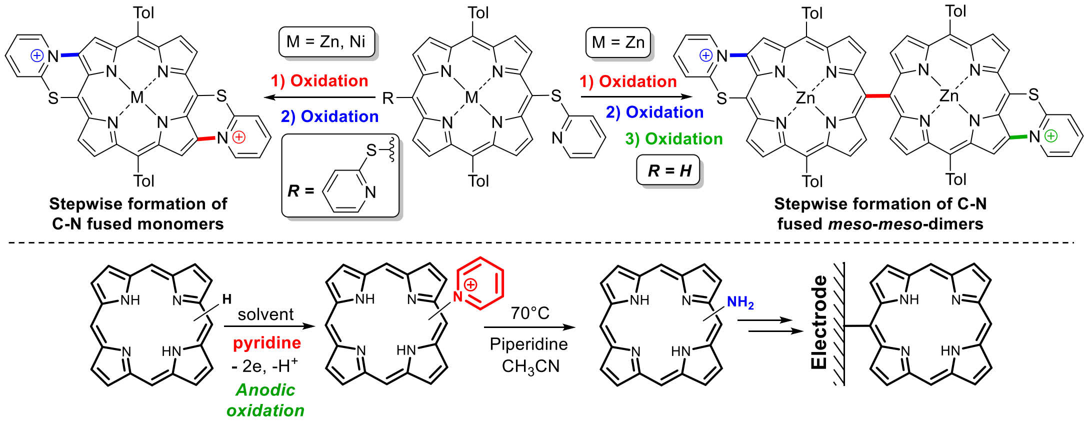
Porphyrins and porphyrin-based materials are currently used in various fields and for many applications because of their interesting physico-chemical properties. Indeed, these materials are part of different devices for non-linear optical and optical limiting devices, photoluminescent biosensors, electrochemical or spectrometric sensors, molecular electronic junctions, dye-sensitized solar cells and electrocatalytic systems [1].
Our research is focused on the (electro)functionalization of porphyrins, the electrosynthesis of new porphyrin-based materials as well as their possible applications. Examples of oxidative C-N fusion reaction of pyridinyl-porphyrins [2], one-pot electrochemical amination [3] as well as electrografting of primary amino-porphyrins *via* the *in situ* formation of the corresponding diazonium-porphyrins will be presented [4].



REFERENCES

1. K. M. Kadish, K. M. Smith, R. Guilard (Eds.), *The Handbook of Porphyrin Science*. World Scientific: Singapore, **2010-16**; Vol. 1-46.
2. Berthelot, M.; Hoffmann, G.; Bousfiha, A.; Echaubard, J.; Roger, J.; Cattey, H.; Romieu, A.; Lucas, D.; Fleurat-Lessard, P.; Devillers, C. H. *Chem. Commun.* **2018**, *54*, 5414, doi: 10.1039/c8cc01375f.
3. Bousfiha, A., Dimé, A. K. D., Mankou-Makaya, A., Echaubard, J., Berthelot, M., Cattey, H., Romieu, A., Roger, J., Devillers, C. H., *Chem. Commun.*, **2020**, 56, 884 - 887, doi: 10.1039/c9cc07351e.
4. S. Hebié, C. H. Devillers, S. Fournier, D. Lucas, *ChemElectroChem* **2016**, *3*, 45, doi: 10.1002/celc.201500496.

Rational Design of Electrocatalyst for CO_2 Reduction

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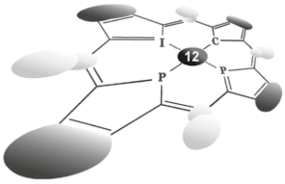
The electrocatalytic CO_2 reduction reaction (CO_2RR) to generate fixed forms of carbons that have commercial value is a lucrative avenue to ameliorate the growing concerns about the detrimental effect of CO_2 emissions as well as to generate carbon-based feed chemicals, which are generally obtained from the petrochemical industry. The area of electrochemical CO_2RR has seen substantial activity in the past decade, and several good catalysts have been reported. While the focus was initially on the rate and overpotential of electrocatalysis, it is gradually shifting toward the more chemically challenging issue of selectivity. CO_2 can be partially reduced to produce several C1 products like CO, HCOOH, CH_3OH, etc. before its complete 8e–/8H+ reduction to CH4. In addition to that, the low-valent electron-rich metal centers deployed to activate CO2, a Lewis acid, are prone to reduce protons, which are a substrate for CO_2RR, leading to competing hydrogen evolution reaction (HER). Similarly, the low-valent metal is prone to oxidation by atmospheric O_2 (i.e., it can catalyze the oxygen reduction reaction, ORR), necessitating strictly anaerobic conditions for CO_2RR. Not only is the requirement of O_2^- free reaction conditions impractical, but it also leads to the release of partially reduced O2 species such as $O_2^–$, H_2O_2, etc., which are reactive and result in oxidative degradation of the catalyst. In this presentation, mechanistic investigations of CO_2RR by detecting and, often, chemically trapping and characterizing reaction intermediates are used to understand the factors that determine the selectivity in CO_2RR. The spectroscopic data obtained from different intermediates have been identified in different CO_2RR catalysts to develop an electronic structure selectivity relationship that is deemed to be important for deciding the selectivity of $2e^–/2H^+$ CO_2RR. The roles played by the spin state, hydrogen bonding, and heterogenization in determining the rate and selectivity of CO_2RR (producing only CO, only HCOOH, or only CH4) are discussed using examples of both iron porphyrin and non-heme bioinspired artificial mimics. In addition, strategies are demonstrated where the competition between CO_2RR and HER as well as CO_2RR and ORR could be skewed overwhelmingly in favor of CO_2RR in both cases.

REFERENCES

1. Sk Amanullah, P. Saha, A. Dey* Selectivity in Electrochemical CO2 Reduction Acc. *Chem. Res.* 2022, 55, 134–144



Alzheimer's Disease: Reactive Intermediates

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Alzheimer's disease (AD) is a neurodegenerative disorder that has generally been associated with the accumulation of amyloid beta (Aβ) peptides and formation of partially reduced oxygen species (PROS) catalyzed by heme and Cu bound Aβ active sites in the brain. Degradation of neurotransmitters is another hallmark feature of AD. The heme bound Aβ peptides can act as peroxidases and degrade neurotransmitters like serotonin through reactive intermediates like compound 0 and compound I, which have been trapped and characterized. Cu bound Aβ peptides are also found to catalyze the oxidation of serotonin in the presence of H_2O_2. While both, a Cu(II)-OOH species and a dimeric, EPR silent, Cu_2O_2 bis-μ-oxo species are formed under the reaction conditions, the Cu(II)-OOH species is the reactive intermediate responsible for serotonin oxidation. Second sphere amino acid residues play significant roles in the reactivities exhibited by these metal-Aβ complexes.

REFERENCES

1. Nath, Arnab, K.; Ghatak, Arnab; *Dey, Abhishek; *Dey, Somdatta Ghosh. Intermediates involved in serotonin oxidation catalyzed by Cu bound Aβ peptides. *Chem. Sci.* **12**, 1924-1929, 2021.
2. Roy, Madhuparna; Nath, Arnab, K.; Pal, Ishita; *Dey, Somdatta Ghosh. Peroxidases Activity of Heme-Aβ complexes. *Chem. Comm.* Featured Article, **56**, 4505-4518, 2020.
3. Pal, Ishita; Nath, Arnab, K.; Roy, Madhuparna; Seal, Manas; Ghosh, Chandradeep; *Dey Abhishek;*Dey, Somdatta Ghosh. Formation of Compound I in Heme bound Aβ-peptides relevant to Alzheimer's Disease. *Chem. Sci.* **10**(36), 8405-8410, 2019.

Hybrid Porphyrin Materials for Electric Impedance Based Sensor Arrays

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Porphyrins and corroles have been used in the last two decades to prepare sensor arrays for a variety of applications [1,2]. The extended chemical interactivity of these molecules makes possible the measurement of complex patterns of volatile compounds. The interplay between metal ion, aromatic ring, peripheral compounds and molecular arrangement establishes unique selectivity patterns which are fundamental elements for sensor array design and development. Films of porphyrins and corroles can be adequately applied to inorganic surfaces enabling different kinds of chemical sensors each based on a diverse physical transduction. Among them, mass transducers, such as Quartz Microbalances (QMBs), have been found particularly suitable for several applications. QMBs do not select amidst the interaction mechanisms, rather it considers the whole bouquet of interactions involving the volatile compounds and the sensitive layer. Porphyrins and corroles coated QMB sensor arrays have been successfully used in several applications, and in particular to investigate the relationships between human volatilome and pathologies in-vivo (e.g. breath analysis), in human samples (e.g. urines and blood) and in-vitro (e.g. cell cultures). Recent results include the diagnosis of kidney cancer from urines [3], COVID-19 from blood serum [4], and the *Plasmodium falciparum* infected red blood cells[5].

In the last years, we have been interested in replicating the behavior of QMB sensor arrays with other transduction principle which enables a more simple sensor system design and even the integration of sensors in wearable supports[6]. To this regard simplest sensors are those based on electric impedance variation. For this scope, porphyrinoid have been grafted onto the surface of nanostructures that can provide a change of impedance as a result of the chemical interaction between porphyrinoids and volatile compounds. For instance, layers of porphyrinoids coated ZnO nanoparticles shown sensitivity towards a large spectra of compounds [7]. Exploiting the optical properties of porphyrins, the sensitivity of this sensors can be triggered by light. As a result, these devices show a negative sensitivity to electron donor compounds (e.g. amines) and a positive sensitivity respect to other compounds. This property can be fruitfully exploited in sensor arrays configuration to classify complex samples such as foods and furthermore to detect spoilage processes. Another example is provided by porphyrnoids coated silica nanoparticles. In this case, the dielectric properties of silica are exploited to develop capacitive sensors whose capacitance is modulated by the absorption of volatile compounds. These sensors retain the chemical sensitivity properties of porphyrins allowing for instance to reproduce the results of the QMB sensors in the identification of COVID-19 blood serum samples.

REFERENCES

1. R. Paolesse, S. Nardis, D. Monti, M. Stefanelli, C. Di Natale, Chem. Rev. 117 (2017) 2517–2583. https://doi.org/10.1021/acs.chemrev.6b00361.
2. C. Di Natale, C.P. Gros, R. Paolesse, Chem. Soc. Rev. (2022). https://doi.org/10.1039/d1cs00662b.
3. M. Murdocca, F. Torino, S. Pucci, M. Costantini, R. Capuano, C. Greggi, C. Polidoro, G. Somma, V. Pasqualetti, Y.K. Mougang, C. Di Natale, F.C. Sangiuolo, Cancers. 13 (2021). https://doi.org/10.3390/cancers13164213.
4. Y.K. Mougang, L. Di Zazzo, M. Minieri, R. Capuano, A. Catini, J.M. Legramante, R. Paolesse, S. Bernardini, C. Di Natale, IScience. 24 (2021) 102851. https://doi.org/10.1016/j.isci.2021.102851.
5. R. Capuano, I. Khomenko, F. Grasso, V. Messina, A. Olivieri, L. Cappellin, R. Paolesse, A. Catini, M. Ponzi, F. Biasioli, F. Biasioli, C. Di Natale, Sci. Rep. 9 (2019). https://doi.org/10.1038/s41598-019-48732-x.
6. L. Di Zazzo, G. Magna, M. Lucentini, M. Stefanelli, R. Paolesse, C. Di Natale, Chemosensors. 9 (2021). https://doi.org/10.3390/chemosensors9120356.
7. G. Magna, M. Muduganti, M. Stefanelli, Y. Sivalingam, F. Zurlo, E. Di Bartolomeo, A. Catini, E. Martinelli, R. Paolesse, C. Di Natale, ACS Appl. Nano Mater. 4 (2021) 414–424. https://doi.org/10.1021/acsanm.0c02754.

Mono- and Heteropentanuclear In(III) Pyrazinoporphyrazine Complexes: Synthesis, Physicochemical and Photoactivity Studies

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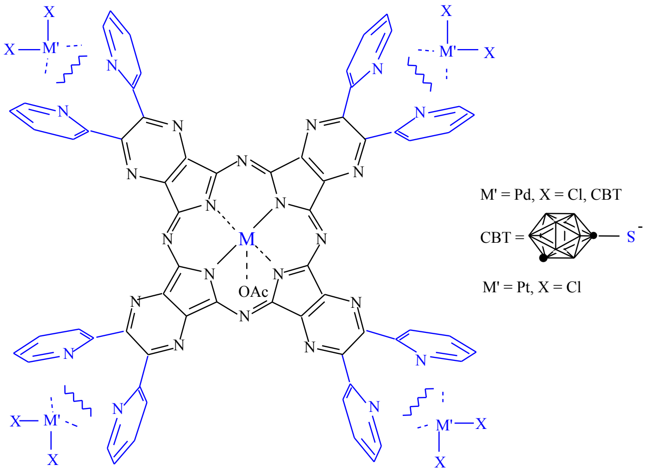
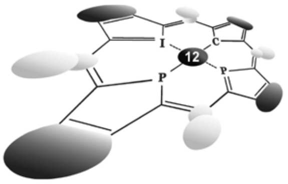
The macrocyclic octapyridinotetrapyrazinoporphyrazine In^{III} complex of formula $[Py_8TPyzPzIn(OAc)]\cdot 8H_2O$, prepared by reaction of the free ligand $[Py_8TPyzPzH_2]\cdot 2H_2O$ [1] with $In(OAc)_3$, is a stable-to-air species of which the structure has been studied by its X-ray powder diffraction and mass spectra and characterization made by IR and UV-visible spectral measurements [2]. The complex has been proven to be of potential interest for its response as an anticancer agent in the field of photodynamic therapy (PDT), the value of $\Phi_\Delta = 0.55$ (in DMF) being in the range of 0.4–0.6 of similar phthalocyanine and porphyrazine analogs [3] and qualifying the species as a highly efficient anticancer agent. Parallel studies, including photoactive behaviour in PDT, have been extended to the mononuclear octacation $[(2\text{-}Mepy)_8TPyzPzIn(OAc)]^{8+}$ (salted by iodide ions), and to the heteropentanuclear derivatives of formula $[(M'Cl_2)_4Py_8TPyzPzIn(OAc)]\cdot xH_2O$ (M' = Pd^{II}, x = 8; Pt^{II}, x = 1)) and $[\{(Pd(CBT)_2)_4\}Py_8TPyzPzIn(OAc)]\cdot 19H_2O$ (CBT = *m*-carborane-1-thiolate anion) (see Figure).



REFERENCES

1. Donzello, M. P.; Ou, Z.; Monacelli, F.; Ricciardi, G.; Rizzoli,| C.; Ercolani, C.; Kadish, K. M. *Inorg. Chem*. **2004**, *43*, 8637-8648.
2. Donzello, M. P.; Capobianco, G.; Pettiti, I.; Ercolani, C.; Stuzhin, P. A. *Molecules* **2022**, 27, 849-866.
3. a) Nyokong, T. *Coord. Chem. Rev*. **2007**, *251*, 1707-1722. b) Machacek, M.; Cidlina, A.; Novakova, V.; Svec, J.; Rudolf, E.; Miletin, M.; Kučera, R.; Simunek, T.; Zimcik, P. *J. Med. Chem*. **2015**, *58*, 1736-1749.



Peptide ‘Corrination’ for the mitigation of CNS associated side-effects of GLP-1 receptor agonists

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The hypophagia and nausea/malaise effects produced by existing GLP-1R agonists are reported to require penetrance and direct action in the CNS [1-4]. Thus, we sought to create a GLP-1R agonist with reduced brain penetrance but that retained *at least* a comparable pharmacodynamic profile on pancreatic GLP-1R populations [5]. Our recent published reports [6-7], along with preliminary data discussed in this talk, show that conjugation of vitamin B12 (B12) or dicyanocobinamide (Cbi) (so called ‘corrination’ conjugates) with the potent (EC_{50} ~30 pM) GLP-1R agonist Exendin-4 (Ex4), namely B12-Ex4 and Cbi-Ex4, produces hypoglycemia in a glucose tolerance test in *both* mouse and rat models *without* producing hypophagia or illness-like behaviors. Further, we show in the musk shrew [*Suncus murinus*], a mammal capable of emesis, that B12-Ex4 or Cbi-Ex4 retain a hypoglycemic profile with a virtual absence of emetic events compared to the profound emesis produced by native Ex4.

‘Corrination’ overall offers broad clinical potential extending to any disease/syndrome where ONLY a peripheral (non-CNS) site-of-action is desired for any peptide-based biological therapeutic to reduce the profile of adverse events that may impair clinical application and disease treatment.

REFERENCES

1. Kanoski SE, Fortin SM, Arnold M, Grill HJ, Hayes MR. Peripheral and central GLP-1 receptor populations mediate the anorectic effects of peripherally administered GLP-1 receptor agonists, liraglutide and exendin-4. *Endocrinology* 2011;152:3103-12.
2. Sisley S, Gutierrez-Aguilar R, Scott M, D'Alessio DA, Sandoval DA, Seeley RJ. Neuronal GLP1R mediates liraglutide's anorectic but not glucose-lowering effect. *J. Clin Invest* 2014;124:2456-63.
3. Secher A, Jelsing J, Baquero AF, et al. The arcuate nucleus mediates GLP-1 receptor agonist liraglutide-dependent weight loss. *J. Clin Invest* 2014;124:4473-88.
4. Kanoski SE, Rupprecht LE, Fortin SM, De Jonghe BC, Hayes MR. The role of nausea in food intake and body weight suppression by peripheral GLP-1 receptor agonists, exendin-4 and liraglutide. *Neuropharmacology* 2012;62:1916-27.
5 Mietlicki-Baase EG, Liberini CG, Workinger JL, et al. A vitamin B12 conjugate of exendin-4 improves glucose tolerance without associated nausea or hypophagia in rodents. *Diabetes Obes Metab* 2018.
6. IC Tinsley, T Borner, MKL Swanson, OG Chepurny, SA Doebley, V Kamat, R.P. Doyle et al., Synthesis, Optimization, and Biological Evaluation of Corrinated Conjugates of the GLP-1R Agonist Exendin-4. *Journal of Medicinal Chemistry* 2021; 64 (6), 3479-3492.
7. T Borner, JL Workinger, IC Tinsley, SM Fortin, LM Stein, OG Chepurny, RP Doyle et al., Corrination of a GLP-1 receptor agonist for glycemic control without emesis. *Cell reports* 2020, 31(11), 107768.

Carbazole-Annelated Mono and Binuclear Porphyrazines: Optical and Photochemical Properties

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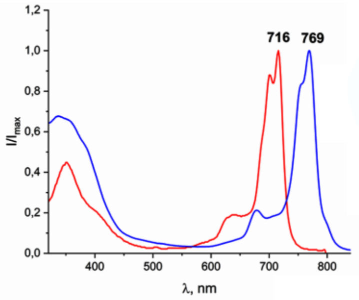
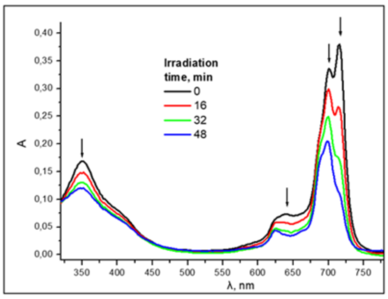
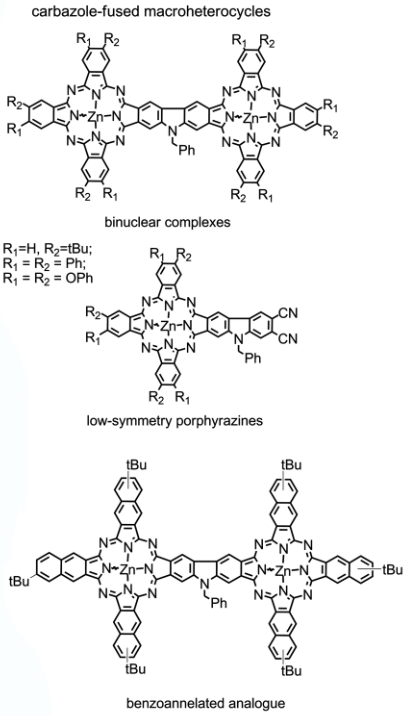
In the present study, the synthetic approach to a novel class of planar binuclear porphyrazines with carbazole spacer was developed. By the optimization of the reaction conditions yields up to 52% were achieved. Low symmetry A_3B-type complexes with carbazole moiety were separated and identified. The extension of the periphery of binuclear complexes results in linear benzoannelated analogs which demonstrate the bathochromic shift of the main absorption band. The electrochemical and spectroelectrochemical studies were conducted for target complexes. The target binuclear compounds tend to easier oxidation compared to monoporphyrazines. Singlet oxygen quantum yields were measured for the series of binuclear phthalocyanines and it was found that they are comparable with binuclear phthalocyanines sharing a common benzene ring (Φ_Δ=10-15%).



red line - binuclear porphyrazine;
blue line - benzoannelated analogue



Photodegradation of binuclear porphyrazine



The photodegradation of binuclear complexes was investigated using UV-Vis spectroscopy and mass spectrometry. It was found that photodegradation is a stepwise process passed the stage of destruction of the aromatic bridge.

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Engineering P450s to Alleviate a Bottleneck to Lignin Demethylation

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Cytochrome P450s are champion catalysts due to their versatility, robustness, and malleability. In the first of a trilogy of papers, we described a P450 system capable of oxidatively demethylating the guaiacol subunit of lignin – a chemically heterogeneous, abundant plant cell wall polymer that currently is burned as a waste product. To date, O-demethylation has served as a bottleneck for biocatalytic conversion of lignin into useful chemical precursors such as protocatechuic acid. Our work identified a potential solution to the demethylation problem for one of the most abundant lignin subunits. However, guaiacol – the compound that gives barrel-aged whisky its smoky flavour – is not the only O-methylated lignin constituent. Related syringol and vanillin monomers are also abundant. The use of engineered microbial systems as composite biocatalysts, a process known as "funnelling" demands that all of the substrate components be dealt with in order to avoid poisoning the bioreactor. Using structure-guided engineering, we were able to selectively modify the active site of the guaiacol demethylase to tune its reactivity toward these alternate substrates. Taken together, this work constitutes a biocatalytic hat trick in which first the native substrate guaiacol, followed shortly afterwards by syringol and then vanillin, have been successfully corralled into the P450 funnel.

REFERENCES

1. Mallinson, DuBois, Beckham, McGeehan *et al.* 2018 A promiscuous cytochrome P450 aromatic O-demethylase for lignin bioconversion *Nature Communications* 9:2487.
2. Machovina, Beckham, McGeehan, DuBois *et al.* 2019 Enabling microbial syringol conversion through structure-guided protein engineering *Proc. Natl. Acad. Sci USA* 116, 13970–13976.
3. Ellis, Beckham, McGeehan, DuBois *et al.* 2021 Engineering a cytochrome P450 for demethylation of lignin-derived aromatic aldehydes *JACS Au* 1, 252−261.

Phthalocyanines-based systems for health

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Using wavelengths belonging to one of the phototherapeutic window for photodynamic therapy treatment has two crucial advantages: a deeper tissue penetration of light, without affecting endogenous chromophores. In this regard, phthalocyanines, with their intense absorption around 700 nm, are ideal.

Our works on the design and synthesis of phthalocyanines-based systems for health (mainly PDT) follow several directions that will be presented:
- new water-solubilising substitution pattern
- improvement of singlet oxygen generation
- active targeting strategies
- combination with other therapeutically active molecules
- nano-sizing, covalent or not
- theranostics.

REFERENCES

1. Pui-Chi Lo, M. Salomé Rodriguez-Morgade, Dennis K. P. Ng*, Tomas Torres*, Ravindra Pandey* and Fabienne Dumoulin*, *Chemical Society Reviews,* **2020**, 49, 1041-1056
2. Eda Gazel Pehlivan, Yıldız Ek, Derya Topkaya, Uygar Halis Tazebay* and Fabienne Dumoulin*, *J. Porphyrins Phthalocyanines* **2019**, *23*, 1587-1591
3. Gülçin Ekineker, Christophe Nguyen, Sumeyra Bayir, sofia dominguez-gil, Umit Isci, Morgane Daurat, Anastasia Godefroy, Laurence Raehm, Clarence Charnay, Erwan Oliviero, Vefa Ahsen, Magali Gary-Bobo*, Jean-Olivier Durand and Fabienne Dumoulin* *Chem. Commun.* **2019**, *55*, 11619-11622
4. Hoay Yan Cheah, Elena Gallon, Fabienne Dumoulin, See Ziau Hoe, Nina Japundžić-Žigon, Sofija Glumac, Hong Boon Lee, Prem Anand, Lip Yong Chung, Maria Jesus Vicent and Lik Voon Kiew, *Mol. Pharmaceutics* **2018**, *15*, 2594-2605
5. M. Tarhouni, D. Durand, E. Önal, D. Aggad, Ü. İşci, G. Ekineker, F. Brégier, B. Jamoussi, V. Sol, M. Gary-Bobo and F. Dumoulin* *J. Porphyrins Phthalocyanines* **2018**, *22*, 552–561
6. Chiara Mauriello-Jimenez, Maxime Henry, Dina Aggad, Laurence Raehm, Clarence Charnay, Xavier Cattoen, Michel Wong Chi Man, Serkan Alpugan, Vefa Ahsen, Deniz Kutlu Tarakcı, Philippe Maillard, Marie Maynadier, Marcel Garcia, Fabienne Dumoulin*, Magali Gary-Bobo*, Jean-Luc Coll, Véronique Josserand* and Jean-Olivier Durand* *Nanoscale, **2017**, 9, 16622-16626*

Organosilica Nanoparticles for Photodynamic Therapy and siRNA Delivery.

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Organosilica nanoparticles have attracted much attention for nanomedicine applications due to their biocompatibility, flexible functionalisation, tunable pore size and diameter. These nanoparticles are different from well-known mesoporous silica nanoparticles (MSN). Indeed the organic part represent 80% of the framework, therefore, they present improved properties in terms of drug loading capacities, biocompatibility than MSN. We describe here mesoporous organosilica nanoparticles engineered for siRNA delivery and two-photon photodynamic therapy. The photosensitizers were located in the walls of the nanoparticles as J aggregates, letting the porosity free for siRNA loading. Combined with two-photon photodynamic therapy, photochemical internalization of siRNA was observed. Alternatively, non-porous organosilica nanoparticles of small size (10 nm hydrodynamic diameter), made of J aggregates of silylated porphyrins, and functionalized with mannose were prepared. These nanoparticles were injected in the blood stream of MDA-MB-231 breast tumor-xenograted models of zebrafish embryos. 1.5h after the injection, the tumor was irradiated with focused two-photon light (3 scans of 1.57 s). Two days after, the evolution of the tumor was monitored and two-photon PDT allowed a reduction of the tumor of 75%.The mechanism of cell death involved caspase 3 and thus apoptosis of the cancer cells.

REFERENCES

1. S. Dib, D. Aggad, C. Mauriello Jimenez, A. Lakrafi, G. Hery, C. Nguyen, D. Durand, A. Morère, K. El Cheikh, V. Sol, V. Chaleix, S. Dominguez Gil, K. Bouchmella, L. Raehm, J.-O. Durand, M. Boufatit, X. Cattoën, M. Wong Chi Man, N. Bettache and M. Gary-Bobo, *CANCER REPORTS*, 2019, **2**, e1186.
2. C. Mauriello Jimenez, D. Aggad, J. G. Croissant, K. Tresfield, D. Laurencin, D. Berthomieu, N. Cubedo, M. Rossel, S. Alsaiari, D. H. Anjum, R. Sougrat, M. A. Roldan-Gutierrez, S. Richeter, E. Oliviero, L. Raehm, C. Charnay, X. Cattoen, S. Clement, M. Wong Chi Man, M. Maynadier, V. Chaleix, V. Sol, M. Garcia, M. Gary-Bobo, N. M. Khashab, N. Bettache and J. O. Durand, *Adv. Funct. Mater.*, 2018, **28**, 1800235.

Lanthanides and porphyrins on surfaces

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Lanthanide elements play a pivotal role in modern science and technology, with impact in light emitting devices, lasers, nanomagnetism, and quantum information [1]. In this talk, I will revise our recent efforts regarding the metallation of porphyrinoid species on surfaces, targeting to achieve unprecedented metal-organic architectures, which could exploit the functionalities of lanthanides in a coordinative environment [2-3].

REFERENCES

1. *Accounts of chemical research* 51, 365-375, 2018
2. *Journal of the American Chemical Society* 139, 14129-14136, 2017
3. *Nanoscale* 13, 8600-8606, 2021

Design of Aerogel-based Electrocatalysts for Oxygen Reduction Reaction in Fuel Cells

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In the past couple of decades great advancements have been made in the development of PGM-free catalysts based on earth-abundant elements, nitrogen, carbon and transition metals (usually Fe or Co), inspired by biological systems such as porphyrins and phthalocyanines. In order to overcome the poor stability and low catalytic activity of transition-metal complexes, a new class of high temperature-treated (HT-treated) catalysts, composed of the same elements, i.e., a transition metal, carbon and nitrogen, was developed. Although HT-treated PGM-free catalysts exhibit improved activity and stability, their performance remains inferior to PGM catalysts, calling for further improvements to make them a viable alternative to the state-of-the-art materials.

In this work, we designed, synthesized and characterized ORR catalysts based on iron, carbon and nitrogen in a well-defined, high surface-area covalent framework (COF) of aerogels. Aerogels are ultralight, porous materials, with ultra-low density and high void volume (> 97%), also known for their unique physicochemical properties such as high porosity, controllable pore size and surface area, low thermal conductivity, just to name a few. The variety of precursors used for aerogel synthesis makes them promising candidates for a wide range of applications in catalysts, capacitors, insulators, absorbents, and many more. In the context of electrocatalysis of fuel cell reactions, carbon-aerogels have been mostly used so far as catalyst supports for PGM and PGM-free catalysts.

In their inorganic form, aerogels can have ultra-high catalytic site density, high surface area, and tunable physical and chemical structures - all very important features for a heterogeneous catalyst. In this talk, we will discuss the synthesis and electrocatalytic properties of an iron-porphyrin aerogel. 5,10,15,20-(tetra-4-aminophenyl)porphyrin (H2TAPP) and Fe(II) were used as the building blocks of the aerogel, which was later heat-treated at 600 °C to enhance electronic conductivity and catalytic activity while preserving its macro-structure. The resulting material has a very high concentration of atomically dispersed catalytic sites (4.01·1019 sites cm-3), capable of catalyzing the oxygen reduction reaction in alkaline solution (E_{onset} = 0.93 V vs. RHE, TOF = 0.2 e- site-1 s-1 at 0.8 V vs. RHE). At the end of the talk, I will also show some of our recent results with other types of aerogels, some for different applications.

Plasticity in the Mode of Action of B_{12}-based Photoreceptors

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CarH is the prototype of a new and large family of photoreceptors that are widely distributed in many bacterial species and that use the form of vitamin B_{12} known as coenzyme B_{12} or AdoCbl (5'-deoxyadenosylcobalamin) as their chromophore [1]. Typically, they repress their own expression and that of genes for carotenoid synthesis in the dark by binding to operator DNA as AdoCbl-bound tetramers, whose light-induced disassembly relieves repression [1-4]. Structures of *Thermus thermophilus* CarH provided high-resolution snapshots of the dark and light states, and of a unique DNA-binding mode where three out of four DNA-binding domains contact an operator comprising three tandem 11-bp direct repeats [2]. I will present our recent results highlighting a notable plasticity in oligomerization, DNA binding and/or operator architecture of CarH photoreceptors, which may be important for their biological functions and development as optogenetic tools [3,4,5].

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REFERENCES

1. Ortiz-Guerrero JM, Polanco MC, Murillo FJ, Padmanabhan S, Elías-Arnanz M (2011) *Proc Natl Acad Sci USA* 108, 7565-7570.
2. Jost M, Fernández-Zapata J, Polanco MC, Ortiz-Guerrero JM, et al (2015) *Nature* 526: 536-541.
3. Padmanabhan S, Jost M, Drennan CL, Elías-Arnanz M (2017) *Annu Rev Biochem* 86: 485-514.
4. Fernández-Zapata J, Pérez-Castaño R, Aranda J, Colizzi F et al (2018) *J. Biol Chem* 293: 17888-17905.
5. Padmanabhan S, Pérez-Castaño R, Elías-Arnanz M (2019) *Curr Opin Struct Biol* 57: 47-55.

Stereoselective olefin cyclopropanation reactions with engineered hemoprotein catalysts

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Expanding the reaction scope of biological catalysts beyond the realm of enzymatic transformations occurring in nature can create new opportunities for the exploitation of biocatalysis for organic synthesis and sustainable chemistry. In this lecture, we will present recent progress made by our group toward the design and application of engineered myoglobins and other hemoprotein scaffolds for catalyzing abiological carbene transfer reactions, with an emphasis on olefin cyclopropanation reactions. These efforts have led to the development of efficient and stereoselective biocatalysts for the asymmetric synthesis of a variety of chiral cyclopropane scaffolds, including transformations not previously accessible with synthetic carbene transfer catalysts. These biocatalytic strategies could be leveraged to enable the stereoselective synthesis of core motifs in drugs and bioactive natural products at the preparative scale and they could be integrated into chemoenzymatic schemes for the generation of structurally diverse and stereochemically rich scaffolds of high value for medicinal chemistry and natural product synthesis.

ORALS

A Mixed Metal Porphyrinic Metal Organic Framework for Photocatalytic Applications

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Porphyrin-based Metal Organic Frameworks (MOFs) are being extensively investigated as functional materials with properties originating both from the porphyrinic linker and the metallic building unit of the framework [1]. Chemical stability is a prerequisite for any material use but is also a challenge for coordination-based compounds, especially regarding stability to hydrolysis [2]. For this purpose tailor-made porphyrins with original coordinating functions have been recently developed [3], that extended the coordination chemistry well beyond carboxylates.

In our quest to stable functional materials, we recently reported an especially robust polyphenolate porphyrin-based framework: MIL-173(Zr) [4]. This material was proved to be active in several catalytic transformations and in view to upgrade the photocatalytic features a modification of the inorganic unit was performed, to introduce TiO_x units, thus impacting the band gap and photophysical properties. MIL-173 was modified through chemical synthesis: using a mixture of Zr and Ti precursors we demonstrate the synthesis of a mixed metal Ti/Zr based MOF with a finely tuneable inorganic composition (Figure 1). The structure, morphology, porosity and light absorption properties evolution were studied with increasing Ti content. Photocatalytic activity is assessed for variable Ti content in the MOF.

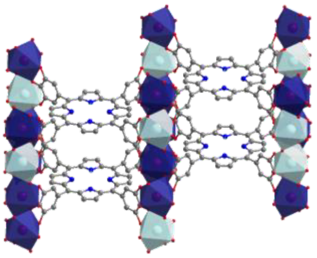

Figure 1: mixed-metal MIL-173 metal organic framework

REFERENCES

1. X. Zhang *et al.*, Coord. Chem. Rev. **429**, 213615 (2021).
2. A. Fateeva *et al.*, Angew. Chem.-Int. Ed. **51**, 7440 (2012).
3. S. De, T. Devic, and A. Fateeva, Dalton Trans **50**, 1166 (2021).
4. G. Mouchaham *et al.*, Chem. Commun. **53**, 7661 (2017).

SubPc – Scaffolding

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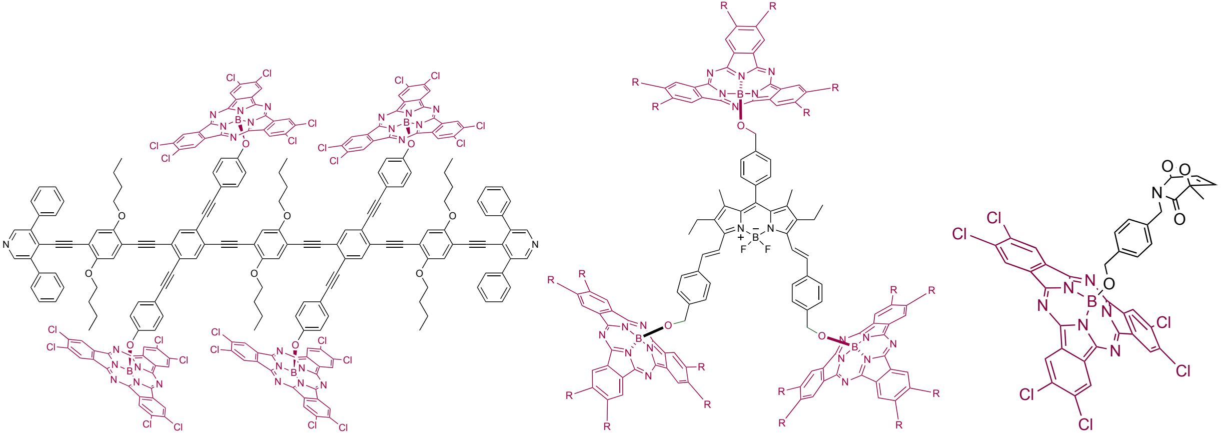
The cone-shaped subphthalocyanines (SubPcs) have emerged as promising functional chromophores with an intriguingly broad application profile that is driven by their synthetic accessibility and their relative ease of handling in combination with impressive solar light harvesting and/or photooxidative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

Porphyrin photosensitizers for biological applications

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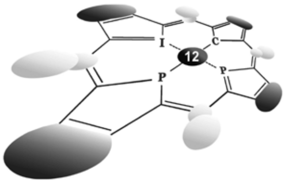
Tetrapyrrolic macrocycles are a ubiquitous class of compounds in nature with unique physicochemical properties and a stablished role in crucial biological functions. The adequate functionalization of these natural or synthetic macrocycles at *meso* and/or *beta*-pyrrolic positions or their immobilization on different supports are responsible for their successful applications in several field. In particular, some of these derivatives have shown remarkable properties and significant potential to be used as photosensitizers in photodynamic therapy against tumoral cells, microbial cells in planktonic and biofilms forms, viruses and parasites [1-3]. In this communication, an overview of some of the recent synthetic advances obtained in our group to obtain immobilized and non-immobilized *meso*-arylporphyrins derivatives and applications related with their photodynamic efficiency under different contexts will be addressed and discussed [4-7].

Acknowledgements: The authors thank the University of Aveiro and FCT/MCT for the financial support provided to LAQV-REQUIMTE (UIDB/50006/2020) and to the Projects PREVINE - FCT-PTDC/ASP-PES/29576/2017 through national funds (OE) and GT-LightUP-FCT-PTDC/QUI-QFI/29319/2017 where applicable co-financed by the FEDER-Operational Thematic Program for Competitiveness and Internationalization-COMPETE 2020, within the PT2020 Partnership Agreement. Thanks are also due to the Portuguese NMR and Mass Networks.

REFERENCES

1. Mesquita M.Q., Dias C.J., Neves M.G.P.M.S., Almeida A. Faustino M.A., The Role of Photoactive Materials Based on Tetrapyrrolic Macrocycles in Antimicrobial Photodynamic Therapy, Handbook of Porphyrin Science. Vol 46, chapter 4 February 2022, 201-277. https://doi.org/10.1142/9789811246760_0221
2. M.Q. Mesquita, C.J. Dias, M.G.P.M.S. Neves, A. Almeida, M.A.F. Faustino *Molecules*, **2018**, 23(10), 2424.
3. M. Q. Mesquita, C.J. Dias, S. Gamelas, M. Fardilha, M.G.P.M.S. Neves, A. Almeida, M.A.F. Faustino. A*n Acad Bras Cienc*. **2018**, 90(1), 1101-1130.
4. K.A.D.F. Castro, L.D. Costa, J.A. Prandini, J.C. Biazzotto, A.C. Tomé, M.R. Hamblin, M.G.P.M.S. Neves, M.A.F. Faustino, R.S. da Silva, *Chem. Eur J.*, **2021**, 27
5. M.Q. Mesquita, A.R. Ferreira, M.G.P.M.S. Neves, D. Ribeiro, M. Fardilha, M.A.F. Faustino, *J. Photochem. Photobiol. B: Biol*, **2021**, 223, 112301
6. K.A.D.F. Castro, G.T.P. Brancini, L.D. Costa, J.C. Biazzotto, M.A.F. Faustino, A.C. Tomé, M.G.P.M.S. Neves, A. Almeida, M.R. Hamblin, R.S. et al., *Photochem. Photobiol. Sci*., **2020**, *19*, 1063-1071
7. C.J. Dias, I. Sardo, N.M.M. Moura, J. Felgueiras, M.G.P.M.S. Neves M. Fardilha, M.A.F. Faustino, *Dyes Pigm.*, **2020**, *173*, 107996.



Application of Porphyrin and Phthalocyanine Glycodendritic Conjugates in Biomedicine

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Photosensitizers (PSs), such as phthalocyanines and porphyrins, are chemicals that are activatable by light of a specific wavelength. Several PSs have been used in photodynamic therapy to treat a variety of diseases, including central serous retinopathy, age-related macular degeneration, and certain solid tumors [1-3].

Exosomes are small vesicles (30-150 nm) that are released into the extracellular space by most cells. They play a crucial role in cell-cell communication, by carrying a variety of bioactive molecules (e.g. lipids, proteins, and genetic material). Exosomes are suitable for PS delivery because of their inherent features, including low immunogenicity and toxicity, as well as their intrinsic ability to cross biological barriers.

Due to the ability to recognize carbohydrate-binding proteins overexpressed in the diseased tissue, incorporation of different carbohydrates at the periphery of PSs' core improves their solubility and provides a molecular-targeted method of delivering PDT-mediated toxicity [4-7].

This talk will cover the putative use of exosomes as PSs carriers and delivery systems, as well as the mechanisms underlying phototoxic effects of galactose-PSs conjugates, including the mechanisms of their internalization and the impact of cytoskeleton disorganization in PDT-induced cell death.

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REFERENCES

1. Josefsen LB and Boyle RW, *Theranostics*, 2012, 2: 916.
2. Iacono P, Da Pozzo S, Varano M, Parravano M. *Pharmaceuticals*, 2020, 12
3. Battaglia Parodi M, La Spina C, Berchicci L, Petruzzi G and Bandello F. *Dev Ophthalmol*, 2015, 55: 330-336.
4. Pereira PMR, Silva S, Bispo M, Zuzarte M, Gomes C, Girão H, Cavaleiro JAS, Ribeiro CAF, Tomé JPC and Fernandes R, *Bioconjug. Chem*, 2016, 27: 2762.
5. Pereira PMR, Silva S, Ramalho JS, Gomes CM, Girão H, Cavaleiro JAS, Ribeiro CAF, Tomé JPC and Fernandes R, *Eur J Cancer*, 2016, 68: 60.
6. Fernandes SRG, Fernandes R, Sarmento B, Pereira PMR and Tomé JPC. *Org Biomol Chem*, 2019, 17: 2579.
7. Pereira PMR, Parada B, Ribeiro-Rodrigues TM, Fontes-Ribeiro CA, Girão H, Tomé JPC and Fernandes R. *Mol Pharmaceutics*, 2020, 17: 2145.

Synthesis and Photophysical Study of a (Perylenediimide-Azobenzene)$_2$Silicon Phthalocyanine Pentad

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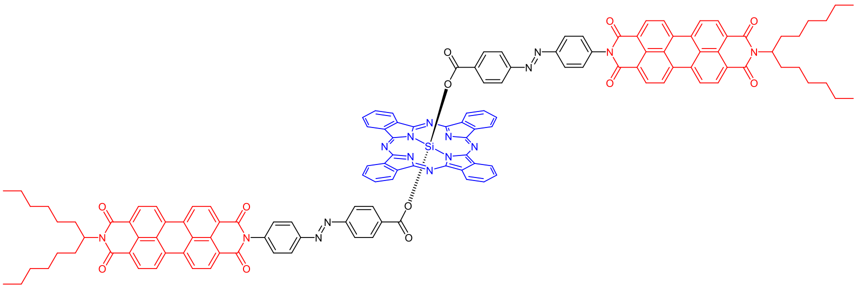
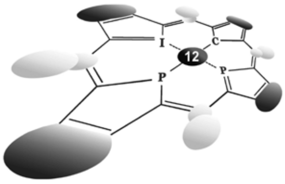
Photoinduced electron transfer is a key step in natural photosynthesis, but also in artificial photosynthesis and organic photovoltaics. As a consequence, it has received great scientific attention. Our groups have dedicated many efforts to the study of such charge-separated states by bonding, for example, phthalocyanines (Pcs) [1] and perylenediimides (PDIs) [2] in different stoichiometries and geometries, thus generating charge-separated states with lifetimes in the hundreds of microseconds range [3]. Recently, we have initiated the photophysical study of PDI-azobenzene ensembles [4], which contain a photoisomerizable azo group, obtaining exciting results. Herein, we will present the extension of these studies to pentads containing both phthalocyanines and azobenzene-PDIs.



This research was supported by the European Regional Development Fund "A way to make Europe" and the Spanish Ministerio de Ciencia e Innovación/Agencia Estatal de Investigación (PID2019-109200GB-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.

REFERENCES

1. *Phthalocyanines: Properties and Applications*, C. C. Leznoff, A, B. P. Lever, Eds.; VCH Publishers, Weinheim, 1990-1996, Vol. 1-4.
2. F. Würthner, C. R. Saha-Möller, B. Fimmel, S. Ogi, P. Leowanawat, D. Schmidt, *Chem. Rev.* **2016**, 116, 962.
3. (a) V. Navarro-Pérez, A. M. Gutiérrez-Vílchez, J. Ortiz, Á. Sastre-Santos, F. Fernández-Lázaro, S. Seetharaman, M. J. Duffy, P. A. Karr, F. D'Souza, *Chem. Commun.* **2019**, 55, 14946; (b) N. Zink-Lorre, E. Font-Sanchis, S. Seetharaman, P. A. Karr, Á. Sastre-Santos, F. D'Souza, F. Fernández-Lázaro, *Chem. Eur. J.* **2019**, 25, 10123.
4. N. Zink-Lorre, S. Seetharaman, D. Gutiérrez-Moreno, F. Fernández-Lázaro, P. A. Karr, F. D'Souza, *Chem. Eur. J.* **2021**, 27, 14996.



Linking magnetically induced currents to spectroscopic properties

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Theoretical studies are often applied to complement experiments that aim at synthesizing porphyrinoids with distinct properties. It has been shown, that systematic studies of magnetically induced currents are very useful in this context.[1,2] The computational approach used here is the gauge including magnetically induced current density method (GIMIC).[3,4] Numerical integration of the current flow around molecular rings and along selected chemical bonds can be used for determining current pathways and the degree of aromaticity of various molecules according to the magnetic criterion.[1-4] It has also been found that the integrated current strength susceptibility and optical properties of antiaromatic porphyrinoids are related.[5,6]
A new feature in GIMIC is to calculate numerically the magnetizability of a molecule from the current density.[7] A new methodology for calculating, analyzing, and visualizing nuclear magnetic shielding densities which are calculated from the current density has been developed and made available in GIMIC. Atomic contributions to nuclear magnetic shielding constants can be estimated, using a Becke partitioning scheme.[8] First applications on prototypical aromatic and antiaromatic porphyrinoids showed that the new approach can be used to determine spacial contributions to ^{1}H NMR magnetic shieldings paving the way to a better understanding of the latter.[9] Three dimensional visualizations of the current density as streamlines including 3D animations of the current flow are by now also feasible and very recent work will be highlighted in this context.[10-14]

REFERENCES

1. D. Sundholm, H. Fliegl and R. J. F. Berger, *Wiley Interdisciplinary Reviews (WIREs),* **6**, 639-678 (2016).
2. H. Fliegl, R. R. Valiev, F. Pichierri and D. Sundholm, *Chem. Modell.,* **14**, 1-42, (2018).
3. J. Jusélius, D. Sundholm and J. Gauss, *J. Chem. Phys.,* **121**, 3952-3963 (2004).
4. H. Fliegl, S. Taubert, O. Lehtonen and D. Sundholm, *Phys. Chem. Chem. Phys.,* **13**, 20500-20518 (2011).
5. R. R. Valiev, H. Fliegl and D. Sundholm, *Phys. Chem. Chem. Phys*., **19**, 25979-25988, (2017).
6. R. R. Valiev, H. Fliegl and D. Sundholm, *Chem. Comm.,* **53**, 9866-9869, (2017).
7. S. Lehtola, M. Dimitrova, H. Fliegl and D. Sundholm, *J. Chem. Theory Comput.,* **17**, 1457, (2021).
8. R. K. Jinger, H. Fliegl, R. Bast, M. Dimitrova, S. Lehtola and D. Sundholm, *J. Phs. Chem.A,* **125**, 1778, (2021).
9. H. Fliegl, M. Dimitrova, R. J. F. Berger, D. Sundholm, *Chemistry*, **3**, 1005, (2021).
10. A. Nishiyama, M. Fukuda, S. Mori, K. Furukawa, H. Fliegl, H. Furuta and S. Shimizu, *Angew. Chem. Int. Ed.,* **57**, 9728-9733, (2018).
11. R. R. Valiev, H. Fliegl and D. Sundholm, *Phys. Chem. Chem. Phys.,* **20**, 17705-17713, (2018).
12. H. Omori, S. Hiroto, Y. Takeda, H. Fliegl, S. Minakata and H. Shinokubo, *J. Am. Chem. Soc.,* **141**, 4800-4805, (2019).
13. R. Nozawa, J. Kim, J. Oh, A. Lamping, Y. Wang, S. Shimizu, I. Hisaki, T. Kowalczyk, H. Fliegl, D. Kim, H. Shinokubo, *Nature Comm.,* **10**, 3576, (2019).
14. H. Kawashima, S. Ukai, R. Nozawa, N. Fukui, G. Fitzsimmons, T. Kowalczyk, H. Fliegl and H. Shinokubo, *J. Am. Chem. Soc*., **143**, 10676, (2021).

Radical–Triplet Pair Interactions: New Tools for Mechanistic Photochemistry

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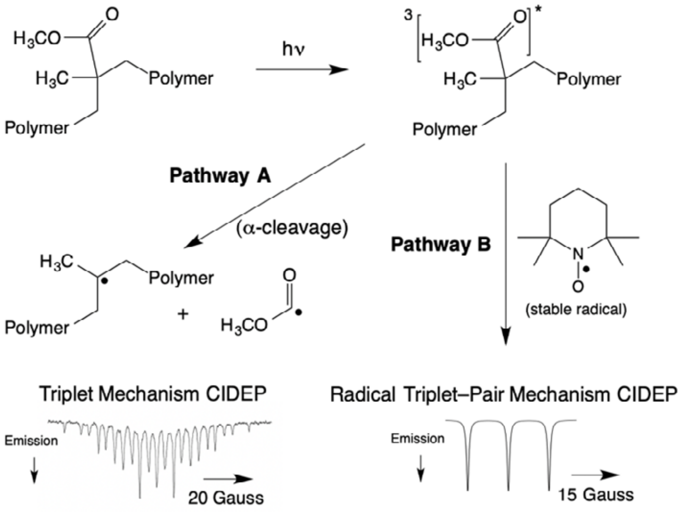
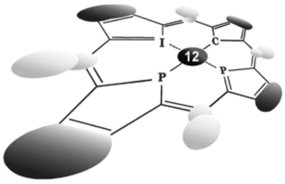
Organic and inorganic photoexcited states often lead to free radicals that have strong chemically induced electron spin polarization (CIDEP), easily detected on the sub-microsecond time scale using time–resolved (CW) electron paramagnetic resonance spectroscopy (TREPR). Of the four known CIDEP mechanisms (radical pair mechanism (RPM), spin–correlated radical pair mechanism (SCRPM), triplet mechanism (TM), and radical–triplet pair mechanism (RTPM), the latter is by far the least understood theoretically but may prove to be the most useful of all of them. Radical-triplet pairs involve electron spin state mixing and sometimes quenching of triplet states by stable doublet state free radicals such as nitroxides. This process can be extended to the study of stable nitroxide biradicals. The RTPM is attractive for investigation of excited state and radical dynamics for reasons: 1) the process is overall non-destructive, i.e., the triplet and the nitroxide eventually return to their electronic ground states with Boltzmann spin state populations, and 2) the resulting spectrum reports spin state information from the unobserved excited triplet state through the nitroxide, the intensity of which can be related to encounters between the two, driven by *translational* motion. Simultaneously, the recorded TREPR spectrum of the nitroxide contains line shape information related to *rotational* motion. The ability to observe and record both types of motion, especially in heterogeneous systems such as micelles, vesicles, bubbles, and emulsions is highly advantageous, particularly when one notes that polarity and order parameters can also be extracted by spectral simulation.

In this talk I will give an overview of all four CIDEP mechanisms and introduce the intricate features of the RTPM, with examples from my laboratory and others to show how structural, dynamic and kinetic information can be obtained in both organic and inorganic systems, specifically metal-coordinated porphyrins. I will use this overview as a platform to suggest new pathways that can exploit the RTPM for the investigation of more complex systems such as dye-sensitized solar cells, structured fluids, and the physiochemical properties of commercially important polymers.





Is Aromaticity Related to Transmission Properties? A Survey on Porphyrinoids

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Porphyrinoids have been fascinating target molecules for potential applications in molecular electronics.[1–3] Although porphyrinoids have been used for fabricating different molecular devices [4–6] a systematic study that defines the relationships between their structural characteristics and their transmission properties has not been performed yet. Some evidence suggests that aromaticity of Porphyrinoids may affect their conductivity,[7] but is it a general trend? Aromatic porphyrinoids often have a larger HOMO-LUMO gap compared to their antiaromatic counterparts. This might justify the abovementioned hypothesis. To examine possible relationship between the aromatic character of porphyrinoids and their transmission properties a diverse set of porphyrinoids which are known to have aromatic and antiaromatic characters were selected. Transmission properties of these systems along with their magnetic aromaticity as defined by the strengths of their induced magnetic currents are assessed within the context of density functional theory (DFT) and DFT-coupled nonequilibrium Green's function (DFT-NEGF). Here we represent our finding to solve this mystery.

REFERENCES

1. M. Jurow, A. E. Schuckman, J. D. Batteas, C. M. Drain, *Coordination Chemistry Reviews* **2010**, *254*, 2297–2310.
2. W. Liu, S. Yang, J. Li, G. Su, J.-C. Ren, *WIREs Computational Molecular Science* **2021**, *11*, e1511.
3. M. Jirásek, H. L. Anderson, M. D. Peeks, *Acc. Chem. Res.* **2021**, *54*, 3241–3251.
4. A. C. Aragonès, A. Martín-Rodríguez, D. Aravena, J. Puigmartí-Luis, D. B. Amabilino, N. Aliaga-Alcalde, A. González-Campo, E. Ruiz, I. Díez-Pérez, *Angewandte Chemie International Edition* **2020**, *59*, 19193–19201.
5. H. M. Sturmeit, I. Cojocariu, A. Windischbacher, P. Puschnig, C. Piamonteze, M. Jugovac, A. Sala, C. Africh, G. Comelli, A. Cossaro, A. Verdini, L. Floreano, M. Stredansky, E. Vesselli, C. Hohner, M. Kettner, J. Libuda, C. M. Schneider, G. Zamborlini, M. Cinchetti, V. Feyer, *Small* **n.d.**, *n/a*, 2104779.
6. X. Yao, M. Vonesch, M. Combes, J. Weiss, X. Sun, J.-C. Lacroix, *Nano Lett.* **2021**, *21*, 6540–6548.
7. S. Fujii, S. Marqués-González, J.-Y. Shin, H. Shinokubo, T. Masuda, T. Nishino, N. P. Arasu, H. Vázquez, M. Kiguchi, *Nat Commun* **2017**, *8*, 15984.

From NIR-responsive porphyrin arch-tapes to non-planar PBI derivatives and a NIR-responsive C_{70}-fragment

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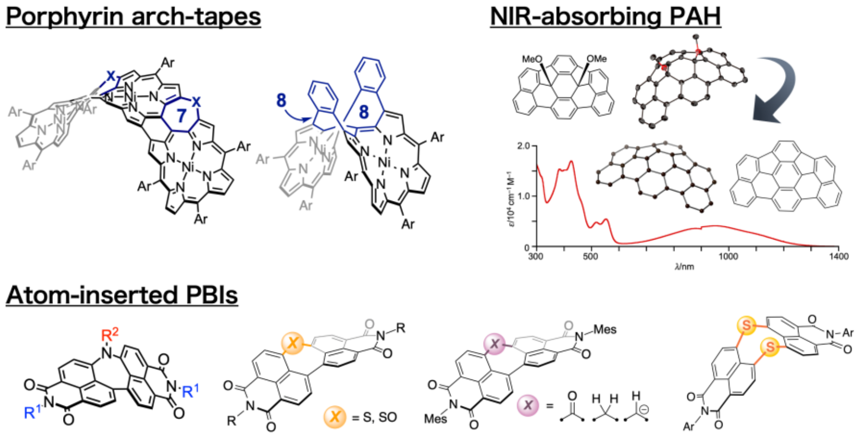
During my Ph. D course in Kyoto University under the supervision of Prof. Osuka, I synthesized non-planar fused porphyrin oligomers, so-called porphyrin arch-tapes.[1] The key to realizing the curvature is the conceptual insertion of atoms between porphyrin units, which distorts the structure. My current project started four years ago based on this experience. In this presentation, I will talk about the details of my current project and how I launched it.

The development of novel π-conjugated molecules is an attractive research topic in modern organic chemistry because this approach leads to various future applications. I believe that the most important to create original molecules is the concept for molecular design. Accordingly, I felt that "insertion of atoms" should be potentially more general, thus affording various unique molecules. With this idea, I designed atom-inserted perylene bisimides (PBIs).[2] These molecules exhibited unique properties due to the non-planar structures and inserted atoms.

I also expanded my molecular design to "inner-modification" and designed internally functionalized bowl-shaped aromatic hydrocarbons.[3] After synthesizing these molecules, I realized that their main skeleton is a new C_{70}-fragment, *as*-indaceno[3,2,1,8,7,6-*ghijklm*]terrylene. The hydrogen-substituted derivative was oxidized, which afforded *as*-indacenoterrylene. Surprisingly, *as*-indacenoterrylene exhibited NIR-absorption tailing to 1300 nm.



REFERENCES

1. (a) *J. Am. Chem. Soc.* **2017**, 139, 9075; (b) *Angew. Chem. Int. Ed.* **2018**, 57, 6304; (c) *Bull. Chem. Soc. Jpn.* **2018**, 91, 1131.
2. (a) *J. Am. Chem. Soc.* **2019**, 141, 19807; (b) *J. Am. Chem. Soc.* **2020**, 142, 11663; (c) *Asian J. Org. Chem.* **2021**, 10, 541; (d) *Angew. Chem. Int. Ed.* **2021**, 60, 15838.
3. *Nat. Commun.* **2020**, 11, 3873.

Modulation of Aromatic Circuits in the Triply Fused N-Confused Porphyrin Dimer System

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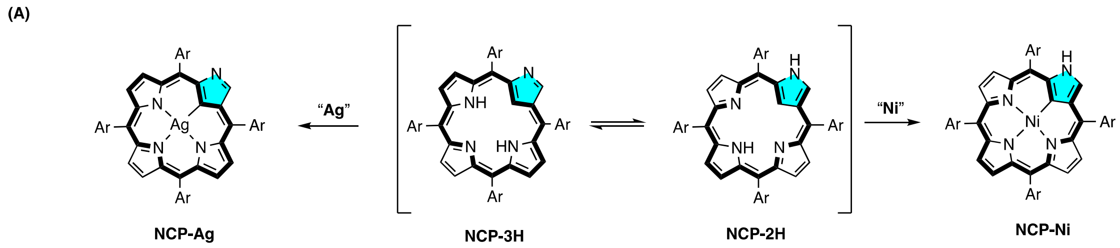
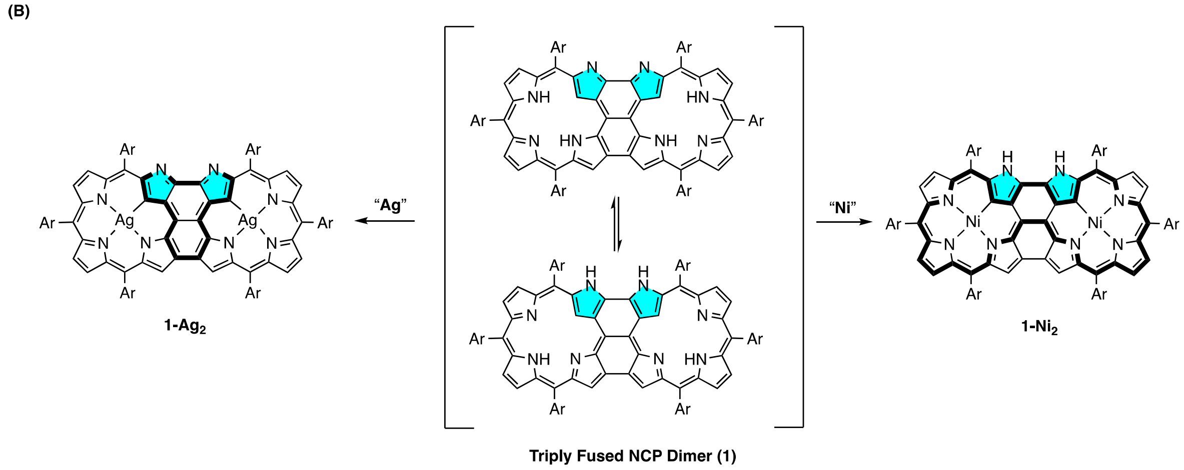
The aromaticity of the planar porphyrinoids is usually controlled by the number of electrons in the π-conjugated circuits and is readily altered by modulating the π-circuits upon oxidation and reduction. In the N-confused porphyrin, however, the π-conjugation pathways can be modulated by NH tautomerism (**NCP-3H** and **NCP-2H**). The circuits can be fixed by metalation (e.g., **NCP-Ag** and **NCP-Ni**). As the α-position of the confused pyrrole ring could serve as a turnout point of the π-conjugation pathways,[1] it is interesting to investigate the aromaticity in the triply fused dimer system.[2] In this presentation, the aromaticity of bismetal complexes of confused porphyrinoid systems, α-α’, *meso-meso*, β-β’ triply linked N-confused porphyrin dimer (**1**) will be discussed.





REFERENCES

1. T. Ishizuka *et al. J. Phys. Chem.* **2020**, *124*, 5756–5769.
2. Tsuda *et al. Angew. Chem. Int. Ed.* **2000**, *39*, 2549–2552.

CO_2 Cycloaddition to Three-membered Rings Mediated by Porphyrin-based Catalysts

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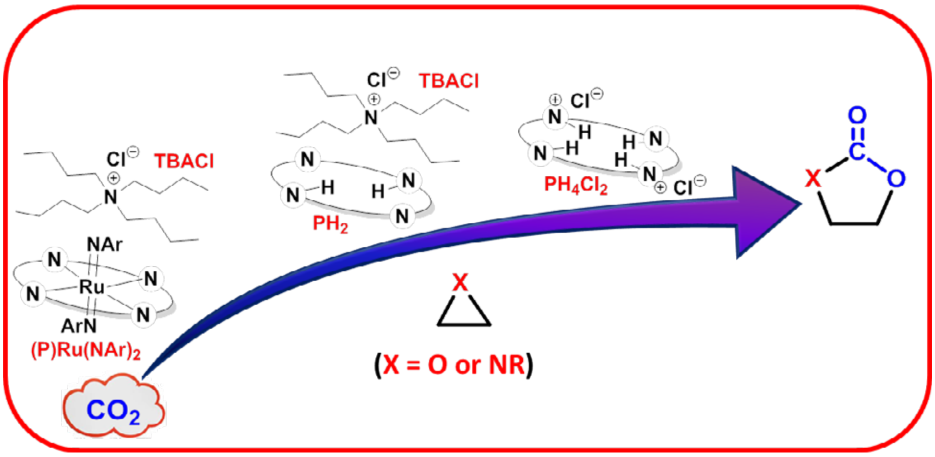
Aziridines, as well as epoxides, can be reacted with CO_2 to synthesize, by cycloaddition reaction, oxazolidinones and cyclic carbonates, respectively. Several catalysts promote these reactions, which permit the formation of high-added value fine chemicals by using a waste such as CO_2 as starting material and applying a 100% atom economic procedure.

Even if both reactions are efficiently promoted by porphyrin-based catalysts [1] and aziridines are structurally analogous to epoxides, the CO_2 insertion into aziridines has been less studied. We are currently investigating the synthesis of oxazolidinones and cyclic carbonates by fine-tuning the nature of the catalyst in order to maximize the eco-compatibility of the employed procedure. It is well known that these reactions occurred thanks to the synergic action of an electrophilic catalyst, usually a metal complex, and nucleophilic co-catalyst such as a salt.

Our recent studies have revealed that the presence of a transition metal into the porphyrin core is not required to afford good catalytic performances ((P)Ru(NAr)$_2$/TBACl) [2] can be replaced by PH_2/TBACl [3]) and also that the addition of a co-catalyst salt can be avoided by using a bifunctional catalyst, which presents the nucleophilic agent as the counterion of the protonated tetrapyrrolic ring (PH_2/TBACl can be replaced by PH_4Cl_2[4]).



DFT calculations have clarified the occurrence of different mechanisms when different porphyrin catalysts were used as promoters.

REFERENCES

1. D. Intrieri, C. Damiano, P. Sonzini, E. Gallo *J. Porphyrins Phthalocyanines* **2019**, 23, 305.
2. a) D. Carminati, E. Gallo, C. Damiano, A. Caselli, D. Intrieri *Eur. J. Inorg. Chem.* **2018**, 5258. b) C. Damiano, P. Sonzini, D. Intrieri, E. Gallo *J. Porphyrins Phthalocyanines* **2020**, *24*, 809.
3. a) P. Sonzini, C. Damiano, D. Intrieri, G. Manca, E. Gallo *Adv. Synth. Catal.* **2020**, *362*, 2961. b) C. Damiano, P. Sonzini, G. Manca, E. Gallo *Eur. J. Org. Chem.* **2021**, 2807.
4. Manuscript in preparation.

Insights into the regulation of light-induced cytotoxicity in photoactive nanomaterials

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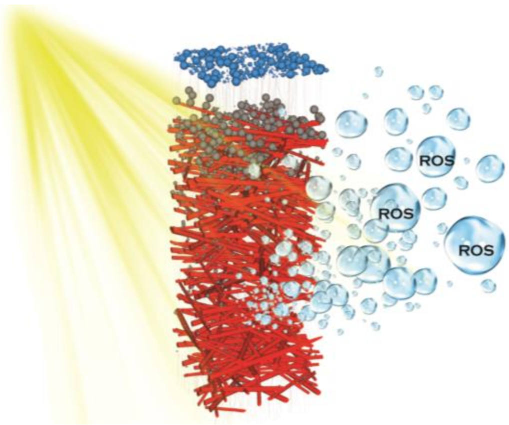
The demand for photofunctional antimicrobial nanomaterials is increasing rapidly in different fields of medicine and biotechnology.[1-3] Though there are many reports showing that such nanoporous surfaces exhibit very strong antibacterial and antiviral effects upon irradiation, major regulators of activity are still largely unverified and the requirements for effective antimicrobial action remain controversial. Design and synthesis of photoactive compounds that could be used as structural components of nanoscale materials as well as structure-activity relationships of fabricated nanomaterials will be presented.[4, 5]



REFERENCES

1. Galstyan, A., Schiller, R. & Dobrindt, U. (2017) Boronic Acid Functionalized Photosensitizers: A Strategy To Target the Surface of Bacteria and Implement Active Agents in Polymer Coatings, Angew Chem Int Ed. 56, 10362-10366.
2. Galstyan, A. (2021) Turning Photons into Drugs: Phthalocyanine-Based Photosensitizers as Efficient Photoantimicrobials, Chem Eur J. 27, 1903-1920.
3. Galstyan, A., Ricker, A., Nüsse, H., Klingauf, J. & Dobrindt, U. (2020) Exploring the Impact of Coordination-Driven Self Assembly on the Antibacterial Activity of Low-Symmetry Phthalocyanines, ACS Applied Bio Materials. 3, 400-411.
4. Strokov, K., Schäfer, A. H., Dobrindt, U. & Galstyan, A. (2020) Facile Fabrication of Silicon(IV)Phthalocyanine-Embedded Poly(vinyl alcohol)-Based Antibacterial and Antifouling Interfaces, ACS Appl Bio Mater. 3, 3751-3760.
5. Galstyan, A., Majiya, H. & Dobrindt, U. (2022) Regulation of photo triggered cytotoxicity in electrospun nanomaterials: role of photosensitizer binding mode and polymer identity, Nanoscale Advances. 4, 200-210.

Self-assembled Photosensitisers for Photodynamic Therapy

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Photodynamic therapy (PDT) has become a clinically promising approach for the treatment of a wide range of cancers and other diseases due to its spatiotemporal selectivity and non-invasive nature. However, the use of traditional molecular PSs has inherent drawbacks that hamper the full development of PDT, as the combination of poor transport, low tumour selectivity and the "always-on" property generally leads to post-treatment risks associated with harmful photosensitisation.

In this context, the use of supramolecular assemblies would allow, with less arduous synthetic effort, to build well-defined dynamic and adaptable structures whose size can be controlled by changing different external parameters like temperature or concentration. Moreover, supramolecular PSs offer the possibility to precisely control not only the internalization, but also the ROS generation via contact- or self-quenching of the PSs.

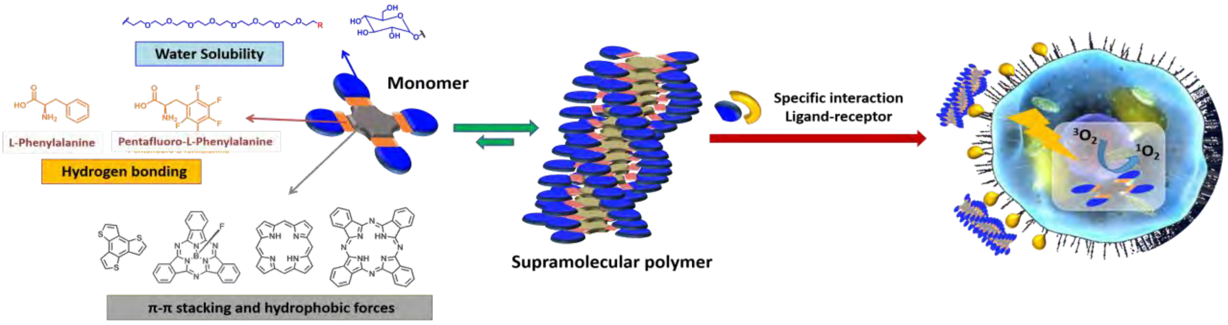

Figure 1. Schematic representation of the monomers, their self-assembly and applications.

The lecture will discuss new strategies on the design, synthesis and self-assembly study of different monomeric photosensitizers in aqueous media and the advantages when employing the resulting supramolecular assemblies in PDT or photothermal therapy. [1, 2]

REFERENCES

1. N. M. Casellas, S. Pujals, D. Bochicchio, G. M. Pavan, T. Torres, L. Albertazzi, M. García-Iglesias, *Chem Commun*, **2018**, *54*, 4112.
2. N. N. M. Casellas, L. Albertazzi, S. Pujals, T. Torres, M. García-Iglesias*, Chem. Eur. J. 2021, 27, 11056.
3. N. M. Casellas, G. Dai, E. Y. Xue, A. Fonseca, D. K. P. Ng, M. García-Iglesias*, T. Torres. *Chem Commun.* **2021**, DOI: 10.1039/D1CC05977G.
4. N. M. Casellas, G. Dai, M. J. Vicente-Arana, D. K. P. Ng, T. Torres, M. García-Iglesias, **2021**, *Submitted*.

Elucidation of Chemical Structure and Evaluation of the Intramolecular Charge-Transfer Properties in Carbazolyl Oxy-Phosphorous Tetrabenzotriazacorrole (Cz-TBC) and its Tertiary Analogue as Multifunctional Materials

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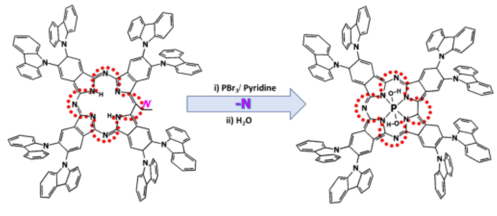
Tetrabenzotriazacorroles (TBCs) are one of the most well-known and successful artificial dyes and pigments in modern materials chemistry. These push-pull effect designed molecules have attracted a great deal of interest in materials sciences due to their unique optical and electronic properties.[1, 2] Moreover, introduction of a phosphorus(V) atom into simple (known) tetrabenzotriazacorrole macrocycles is not necessarily difficult and can generate changes in the structural and optical properties. Here, two new tetrabenzotriazacorroles (TBCs) with phosphorus(V) metal centers substituted with either carbazole units or *t*-butyl groups are presented that demonstrate the potential of tuning the acceptor unit to enhance the photophysical properties. Optical properties are discussed based on a combination of experimental absorption spectra, electrochemical properties, and theoretical molecular orbital calculations. These complexes are relatively easy to synthesize from their metal-free analogues. Chemical modification of metal-free carbazolyl-phthalocyanine derivatives tunes the emission behavior from triplet states by changing the geometry of the intramolecular charge transfer (ICT) state. The novel carbazolyl TBC (Cz-TBC) demonstrated both room temperature phosphorescence (RTP) and T-T annihilation. Time resolved spectroscopy and time-dependent density functional theory (TDDFT) were utilized to investigate both structures and to demonstrate the roles of ICT states in the underlying photophysics.

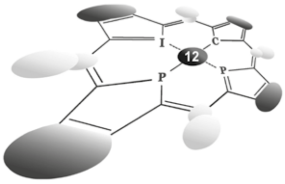


Octa-carbazolyl metal free Phthalocyanine (Pc)
18-π electrons

Octa-carbazolyl Tetrabenzotriazacorrole (TBC)
18-π electrons

REFERENCES

1. Ghazal B, Azizi K, Ewies EF, Youssef ASA, Mwalukuku VM, Demadrille R, et al. Push-Pull Zinc Phthalocyanine Bearing Hexa-Tertiary Substituted Carbazolyl Donor Groups for Dye-Sensitized Solar Cells. Molecules. 2020; 25 (7).
2. Majeed SA, Ghazal B, Nevonen DE, Goff PC, Blank DA, Nemykin VN, et al. Evaluation of the Intramolecular Charge-Transfer Properties in Solvatochromic and Electrochromic Zinc Octa(carbazolyl)phthalocyanines. Inorganic Chemistry. 2017; 56 (19):11640-53.



Antimicrobial Strategies for Infection Prevention: Photodynamic and Photothermal Materials

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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 two approaches for pathogen reduction: antimicrobial photodynamic inactivation (aPDI) and antimicrobial photothermal inactivation (aPTI). *In vitro* aPDI studies were performed against bacteria and viruses employing photosensitizer-embedded or conjugated nanofibrillated cellulose, polyacrylonitrile or nylon nanofibers, dual-dyed wool/acrylic 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. As an alternative strategy, we have embedded the photothermal photosensitizer molybdenum disulfide (MoS_2) into bacterial cellulose (BC) by a facile *in situ* growth followed by a dip-coating process to add a chitosan layer (BC/MoS_2-CS) [5]. When compared with the BC/MoS_2 membrane, which itself showed a 95% reduction of *S. aureus* and 99.9% inactivation of *E. coli*, the addition of chitosan led to a synergistic effect, improving inactivation to 99.998% against *S. aureus* and 99.988% versus *E. coli*. More recently, we have developed dual-coated fabrics employing photosensitizer-luminous powder using silk-screen printing, and demonstrated that this strategy is able to 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.

REFERENCES

1. Alvarado et al. *Green Chemistry* **2019**, *21*, 3424-3435.
2. Peddinti et al. *ACS Appl. Mater. Interfaces* **2018**, *10*, 25955-25959.
3. Ghareeb et al. *Front. Med.* **2021**, *8*, 657837.
4. Peddinti et al. *ACS Appl. Mater. Interfaces* **2021**, *13*, 155-163.
5. Shen et al. *ACS Appl. Mater. Interfaces* **2021**, *13*, 31193–31205.

Thiol-fluoride aromatic substitution: a straightforward entry to new self-assembling peptide-porphyrin conjugates

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[c]*School of Chemistry, University of Edinburgh, Edinburgh, UK*

The ability of tetrapyrroles-peptide conjugates to self-assemble into medium- and long-range ordered supramolecular architectures captivated the interest of scientists worldwide over the last couple of decades. These species provide relatively accessible building blocks to produce environment- and stimuli-responsive materials that display the photochemical/photophysical features of tetrapyrroles. Efforts devoted to this field resulted into a vast and diverse library of conjugates that demonstrated potential for applications in catalysis, light-harvesting and solar cells, sensing, and photodynamic/photoacoustic therapies [1,2].

Several ligation strategies have been used to obtain conjugates of tetrapyrroles to self-assembling peptides [3], including the formation of amides, esters, thioethers, triazine-based conjugations, or the formation of complexes by coordination to the metal ion present in the tetrapyrrole [1].

One approach that received little attention is the nucleophilic displacement of aromatic fluorides by thiols. While this strategy has been a key transformation to decorate perfluoroaryl-substituted tetrapyrroles such as 5,10,15,20-*meso*-tetrakis-pentafluorphenylporphyrin with a variety of substituent (e.g., sugars, heterocycles, etc.) [4], it remains largely under-explored for the conjugation of peptides to porphyrins. Thiols on the side chain of cysteine residues smoothly displace fluorides on perfluorinated arenes [5,6]. The reaction occurs in mild conditions and it targets a relatively low-abundance amino acid, two key features that make it particularly attractive for conjugation of deprotected peptides in solution.

Here we will revisit this approach with a focus on its potential for conjugation of porphyrins to peptides including self-assembling sequences such as bolaamphiphiles [7] and peptide amphiphiles [8].

REFERENCES

1. P. Dognini, C.R. Coxon, W.A. Alves, F. Giuntini, Molecules, 2021, 26, 693
2. Q. Zou, K. Liu, M. Abbas, X. Yan, Adv. Mater., 2016, 1031
3. M. Zelzer, R. V. Ulijn, Chem. Soc. Rev., 2010, 39, 3351
4. I.T.J. Costa, A.C. Tomé, M.G.P.M.S. Neves, J.A.S. Cavaleiro, J. Porphyrins Phthalocyanines, 2011, 15, 1116
5. P. Dognini, P. M. Killoran, S. G. Hanson, L. Halsall, T. Chaudhry, Z. Islam, F. Giuntini, C. R. Coxon, Peptide Science, 2021, 113:e24182
6. W. D. G., Brittain, C. R. Coxon, Chem. Eur. J., 2022, https://doi.org/10.1002/chem.202103305
7. F. Qiu, Y. Chen, C. Tang, Q. Zhou, C. Wang, Y.K. Shi, X. Zhao, Macromol. Biosci., 2008, 8, 1053
8. A. Dehsorkhi, V. Castelletto, I.W. Hamley, J. Pep. Sci., 2014, 20, 453

Iron(III) Superoxide Corrole: Generation, Characterization, and Reactivity with Indole and HAT Substrates

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The activation of dioxygen by heme and related synthetic porphyrinoid complexes is at the heart of numerous catalytic, oxidative processes. The initial step necessarily involves the binding of O_2 to the metal center, forming an activated metal-superoxide species. This talk will focus on our recent results involving the generation of an iron(III) superoxide corrole complex from the reaction of an Fe^{II} precursor and O_2, and the reactivity of this species toward biologically relevant substrates.[1-2] The $Fe^{III}(O_2^{-\bullet})$(corrole) was prepared by using a highly sterically encumbered corrole ligand, combined with low-temperature reaction methods. The new superoxide complex was characterized by UV-vis, ^{1}H NMR, resonance Raman, and Mössbauer spectroscopies. The vibrational data indicated that it is an η^1-superoxo (end-on) iron(III) complex. This species reacts with an indole to give a dioxygenated product as seen in tryptophan and indoleamine dioxygenases, and is also reactive toward H-atom abstraction from a weak O-H bond substrate. These reactions will be discussed regarding their likely mechanisms and implications for the analogous biological dioxygenation and PCET reactivity.

REFERENCES

1. Sacramento, J. J. D.; Goldberg, D. P. *Chem. Commun.* **2020,** *56*, 3089 – 3092.
2. Sacramento, J. J. D.; Albert, T.; Siegler, M.; Moënne-Loccoz, P.; Goldberg, D. P. *Angew. Chem. Int. Ed.,* **2022,** *61,* e202111492.

Host-Guest Chemistry within Novel Porphyrin Nanocages

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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, 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.

REFERENCES

1. IPCC *Climate Change 2013: The Physical Science Basis,* eds Stocker, T. F. *et al.* (Cambridge Univ. Press, 2013).
2. K. M. Kadish *et al. The Porphyrin Handbook*; Academic Press: San Diego, **2000**.
3. A. de Juan, D. González-Rodriguez, M. Garcia-Iglesias, *in preparation*.

Smart materials based on sandwich lanthanide complexes with crown-phthalocyanines

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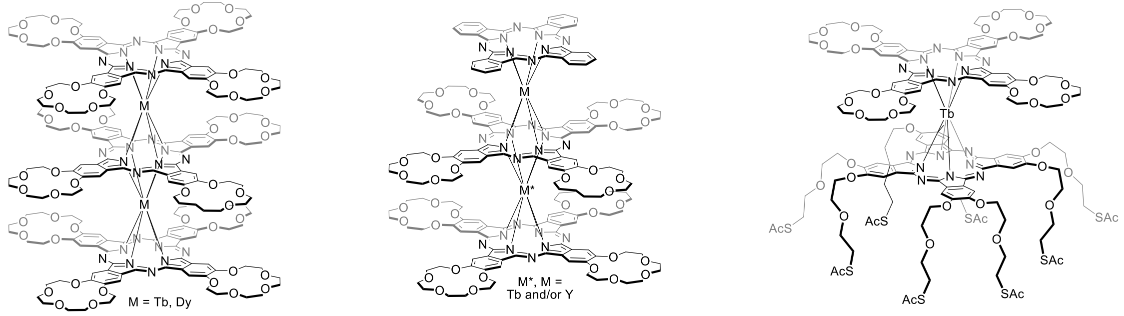
Sandwich lanthanide phthalocyaninates are particularly sensitive to various external physico-chemical stimuli, providing a wide range of responses, including changes in optical and magnetic properties as well as possible changes in the conformational state of stacked ligands. These features make these complexes promising molecular switches and molecular machines [1], and the combination of sandwich scaffolds with chelating crown ether moieties allows to further expand the applications of such smart materials (Figure). Different types of such materials were developed recently in our group and received results will be discussed in the report.

Thus, the introduction of crown ethers into homoleptic Tb(III) and Dy(III) trisphthalocyanates allows their solubilisation in aqueous medium and application as NMR thermosensors in physiological temperature range (303-323 K) due to high temperature sensitivity of lanthanide induced shifts, achieving values of $\Delta\delta/\Delta T$ up to 1.1 and 0.55 ppm/K respectively [2]. Heteroleptic trisphthalocyaninates bearing two adjacent crown-substituted ligands act as receptors which can bind potassium cations. This process results in switching of the coordination polyhedron of the corresponding lanthanide metal centre from square-antiprismatic to square-prismatic. In turn it results in spectacular increase in the axial component of the magnetic susceptibility tensor providing new tool of supramolecular control of magnetic properties of lanthanide complexes [3].

Octopus-like Tb(III) bisphthalocyaninate bearing eight thioacetate-terminated tentacles in one ligand and crown-ether rings in another ligand can form self-assembled monolayers on gold surface. Face-on orientation allows for subsequent binding of crown-phthalocyanine molecules via potassium ion bridges, providing a heterogeneous bilayer with expanded redox-behaviour, where distinct redox-states can be read out using optical density measurements [4]. The proposed approach can be used in wide range of switchable materials, including single-molecule magnets, conductive, and optical devices, etc.



Acknowledgement. This work was supported by Russian Science Foundation (grant 20-63-46026).

REFERENCES

1. Martynov A.G. et al., *Coord. Chem. Rev.* **2019**, *387*, 325–347.
2. Babailov S.P. et al., *Sensors Actuators, A Phys.* **2021**, *331*, 112933.
3. Martynov A.G. et al., *Inorg. Chem.* **2021**, *60*, 9110–9121.
4. Shokurov A.V. et al., *Small* **2022**, *18*, 2104306.

Fluorinated Phthalocyanines with Different Degrees of Perfluoroalkylation and Functional Groups: Synthesis, X-ray Structures, Applications

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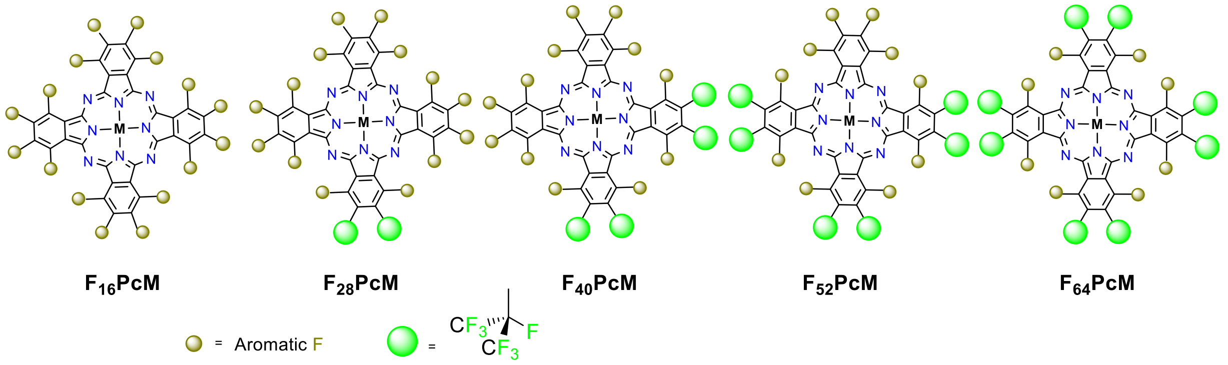
Perfluoroalkyl phthalocyanines, R_fPcM, M = Metal, exhibit high thermal resistance, solubility in organic solvents, single–site behavior and resistance to electrophilic, nucleophilic and radical attacks. The $F_{28}PcM$, $F_{40}PcM$, $F_{52}PcM$, and $F_{64}PcM$ complexes constitute the 1st generation of functional materials, augmented by the introduction of additional functional groups at phthalocyanines molecular periphery, for example $–NR_nR'_m$ groups, R, R' = H, CH_3, n, m $\geq$ 0; n + m = 2. The amino functional groups, which replace a single F, quench energy transfer processes, but their further derivatization, aimed at imparting exocyclic N-lone pair conjugation, restores it. New classes of homo- and heterogeneous electron and energy transfer catalysts are possible.



Interface Chemistry of Expanded and Contracted Oligopyrroles: On-Surface Synthesis and Electronic Properties

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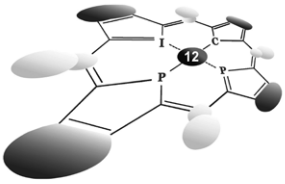
Oligopyrroles and their metal complexes are versatile compounds for surface and interface functionalization. While their monolayers and thin films can often be prepared by physical vapor deposition under vacuum conditions, this approach is limited to chemically and thermally stable molecules. A very flexible alternative is on-surface synthesis, which provides access to species that are too fragile for evaporation or that cannot be made by solution-based synthesis at all. In this contribution, I present latest results obtained using the following strategies for the on-surface synthesis of oligopyrroles: (1) On-surface metalation of pre-deposited free-base porphyrin, phthalocyanine, or corrole ligands. With this approach, monolayers and thin films of metal complexes can be prepared, including over- and understoichiometric alkali metal complexes. (2) Phthalocyanines, naphthalocyanines and their expanded homologs can be prepared by template-directed on-surface synthesis from suitable dinitrile-based precursors. This also includes novel phthalocyanine-based complexes with non-benzenoid and non-alternant topology. (3) On-surface synthesis also gives access to linear open-chain counterparts of phthalocyanines, which represent a novel class of non-cyclic oligopyrroles. Structure, electronic properties and reactivities of the oligopyrrole monolayers and thin films will be discussed on the basis of experimental and theoretical results.



Electronic Relaxation Data and the Importance of Excited State Mixing in Determining the Properties of Compound I

Michael Green[a]

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Recently, a selenolate-ligated P450 compound I (SeP450-I) intermediate was shown to be more reactive towards C-H bonds than its thiolate-ligated counterpart. To gain insight into how the selenolate axial ligand influences the reactivity of compound I, we have investigated the electronic structure of the SeP450-I intermediate using variable temperature Mossbauer (VTM) spectroscopy. Analysis of the VTM data indicate that electronic spin relaxation rates are significantly slower in SeP450-I than in P450-I. Efforts to analyze these and other data in terms of a standard ligand field model indicate that excited state mixing within the ferryl moiety plays an important role in determining electronic properties of compound I species. For SeP450-I, P450-I, and chloroperoxidase compound I, we find that electronic relaxation times correlate with the magnitude of the exchange coupling and track with reactivity towards C-H bonds.

Corroles as precursors of POPs and MIPS Application to the detection of CO and the decontamination of chemical nerve agents

Stéphane Brandès[a], Jian Yang[a], Camille Monot[a], Dimitri Sabat[a], Sandrine Pacquelet[a], Nicolas Desbois[a], Laurie André[a], François Estour[b], Rachid Baati[c] and Claude P. Gros[a]

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Detection of carbon monoxide (CO) at few ppm levels is a critical point for quality control of domestic and industrial environment. CO is responsible for thousands of intoxications and hundreds of deaths *per* year in the world. Moreover, CO is a residual gas found in the industrial dihydrogen used for Proton Exchange Membrane fuel cell, and deactivates the fuel cell prematurely. Corroles have been largely used in sensing applications.[1] Cobalt corroles display high binding affinity for carbon monoxide even in the presence of nitrogen and dioxygen.[2] The affinity of the Co(III) metallocorroles for CO is directly correlated with the Lewis acid character of the metal center. Therefore, structural modifications on the aromatic ring have a direct influence on the reactivity of the metal complex. We have recently obtained very low CO detection level (ppm) using SAW devices functionalized by cobalt corrole deposited as a film on a silica or a gold surface.[3] Our previous work on the synthesis of porous sol-gel materials functionalized by cobalt corroles gave us encouraging results for CO sorption and detection and prompted us to prepare new porous structured materials functionalized by corrole complexes for gas detection applications. Among all the methods of synthesis of porous architectures, organic materials belonging to the POP (Porous Organic Polymer) family are an appealing and original approach in this research field.[4] The synthesis of new POPs functionalized by cobalt corroles (Fig. 1) will be reported. Their selective sorption properties for CO over N_2, O_2 and CO_2 will be also presented.

Preliminary results concerning the design of Molecularly Imprinted Polymers (MIPs) as enzyme mimics for the decontamination of a broad spectrum of pesticides and chemical warfare agents will be also reported.

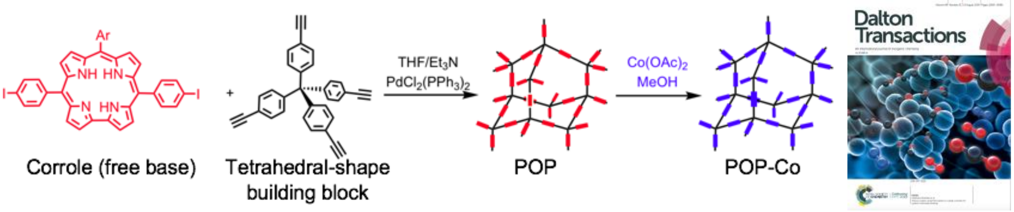

Fig. 1. Synthesis of a POP based on corrole macrocycles

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REFERENCES

1. Di Natale, C.; Gros, C. P.; Paolesse, R., *Chem. Soc. Rev.* **2022**, 000; [2] J.-M. Barbe, G. Canard, S. Brandès, F. Jerôme, G. Dubois, R. Guilard, *Dalton Trans.* **2004**, 1208-1214; [3] Vanotti, M.; Poisson, S.; Soumann, V.; Quesneau, V.; Brandes, S.; Desbois, N.; Yang, J.; Andre, L.; Gros, C. P.; Blondeau-Patissier, V., *Sensors and Actuators B: Chemical* **2021**, (332), 129507. [4] S. Brandès, V. Quesneau, O. Fonquernie, N. Desbois, V. Blondeau-Patissier, C. P. Gros, *Dalton Trans.* **2019**, *48*, 11651-11662 (Front Cover).

Corrole Metal Complexes as Catalysts for Clean Energy Processes

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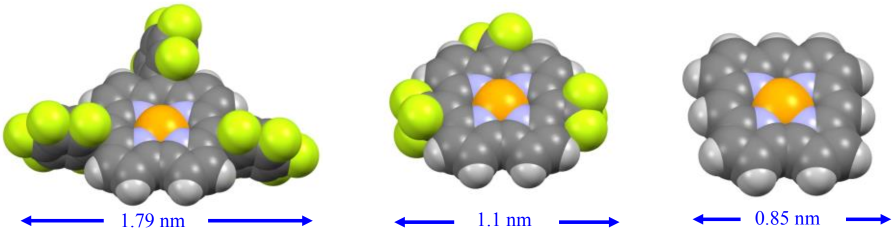
The future of our planet critically depends on the introduction of new or improved strategies for developing non-polluting energy production. Leading approaches are the production of hydrogen gas, development of fuel cells relying on efficient reduction of oxygen and either gaseous or liquid fuels, as well as efficient reduction of carbon dioxide. N4-chelated metal complexes excel in many of these catalytic processes, performed at both homogeneous and heterogeneous conditions. Our contributions to those aspect focused on introducing metallocorroles as catalysts for reduction of protons, oxygen and carbon dioxide, as well as for water oxidation [1-5]. The common motif in these and other publications was to take advantage of the relatively easy functionalization of the macrocyclic periphery for the tuning of properties and reactivity. A significant game changer was most recently disclosed, by reporting synthetic access to corroles with three or two meso-CF_3 substituents and even to the parent corrole with no substituents whatsoever [6]. These developments allow for a focus on the size effect, which according to both hypothesis and fast accumulating results has a very strong effect ("smaller is better") on the performance of electrodes modified by the corresponding metal complexes.



REFERENCES

1. W. Sinha, A. Mizrahi, A. Mahammed, B. Tumanskii and Z. Gross "Reactive Intermediates Involved in Cobalt Corrole Catalyzed Water Oxidation (and Oxygen Reduction)", *Inorg Chem.* **2018**, 57, 478-485.
2. W. Sinha, N. Fridman, Y. Diskin-Posner, L. J. W. Shimon and Z. Gross "Superstructured Metallocorroles for Electrochemical CO_2 Reduction", *Chem. Commun.* **2019**, *55*, 11912-11915.
3. W. Sinha, A. Mahammed, N. Fridman and Z. Gross "Water Oxidation Catalysis by Mono- and Binuclear Iron Corroles" *ACS Catal.* **2020**, *10*, 3764-3772.
4. K. Sudhakar, A. Mahammed, Q.-C. Chen, N. Fridman, B. Tumanskii and Z. Gross "Copper Complexes of CF_3-Substituted Corroles for Affecting Redox Potentials and Electrocatalysis" *ACS Appl. Energy Mater.* **2020**, *3*, 2828-2836.
5. P. Yadav, I. Nigel-Etinger, A. Kumar, A. Mizrahi, A. Mahammed, N. Fridman, S. Lipstman, I. Goldberg, and Z. Gross "Hydrogen Evolution Catalysis, by Terminal Molybdenum-Oxo Complexes", *Iscience* **2021**, *24*, 102924.
6. A. Kumar, P. Yadav, M. Majdoub, I. Saltsman, N. Fridman, S. Kumar, A. Kumar, A. Mahammed and Z. Gross "Corroles: The Hitherto Elusive Parent Macrocycle and its Metal Complexes" *Angew. Chem.* **2021**, *60*, 25097-25103.

Coordination-induced spin state switching of a new complex on surfaces

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Switching the spin of metal-organic complexes on surfaces is attractive for its potential applications in, *e.g.*, molecular spintronics. Intrinsic molecular switches such as spin-crossover complexes so far suffer from fragmentation or loss of functionality upon adsorption on metal surfaces [1] with rare exceptions [2]. Robust metal-organic platforms such as phthalocyanine- or porphyrin-based complexes, on the other hand, rely on external axial ligands to induce spin switching [3]. Yet, adding and removing axial ligands require particular conditions, which tend to affect the selectivity and reversibility of the switching process.
In the present study, we have designed and investigated robust Ni complexes, which can intrinsically switch their coordination state. The switching is based on a mechanical movement of an axial pyridine ligand strapped to a porphyrin. Using x-ray absorption spectroscopy and x-ray diffraction spectroscopy we evidence that the spin and coordination switching are interlocked. Furthermore, employing low-temperature scanning tunnelling microscopy, we show switching of individual Ni complexes in direct contact to a Ag(111) surface. The stability of the two spin and coordination states of the molecules exceeds days at 4 K [4].

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REFERENCES

1. Knaak et al., *J. Phys. Chem. C* 123, 4378 (**2019**).
2. Bairagi et al., *Nat. Commun. 7*, 12212 (**2016**).
3. Wäckerlin et al., *Nat. Commun. 1*, 61344 (**2010**).
4. Köbke et al., *Nat. Nanotechnol. 15*, 18 (**2020**).

Ups and downs in the synthesis of corroles

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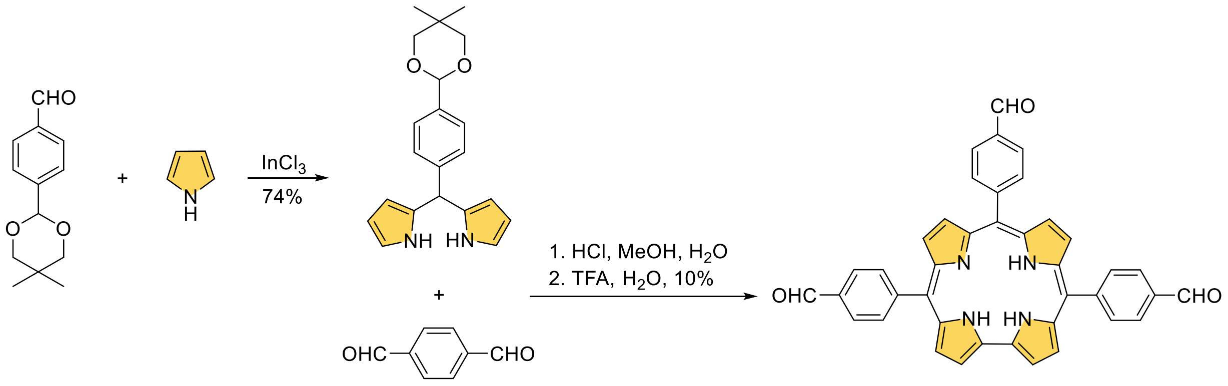
In 1998, it would have been impossible to imagine that only 20 years later the chemistry of one of corroles would expand to create an independent field of study. The synthesis of corroles has undergone incredible changes. From multistep strategies that attracted only practitioners in the field, the procedure has been transformed into a one-pot process from commercially available reagents. The synthesis of *meso*-substituted corroles evolved quickly during the first seven years after Paolesse's and Gross's discovery [1,2]. The methodology which led to *trans*-A_2B-corroles (i.e., corroles bearing substituents A at positions 5 and 15 and substituent B at position 10) from dipyrranes and aldehydes was discovered in 2000 and optimized several times prior to 2006, when we discovered that as long as aldehydes and dipyrranes were relatively small and/or hydrophilic, performing this reaction in a mixture of water and methanol in the presence of HCl allowed the yields to increase from 6-30% to ~55% [3,4]. 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 in the preparation of corroles.

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. We also developed the synthesis of several other corroles possessing reactive functional groups.



REFERENCES

1. Gross, Z.; Galili, N.; Saltsman, I. *Angew. Chem. Int. Ed.* **1999**, *38*, 1427−1429.
2. Paolesse, R.; Jaquinod, L.; Nurco, D. J.; Mini, S.; Sagone, F.; Boschi, T.; Smith, K. M. *Chem. Commun.* **1999**, 1307−1308.
3. Koszarna, B.; Gryko, D. T. *J. Org. Chem.* **2006**, *71*, 3707−3717.
4. Orłowski, R.; Gryko, D.; Gryko, D. T. *Chem. Rev.* **2017**, *117*, 3102-3137.

The polarity reversal strategy based on vitamin B_{12}

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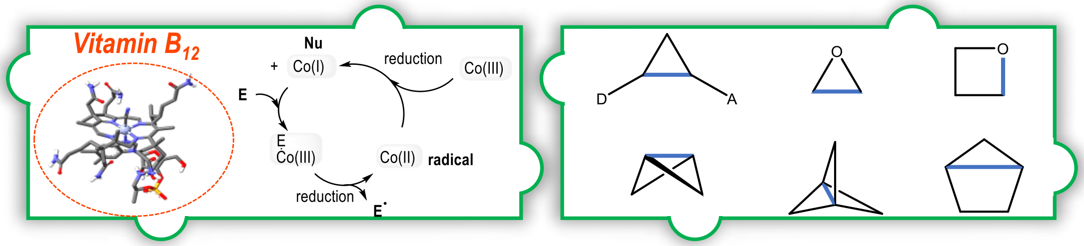
Vitamin B_{12} - a cofactor of many enzymes vital for our life.[1, 2] It is a natural Co-complex and as such has been successfully translated into the field of catalysis. It was shown to promote a collection of various organic reactions.[2, 3] The advantage of using vitamin B_{12} as a catalyst lays in the complete stability of the central cobalt ion and by the definition it is nontoxicity. It has also been well documented that the reaction mechanism usually follows a radical pathway, bringing a new dimension to this already interesting field.



On the other hand, strain-release driven transformations give access to attractive bioisosteric motifs highly prized by medicinal chemists, and they are characteristic to molecules possessing distorted bonds lengths and angles.[4] Their reactivity stemms mainly from an increased energy and destabilization as a result the opening of the strained bond can occur under the action of both nucleophiles, and electrophiles as well as radical species and transition metals. Though the strained bond dominates their reactivity, it is also influenced by the substitution pattern.

The presentation will highlight a successful application of vitamin B_{12} and is derivatives in strain-release functionalizations. The polarity reversal strategy enables regioselective transformations of strained molecules (BCB,[5] epoxides,[6] D-A-cyclopropanes,[7] and oxetanes[8]) into complex building blocks. These processes involve generation of alkylcobalamins via ring-opening of cyclic molecules and subsequent reactions with SOMOphiles and electrophiles. Mechanistic aspects of these transformations will be discussed.

REFERENCES

1. Banerjee, R. Chemistry and Biochemistry of B_{12}, John Wiley & Sons, Inc, 1999
2. K. ó Proinsias, M. Giedyk, D. Gryko, *Chem. Soc. Rev.* **2013**, *42*, 6605-6619.
3. Giedyk, M., Goliszewska, K., Gryko, D. *Chem. Soc. Rev.* **2015**, *44*, 3391-3404.
4. Turkowska, J.; Durka, K.; Gryko, D. *Chem. Commun.* **2020**, *56*, 5718-5734
5. M. Ociepa, A. J. Wierzba, J. Turkowska, D. Gryko, *J. Am. Chem. Soc.* **2020**, *142*, 5355.
6. Potrząsaj, A.; Musiejuk, M.; Chaładaj, W.; Giedyk, M; Gryko, D *J. Am. Chem. Soc.* **2021**, *143*, 9368–9376.
7. Turkowska, J.; Durka, J.; Ociepa, M.; Gryko, D. *Chem. Commun.*, **2021**, DOI https://doi.org/10.1039/D1CC05330B
8. Potrząsaj, A.; Ociepa, M.; Chaładaj, W.; Gryko, D. submitted.

Dynamics and mechanisms of ligand binding to cytochrome P450 3A4

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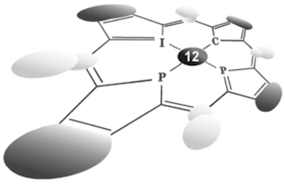
Cytochrome P450 3A4 (CYP3A4) is the dominant P450 enzyme involved in human drug metabolism, and its inhibition may result in adverse interactions or favorably reduce the systemic elimination of poorly bioavailable drugs. I will summarize our recent work aimed at understanding the fundamental aspects of ligand binding and protein dynamics in CYP3A4 in a native-like membrane environment using nanoscale lipid bilayers, or nanodiscs. First, this talk will describe our application of stopped-flow UV-visible spectroscopy coupled to numerical analyses of the kinetic data to delineate fundamental features of the binding mechanism, specifically addressing whether conformational selection or induced fit mechanisms are dominant. Second, our successes applying hydrogen-deuterium exchange mass spectrometry to CYP3A4 nanodiscs will be described. These studies demonstrate that diverse ligands induce distinct changes in CYP3A4 protein dynamics. Finally, we complement these studies with atomistic molecular dynamics simulations of membrane embedded CYP3A4. The observed differences protein-ligand interactions and protein fluctuations provide a structural basis for our interpretation of hydrogen-deuterium exchange experiments and provide novel insight into the functional dynamics of this important enzyme.



Connecting Molecular Electronic Structure and Electron Spin Relaxation for Quantum Information Science

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Quantum devices based on molecules afford unique potential in miniaturization, spatial localization, and tunability through the methods of synthetic chemistry. Unpaired electrons on a molecule constitute a platform for implementing a quantum bit (qubit), the smallest unit of quantum information. However, the utility of such molecular electron spin qubits is intrinsically limited by spin relaxation, which destroys the quantum coherences needed to process information and constitutes the barrier to attaining room temperature quantum devices. While spin relaxation times have been rationalized on the basis of the Debye model, the assumptions behind this model are incompatible with the structure of molecular materials and fail to yield meaningful predictions for slowly-relaxing, highly coherent molecules. This talk will describe our ligand field electron spin dynamics research, which has provided a molecular paradigm to quantitatively evaluate and understand temperature dependent electron spin relaxation. These analyses elucidate the specific vibrational modes that give rise to decoherence in the T_1-limited regime and the critical spin-phonon coupling, chemical bonding, and symmetry factors that engender sustainable molecular coherence at high temperature.

Dissection of Light-Induced Charge Accumulation at a Highly Active Iron-Porphyrin for CO_2 Catalytic Reduction

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Coupling light-triggered single-electron transfer events to multielectron catalysis is one of the most remarkable lessons we can learn from the functioning of the natural photosynthetic apparatus.[1] In the actual context of finding ways to use solar energy to convert H_2O and CO_2 to a renewable energetic vector, chemists want to replicate such photo-driven processes in bioinspired synthetic models to understand and optimize the photocatalytic pattern.[2] To reach this goal, the specific identification and tracking of both short- and long-lived transient species formed by photoinitiated electron transfer are fundamental to determine the mechanistic routes by which charge shifts, charge accumulation, and catalytic events proceed within the photocatalysis context. Although much more complex, these studies are essential to provide the whole panorama of the critical steps in the photocatalytic cycle.

In this context, we pursue an investigation on the light-driven CO_2 to CO conversion featuring a bioinspired iron-porphyrin catalyst bearing urea functions in the second coordination sphere as multipoint hydrogen-bond pillars. The motivation behind the choice of such a catalytic module, was guided by our electrocatalytic study,[3-4] where we have demonstrated that hydrogen-bond interactions induced by these urea groups are involved in different steps of the reaction mechanism such as CO_2 capture and proton transfer leading to a significant enhancement of catalysis. A significant photocatalytic activity is also observed when the catalyst is incorporated in a photocatalytic system comprising a photosensitiser and a sacrificial electron donner. The optimisation of the catalytic system based on the spectroscopic investigation of the different photo-reduced Fe^{II}, Fe^{I} and Fe^{0} states and the identification of the key steps of the reaction mechanism leads to an exceptional photocatalytic performance.

REFERENCES

1. Dau, I. Zaharieva, *Acc. Chem. Res*. **2009**, *42*, 1861-1870.
2. V. Balzani, A. Credi, M. Venturi, *ChemSusChem* **2008**, *1*, 26-58.
3. P. Gotico, B. Boitrel, R. Guillot, M. Sircoglou, A. Quaranta, Z. Halime, W. Leibl, A. Aukauloo, *Angew. Chem. Int. Ed.* **2019**, *58*, 4504-4509.
4. P. Gotico, L. Roupnel, R. Guillot, M. Sircoglou, W. Leibl, Z. Halime, A. Aukauloo, *Angew. Chem. Int. Ed. Engl.* **2020**, *59*, 22451-22455.

The importance of porphyrins in nanoconstructs for enabling therapeutics

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There is an increasing understanding of disease mechanisms and their regulation. Simultaneously there is an increasing recognition that disabling single pathways, when they are believed to be the dominating pathway or targets, will not provide effective long-term cures for disease. Inhibition of a given pathway leads the cancer cell or the pathogen to commandeer compensatory mechanisms for its survival. A combination of therapeutics addressing multiple mechanisms has therefore emerged as a desirable mode of disease management, but in that case pharmacokinetics and dosing now become complex and crucial. While the concept of combination treatment is by no means new, there are some newer emerging approaches to administering combination therapeutics that are exciting. These include the use of nanotechnology and light as a switch, which can provide cytotoxicity while at the same time priming the microenvironment and helping deliver molecules at the right time to the right place. Results from the literature and our own studies in the context of the potential of PDT-inspired combination therapeutics and nanotechnology will be presented.

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Catalysis in Myoglobins Reconstituted with Artificial Metalloporphyrinoids

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Many heme-dependent enzymes have heme *b*, protoporphyrin IX iron complex, as a metal cofactor via non-covalent and coordination interactions. Myoglobin, an oxygen-storage protein, also has the same cofactor, and apomyoglobin is available after removal of the native cofactor under acidic conditions. Over two decades, our group has attempted to convert myoglobin to an artificial enzyme by replacing native heme with an artificial metalloporphyrinod [1-2]. In a series of our works, porphycene, a constitutional isomer of porphyrin is found to be one of the attractive metal ligands. Here, we report the catalytic properties of myoglobins reconstituted with iron porphycene (FePc) and manganese porphycene (MnPc), where two propionate side chains are attached to the porphycene framework.

It is well-known that myoglobin does not catalyze the hydroxylation of inert alkane species as seen in many cytochrome P450s. However, our group has recently found that myoglobin reconstituted with MnPc can catalyze H_2O_2-dependent hydroxylation of alkane species [3] (Fig. 1). For example, ethylbenzene, cyclohexane and propane were converted to the corresponding alcohols via inert C(sp^3)–H bond activation. Interestingly, FePc and manganese porphyrin do not show hydroxylation activities in myoglobin. Spectroscopic studies suggest that Mn(V)Pc-oxo species is a catalysis intermediate. Furthermore, appropriate modification of the heme pocket of myoglobin is found to accelerate the catalysis and enhances the enantioselectivity of ethylbenzene hydroxylation.

Several groups have demonstrated cyclopropanation of olefins catalysed by modified myoglobins where iron protoporphyrin IX was replaced with Ir or Ru protoporphyrin IX. In contrast, we carried out styrene cyclopropanation in the presence of ethyl diazoacetate by myoglobin reconstituted with FePc [4]. Michaelis-Menten kinetics suggests that k_{cat} values of the reconstituted protein are 65-fold higher than that observed by native myoglobin. Stopped-flow experiments provide the transient intermediate of iron-carbenoid species, which supported by theoretical studies.

Recently, our group found that myoglobin reconstituted with FePc can also catalyze other non-redox reactions. In this presentation, we discuss the scope of the catalysis by myoglobin reconstituted with metalloporphycenes.

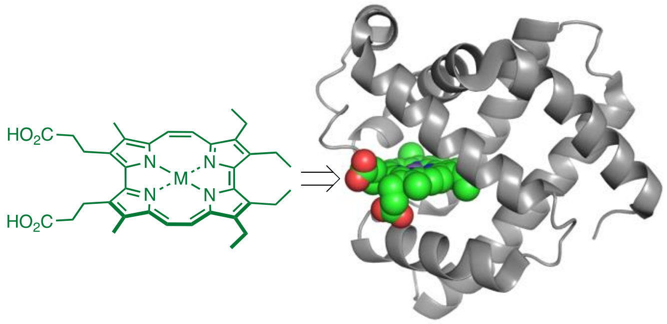

Figure 1. Crystal structure of myoglobin reconstituted with MnPc.

REFERENCES

1. K. Oohora, A. Onoda, T. Hayashi, *Acc. Chem. Res. 52*, 945 (2019).
2. K. Oohora, T. Hayashi, *Dalton Trans. 50*, 1940 (2021).
3. K. Oohora, H. Meichin, Y. Kihira, H. Sugimoto, Y. Shiro, T. Hayashi, J. Am. Chem. Soc. 139, 18460 (2017).
4. K. Oohora, H. Meichin, L. Zhao, M. W. Wolf, A. Nakayama, J.-y. Hasegawa, M. Lehnert, T. Hayashi, *J. Am. Chem. Soc. 139*, 17265 (2017).

Electric Fields and Proton Transfers in Cytochrome c Oxidase Gauged by Time-Resolved IR Spectroscopy

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Cytochrome c oxidase (CcO) is a transmembrane protein complex that reduces molecular oxygen to water while translocating protons across the mitochondrial membrane. Changes in the redox states of its cofactors trigger both O_2 reduction and vectorial proton transfer, which includes a proton loading site yet unidentified. We exploited carbon monoxide as a vibrational Stark effect probe at the binuclear center of CcO from *R. sphaeroides*. The CO stretching frequency was monitored as a function of the electrical potential using Fourier transform infrared (FTIR) absorption spectroelectrochemistry [1]. We observed three different redox states (R_4CO, R_2CO, O), determined their midpoint potentials, and compared the resulting electric field to electrostatic calculations. A change in the local electric field strength of +2.9 MV/cm was derived, which was induced by the redox transition from R_4CO to R_2CO. We performed potential-jump experiments to accumulate the R_2CO and R_4CO species and studied the FTIR difference spectra in the protein fingerprint region. The comparison of experimental and computational result reveals that the key glutamic acid residue E286 is protonated in the observed states and that its hydrogen-bonding environment is disturbed upon the redox transition of heme a_3. In a different set of experiments, we traced electron-coupled proton transfer in CcO by flashing the mixed-valent state R_2CO of CcO reconstituted in nanodiscs. Transient deprotonation of E286 was observed on the μs time scale applying transient spectroscopy with tunable extra cavity quantum cascade lasers (EC-QCL [2]). This kinetics is correlated to the evolution of other vibrational bands indicative of structural changes in the heme and protein moieties. -

REFERENCES

1. Baserga F, Dragelj J, Kozuch J, Mohrmann H, Knapp E-W, Stripp ST and Heberle J (2021). *Front. Chem.* 9:669452.
2. Schultz, B.-J., Mohrmann, H., Lórenz-Fonfría, V.A., Heberle J. (2018). *Spectrochim. Acta A* 188, 666-674.

Stimuli-responsive Porphyrin Cages as Allosteric Receptors and Bimetallic Catalysts

Valérie Heitz

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Porphyrins have been incorporated in many multicomponent systems due to their appealing coordination, electronic and photophysical properties. The synthesis of three-dimensional architectures with metalloporphyrins as active components gave rise to attractive structures for molecular recognition or chemical transformation [1]. By analogy with biological processes, molecular cages that incorporate both binding and regulation sites are appealing systems for an allosteric control of their properties as receptor, catalyst or drug carrier [2].

Our group has developed flexible porphyrin cages with peripheral binding sites able to modulate to a large extent their cavity size with a chemical stimulus [3]. We will discuss the ability of these molecular cages to behave as allosteric receptors and as bimetallic catalysts [4-5].

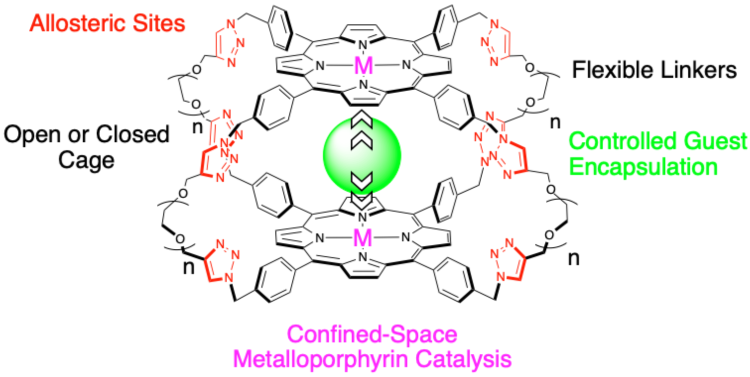

Figure. Flexible cages incorporating porphyrins and peripheral binding sites.

REFERENCES

1. a) S. Durot, J. Taesch, V. Heitz, *Chem. Rev.,* **2014**, *114*, 8542. b) S. H. A. M. Leenders, R. Gramage-Doria, B. de Bruin, J. N. H. Reek, *Chem. Soc. Rev.,* **2015**, *44*, 433
2. a) A. J. McConnell, C. S. Wood, P. P. Neelakandan, J. R. Nitschke, *Chem. Rev.* ***2015**, 115,* 7729. b) C. Kremer, A. Lützen, *Chem. Eur. J.*, **2013**, *19*, 6162.
3. a) J. Taesch, V. Heitz, F. Topic, K. Rissanen, *Chem. Commun.*, **2012**, *48*, 5118. b) L. Kocher, S. Durot, V. Heitz, *Chem. Commun*. **2015**, *51*,13181. c) L. Schoepff, L. Kocher, S. Durot, V. Heitz, *J. Org. Chem.,* **2017**, 82, 5845.
4. a) R. Djemili, L. Kocher, S. Durot, A. Peuronen, K. Rissanen, V. Heitz, *Chem. Eur. J.* **2019**, *25*, 1481. b) L. Zanetti-Polzi, R. Djemili, S. Durot, V. Heitz, I. Daidone, B. Ventura, *Chem. Eur. J.* **2020**, *26*, 17514.
5. L. Schoepff, L. Monnereau, S. Durot, S. Jenni, C. Gourlaouen, V. Heitz, *ChemCatChem*, **2020**, *12*, 5826.

The functional and structural diversity of cytochrome *bd* oxidase, a bacterial defense factor

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The selective reduction of oxygen to water is crucial to life and a central process in aerobic organisms. It is catalyzed by several different enzymes, including cytochrome *bd* oxidases (cyt *bd*) that are solely present in prokaryotes, including several pathogens. The reduction of O_2 occurs at the high spin D-type heme in all cyt *bd* oxidases, that is also the binding site for several ligands from signaling processes, including CO, H_2S and NO. These enzymes play a crucial role in protection against oxidative stress, in virulence, adaptability and antibiotics resistance. The phylogeny of the active subunit has been completely revisited by the recent study of Murali et al. [1] showing an unprecedented structural diversity of this superfamily.

The first structure of cyt *bd* was described for *Geobacillus thermodenitrificans* [2]. Interestingly the *E. coli* cyt *bd* I structure, revealed the heme cofactors in a different spatial position although with homologous primary and secondary structure [3]. In addition, the values of the heme redox potentials have been found to be inverted [4].

In order to get insight into the functional diversity of this enzyme family we performed an electrocatalytic study of cyt *bd from several organisms* in the presence of oxygen and of NO, an important signaling factor. The role of highly conserved acidic residues is analyzed and investigated on the basis of reaction induced FTIR difference spectra. Finally, the question why *E. coli* comprises two highly comparable cytochrome bd oxidases [5] is discussed.

REFERENCES

1. Murali, R., Gennis, RB., Hemp, J. (2021) ISME J. Jun 18.
2. Safarian, S., Rajendran, C., Müller, H., Preu, J., Langer, JD., Ovchinnikov, S., Hirose, T., Kusumoto, T., Sakamoto, J., Michel, H. (2016) *Science* 352(6285): 583-586.
3. Safarian, S., Hahn, A., Mills, DJ., Radloff, M., Eisinger, ML., Nikolaev, A., Meier-Credo, J., Melin, F., Miyoshi, H., Gennis, RB., Sakamoto, J., Langer, JD., Hellwig, P., Kühlbrandt, W., Michel, H. (2019) *Science* 366(6461):100-104
4. Nikolaev, A., Safarian, S., Thesseling, A., Wohlwend, D., Friedrich, T., Michel, H., Kusumoto, T., Sakamoto, J., Melin, F., Hellwig, P. (2021) *Biochim. Biophys. Acta* 1862, 148436.
5. Grauel, A., Kägi, J., Rasmussen, T., Makarchuk, I., Oppermann, S,. Moumbock, A., Wohlwend, D., Müller, R., Melin, F., Günther, S., Hellwig, P., Böttcher, B., and Friedrich, T. (2021) *Nat. Commun.,* 12:6498.

Synthetic heme chalcogenates: Their marked differences and similarities in chemical and physicochemical property

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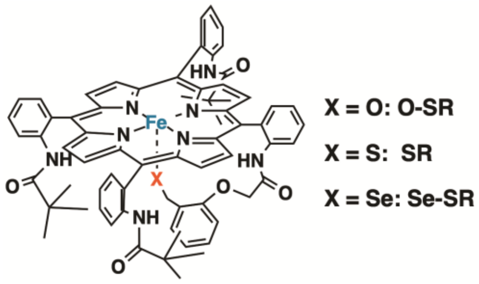
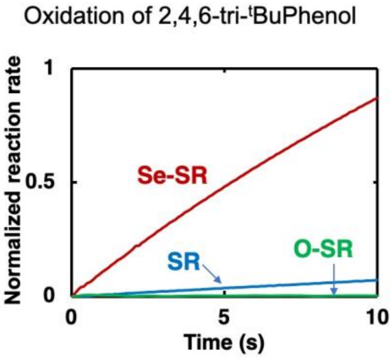
Cytochrome P450 (P450) is a family of heme-containing enzymes that catalyze various types of oxidative processes in steroid biosynthesis and detoxification of xenobiotic compounds, mainly via monooxygenase-type reactions. The relationship between potent catalytic reactivity of cytochrome P450 and electron donative character of axial thiolate ligand has been extensively investigated for long time. We previously succeeded in the synthesis of first synthetic iron porphyrin coordinated by a thiolate (**SR** complex), which can retain its thiolate coordination during catalytic oxidation reaction.[1] Recently, we also synthesized **O-SR** (alcoholate coordination)[2] and **Se-SR** (selenolate coordination) in order to compare effect of axial ligand on the spectroscopic and catalytic properties of iron porphyrin.

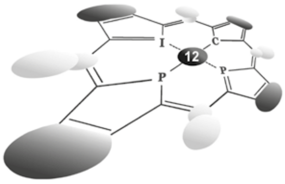
Each electronic absorption spectrum was observed and compared. Binding constants of external ligands were evaluated in each case. **Se-SR** changed its spin state by the coordination of tetrahydrofuran, an weak ligand. N-O Stretching mode of the NO-**Se-SR** complex clearly indicated donative trans-effect of selenolate is larger than thiolate and much larger than alcoholate. Cyclic voltammogram of **Se-SR** revealed that Fe^{III}/Fe^{IV} redox couple of **Se-SR** was lower than that of **SR** but the two potentials were unexpectedly identical in the case of Fe^{II}/Fe^{III} redox couple. Magnetic property of each complex was also evaluated by using SQUID and EPR. At ordinary temperature, the spin state of heme selenolate **Se-SR** is lower ($S = 1/2$ and $A = 5/2$ are mixed) than that of **SR** complex (mainly $S = 5/2$) and **O-SR** ($S = 5/2$) in solid state. Catalytic oxidation reaction using peroxides as oxidants showed below were distinctive differences among **SR**, **O-SR** and **Se-SR** complexes. The catalytic activity of **Se-SR** is 13-fold higher than that of **SR** in substituted phenol oxidation with cumene hydroperoxide, which may reflect the O-O bond cleavage rate.





REFERENCES

1. Higuchi, T.; Uzu, S.; Hirobe, M. *J. Am. Chem. Soc.* **1990**, *112*, 7051-7053.
2. Shirakawa, Y.; Yano, Y.; Niwa, Y.; Inabe, K.; Umezawa, N.; Kato, N.; Hisamatsu, Y.; Higuchi, T. *Inorg. Chem.* **2019**, *58*, 4268-4274.



Sensing and singlet oxygen generation using non-planar tetrapyrroles

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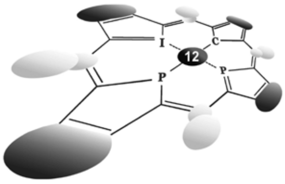
Porphyrins and other tetrapyrroles are highly suitable for sensing operations based on their synthetic flexibility and chromophore structures where an analyte might interact to stimulate some variation in directly observable optical colour or fluorescence emission modulation. Their chromophore structures also allow access to electronic triplet states, which can be harnessed for the generation of singlet oxygen – a highly reactive species useful for photodynamic action against tumours or microorganisms. Here we discuss the sensing activity of several β-substituted porphyrins including not only by the introduction of suitable interacting units but also by the adaptation of non-planar porphyrins for the synthesis of porous structures. The latter are applied for film formation and sensing involving nanomechanical sensors. Selectivity and mechanisms of sensing activity are discussed. We will also introduce new efficient singlet oxygen generating materials based on agglomeration of the OxP chromophore with oxo-Zr(IV) metal-organic frameworks or electron deficient porous polymers. The use of these materials for selective oxidation of organic substrates is demonstrated. Overall, the results demonstrate the efficacy of the chromophore approach to functional materials.



Catalytic Oxygenation Reactions Using Metal Complexes of N-Confused Porphyrins as Catalysts

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The metal complexes of N-confused porphyrins have demonstrated unique coordination chemistry, distinctively different from traditional tetrapyrrolic porphyrin complexes [1,2]. Additionally, the activities of these molecules towards small molecular activities have also been illustrated in several recent reports to show promising results for O_2 activations, nitrite reductions, and nitric oxide to nitrous oxide conversions [3-5]. Although nitric oxide to nitrous oxide conversion, as an example, showed a reactivity with multiple reaction cycles, in general, the catalytic reactions by metal complexes of N-confused porphyrins have not yet been extensively examined. Liu and co-workers firstly reported that manganese N-confused porphyrins can catalyze alkene oxidation reactions in the presence of iodosobenzene as an oxygen atom source [6]. Our group is aiming to develop catalytic reaction systems using N-confused porphyrins complexes as catalysts under greener conditions with either hydrogen peroxide or dioxygen as an oxygen atom source. In this report, we will cover a survey on the unique coordination chemistry of metallo-N-confused porphyrins and present our recent results on mechanistic investigations and catalytic oxygenation reactions of organic molecules using metal complex of N-confused porphyrin as a catalyst.

REFERENCES

1. Maeda, H. ; Ishikawa, Y. ; Matsuda, T. ; Osuka, A. ; Furuta, H. *J. Am. Chem. Soc.* **2003**, *125*, 11822-11823.
2. Chmielewski, P.; Latos-Grażyński L.; Głowiak, T. *J. Am. Chem. Soc.* **1996**, *118*, 5690-5701.
3. Rachlewicz, K.; Wang, S.-L.; Ko, J.-L.; Latos-Grażyński L. *J. Am. Chem. Soc.* **2004**, *126*, 4420-4431.
4. Ching, W.-M.; Chuang, C.-H.; Wu, C.-W.; Peng, C.-H.; Hung, C.-H. *J. Am. Chem. Soc.* **2009**, *131*, 7952-7953.
5. Chuang, C.-H.; W.-F. Liaw; Hung, C.-H. *Angew. Chem. Int. Ed.* **2016**, *55*, 5190-5194.
6. Peng, S.-H.; Mahmood, M. HR; Zou, H.-B.; Yang, S.-B.; Liu, H.-Y. *J. Mol. Catal. A: Chem.* **2014**, *395*, 180-185.

Porphyrins and Corroles for Dye-Sensitized Solar Cells

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In the last decade, porphyrins have made outstanding contribution to performance improvement in dye-sensitized solar cells (DSSCs). Specifically, versatile push-pull type porphyrins have achieved power conversion efficiencies (PCE) over 10% as a result of their improved light-harvesting abilities. Meanwhile, aromatic ring fusion to a porphyrin core is an attractive strategy for highly efficient DSSCs because of its expanded π-conjugation and resultant red-shifted absorption. Nevertheless, aromatic-fused porphyrin sensitizers have suffered rather low cell performances owing to their mismatch of HOMO-LUMO levels, high aggregation tendency, and short lifetime of the excited states. Considering the background, we envisioned that the fusion of substituted methylene-bridged small aromatic ring to a porphyrin core would overcome these drawbacks, improving the cell performance. We designed and synthesized a series of substituted methylene-bridged thiophene-fused porphyrins, **AfZnP**, **DfZnP**, and **DfZnP-*i*Pr**. After optimization, DSSC with the donor-side thiophene-fused **DfZnP-*i*Pr** achieved a PCE of 10.1%, which is comparable to that of DSSC with **GY50** (10.0%), a representative high-performance push-pull type porphyrin. More importantly, co-sensitization of **DfZnP-*i*Pr** with a complementary dye **LEG4** further led to a PCE of 10.7%, which is the highest value ever reported for DSSCs with fused porphyrin sensitizers. Therefore, our methdology will highlight aromatic-fused porphyrins for high-performance DSSCs.

Finding strategies for a high charge separation efficiency is prerequisite for realizing efficient solar energy conversion in photovoltaic and photocatalytic devices. Porphyrinoids, including porphyrins and related macrocycles such as phthalocyanines and corroles, are versatile ligands that can accommodate a single metal atom for most metal ions, and their photophysical and electrochemical properties can be tuned by the metal atom in the cavity. We also evaluated the photovoltaic properties of the DSSCs based on Au^{III}, $\text{Re}^{\text{V}}\text{O}$, and $\text{Os}^{\text{VI}}\text{N}$-corroles with COOH anchoring groups at the *para*- and *meta*-positions of the *meso*-phenyl groups. The DSSCs based on Au^{III}-corrole exhibited a PCE of 4.2%, which is remarkably higher than those for the $\text{Re}^{\text{V}}\text{O}$- and $\text{Os}^{\text{VI}}\text{N}$-corroles. Femtosecond time-resolved transient absorption measurements showed that the electron injection from the excited singlet state competes with intersystem crossing, and that intersystem crossing for Au^{III}-corroles is slower than those for $\text{Re}^{\text{V}}\text{O}$- and $\text{Os}^{\text{VI}}\text{N}$-corroles. Consequently, the high incident photon-to-current efficiencies and resultant short-circuit current densities and PCEs for Au^{III}-corroles are attributed to the high electron injection efficiencies owing to the slower intersystem crossing than $\text{Re}^{\text{V}}\text{O}$- and $\text{Os}^{\text{VI}}\text{N}$-corroles. In addition, the higher PCE for an Au^{III}-corrole with a *meta*-COOH group (4.2%) as opposed to a *para*-COOH group (3.4%) is explained by the stronger Au-TiO_2 interactions supported by XPS measurements and theoretical calculations. These results imply that both the substituents and the metal ion have a large influence on the photovoltaic performances. Overall, DSSCs based on the Au^{III}-corroles were found to exhibit the highest photovoltaic performance among corrole-based DSSCs.

REFERENCES

1. Y. Kurumisawa, T. Higashino, S. Nimura, Y. Tsuji, H. Iiyama, and H. Imahori, *J. Am. Chem. Soc.*, **141**, 9910-9919 (2019).
2. T. Higashino, H. Iiyama, Y. Kurumisawa, and H. Imahori, *ChemPhysChem*, **20**, 2689-2695 (2019).
3. T. Higashino, Y. Kurumisawa, A. B. Alemayehu, R. F. Einrem, D. Sahu, D. M. Packwood, K. Kato, A. Yamakata, A. Ghosh, and H. Imahori, *ACS Adv. Energy Mater.*, **3**, 12460-12467 (2020).
4. H. Imahori, Y. Kobori, and H. Kaji, *Acc. Mater. Res.*, **2**, 501-514 (2021).

Subphthalocyanines for Photocatalytic Hydrogen Evolution

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Hydrogen is a zero-emission energy carrier, which can be used to produce not only fuel and electricity but also value-added chemical feedstock, therefore bearing great potential to address challenges of the dependency on fossil fuels and greenhouse emissions. [3]. Since the photocatalyst-based H_2 production by Fujishima and Honda in 1972, many metal oxide semiconductors have been used as photocatalysts. Although TiO_2 is the most widely used photocatalyst, its absorption in the UV region covering only 4% of the solar emission spectrum limits the efficient use of solar energy. To maximize the productivity of the photocatalyst particularly in the function of solar irradiation, the utilization of photosensitizer to form dye-sensitized photocatalyst is an alternative strategy to increase the yield of solar to fuel conversion.[1] The outstanding properties of subphthalocyanines (SubPcs) such as a high molar extinction coefficient in the visible region good solubility and low aggregation tendency due to their cone-shaped make them very appealing components for artificial photosynthetic devices such as photovoltaic.[2] In this study, a series of SubPcs bearing a carboxylic acid group with different peripheral substituents have been synthesised as dyes to sensitized TiO_2 to investigate the influence of the substituents on the performance of photocatalytic hydrogen evolution. To extend the absorption spectra and minimize the potential aggregation, strong electron-donating and bulky groups were introduced into peripheral positions of SubPcs. Their performances as photosensitizers in photocatalytic H_2 production will be evaluated.

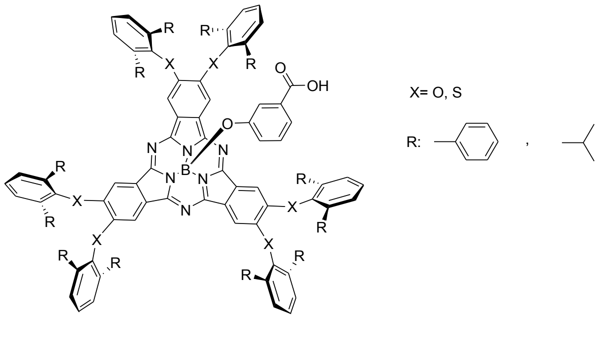

Figure 1. Molecular structure of SubPcs designed for photocatalytic H_2 production

REFERENCES

1. A. Kubacka, M. Fernandez-Garcia, G. Colon, Chem. Rev. 2012, 112, 3, 1555-1614.
2. C.G. Claessens, D. Gonzalez-Rodriguez, M.S. Rodríguez-Morgade, A. Medina, T. Torres, Chem Rev., 2014, 114,2192-277
3. A. C. Yüzer, E. Genc, E. Harputlu, G. Yanalak, E. Aslan, K. Ocakoglu, I. H. Patir and M. Ince, Dalton Trans., 2020,49, 12550-12554.

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ORALS

Calix[3]pyrrole: Synthesis and strain induced reactions

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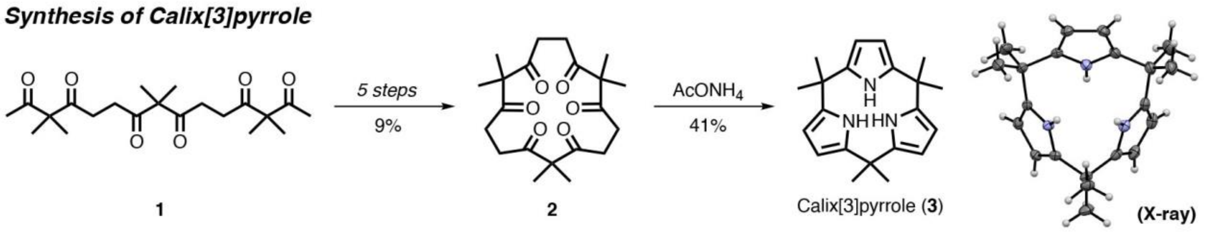
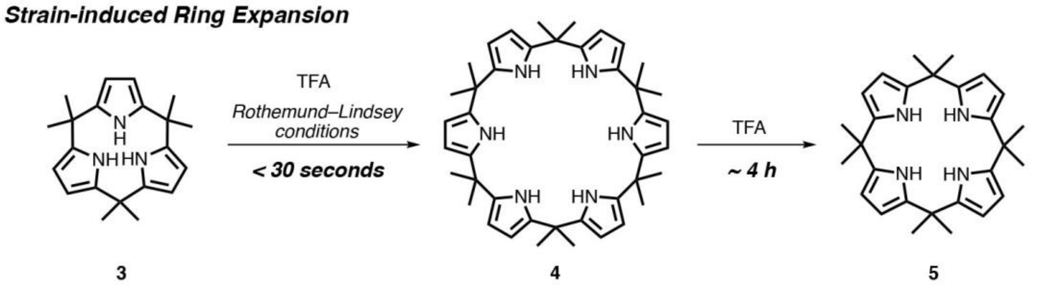
While condensation reactions of pyrrole monomers with aldehydes or ketones often lead to selective formation of tetrapyrrolic macrocycles like porphyrins, the corresponding tripyrrolic macrocycles are not observed. Calix[3]pyrrole, a porphyrinogen-like tripyrrolic macrocycle having three sp^3-carbon linkages, might hold a key to tackle with the long-standing question, but has been missing in porphyrin-related chemistry. Here we show synthesis of calix[3]pyrrole using aliphatic hexaketone as a precursor and its strain-induced ring expansion to calix[4]pyrrole via calix[6]pyrrole.

Linear hexaketone 1[1] was converted to cyclic hexaketone 2 in total 9% yield for 5 steps. Paal–Knorr type pyrrole formation using 2 gave calix[3]pyrrole (3) in 41% yield as a stable solid. Single crystal X-ray diffraction analysis revealed that all the meso-carbon atoms were located out of the mean plane of neighboring pyrrole rings. Such macrocyclic ring strain induced a rapid ring expansion reaction under Rothemund–Lindsey porphyrin cyclization conditions. In the presence of trifluoroacetic acid (TFA), calix[3]pyrrole (3) disappeared within 30 seconds and quantitatively furnished calix[6]pyrrole (4) which slowly converted to calix[4]pyrrole (5) under the same conditions. These findings help explain the absence of tripyrrolic macrocycles during classic porphyrin syntheses [2].





REFERENCES

1. Y. Manabe, M. Uesaka, T. Yoneda, Y. Inokuma, *J. Org. Chem*. **2019**, *84*, 9957.
2. Y. Inaba, Y. Nomata, Y. Ide, J. Pirillo, Y. Hijikata, T. Yoneda, A. Osuka, J. L. Sessler, Y. Inokuma, *J. Am. Chem. Soc.* **2021**, *143*, 12355.

Monomeric and dimeric complexes of phthalocyanines as oxidation catalysts

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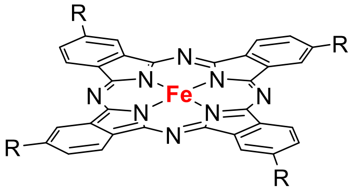
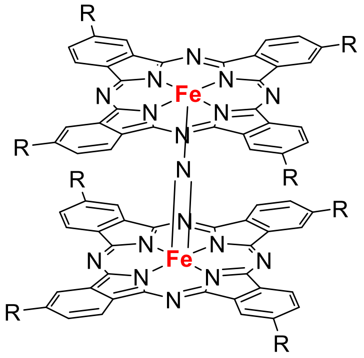
Phthalocyanines can oxidize various organic compounds such as olefins, alcohols, and aromatics [1]. The substitution pattern is crucial to enhance their properties or elucidate some mechanisms.
Extremely stable monomeric sulfonamide substituted iron phthalocyanine oxidized olefins [2].
Two different iron phthalocyanines octa substituted either with electron-withdrawing isobutyl sulfonyl moieties or electron-donating isobutoxy moieties were comparatively tested in oxidation of cyclohexene to assess substituents nature effect [3].

N-bridged diiron dimeric phthalocyanines emerged as powerful oxidation catalysts. These excellent catalysts oxidized methane, benzene, and various organic compounds [1, 4-5].



Monomeric iron phthalocyanine



N-bridged dimeric diiron phthalocyanine

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REFERENCES

1. A. B. Sorokin, *Chem. Rev.* **2013**, *113*, 8152.
2. Ü. İşci, C. Caner, Y. Zorlu, A. G. Gürek, F. Dumoulin and V. Ahsen, *Dalton Trans.* **2014**, *43*, 17916.
3. C. Yüceel, Z. Şahin and Ü. İşci. *J. Porphyr. Phthalocyanines*, 2022, doi.org/10.1142/S1088424621501285
3. Ü. İşci, P. Afanasiev, Jean-Marc M. Millet, E. V. Kudrik, V. Ahsen and A. B. Sorokin, *Dalton Trans.* **2009**, 7410.
4. Ü. İşci, A. S. Faponle, P. Afanasiev, F. Albrieux, V. Briois, V. Ahsen, F. Dumoulin, A. B. Sorokin, S. P. de Visser, *Chem. Sci.*, **2015**, *6*, 5063.

Structural and Functional Characterization of Electron Transfer Complex between Cytochrome *c* and Cytochrome *c* Oxidase

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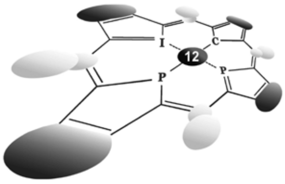
In the respiratory chain of mitochondria, the interprotein electron transfer (ET) reactions promote the proton pumping from matrix to inner membrane space, which is essential for the ATP generation. This ET system is terminated by the four-electron reduction of molecular oxygen (O_2) in cytochrome *c* oxidase (C*c*O), and the ET reaction to C*c*O is mediated by a small hemoprotein, cytochrome *c* (Cyt *c*). Although the structure of the ET complex between Cyt *c* and C*c*O under the turnover conditions is indispensable to examine the regulation mechanism for the ET reaction, the rapid ET reactions after the complex formation of the reduced state of Cyt *c* and the oxidized form of C*c*O have been prevented us from the detailed structural and functional characterization of the "ET-active complex" between Cyt *c* and C*c*O. However, we successfully estimated the structure of the ET complex between Cyt *c* and C*c*O under steady-state turnover conditions by utilizing protein-protein docking simulation combined with the experimentally determined interaction site for C*c*O in Cyt *c* and the Michaelis constants for the ET reaction from various kinds of the Cyt *c* mutants to C*c*O [1]. The complex structure determined by the simulation revealed that the ET distance between the redox centers of two proteins, heme iron of Cyt *c* (Fe_c) and cupper of the $\mathrm{Cu_A}$ site of C*c*O ($\mathrm{Cu_A}$), is nearly 23 Å, which is much longer than that previously suggested. To experimentally confirm the ET distance between two redox centers, the ET rate from Cyt *c* to C*c*O in the complex was measured by using flow-flash measurements. In the flow-flash measurements, carbon monoxide (CO) bound C*c*O was rapidly mixed with the O_2-saturated solution, and, after the mixing, the reduction reaction of O_2 was initiated by irradiating flash light to dissociate CO from C*c*O and to bind O_2. Associated with the O_2 reduction, the ET reaction from Cyt *c* to C*c*O is induced, which can be monitored by the oxidation rate of Fe_c of Cyt *c*. By applying the Marcus equation, the ET distance was estimated to be less than 19 Å, which is substantially shorter than the Fe_c–$\mathrm{Cu_A}$ distance in the simulated complex [1]. This finding allows us to speculate that the "ET-active complex" would have a different binding orientation of Cyt *c* on C*c*O from that in the complex, "energetically stable complex", determined by the previous docking simulation [1]. To structurally characterize the "ET-active complex", a protein-protein docking simulation under the structural restraint of the short Fe_c–$\mathrm{Cu_A}$ distance was applied, which revealed a stable complex structure showing that the Fe_c–$\mathrm{Cu_A}$ distance is ~ 18 Å, corresponding to the ET distance (< 18.6 Å) experimentally determined from the flow-flash measurements. The orientation of Cyt *c* on C*c*O in the "ET-active complex" was significantly different from that in the "energetically stable complex", suggesting the "conformational gating" where the thermal motions of the protein induce the conformational changes of the protein from the most energetically stable structure to the less stable but more active structure of the proteins. In the ET reaction from Cyt *c* to C*c*O, structural fluctuation induced by thermal motions of proteins would be a trigger to the conformational changes to the "ET-active complex". The slower oxidation rate of Cyt *c* by C*c*O under the steady-state turnover conditions also supports the "conformational gating" mechanism, where the rate for the conformational changes from the "energetically stable complex" to the "ET-active complex" would be the rate-determinant step for the ET reaction from Cyt *c* to C*c*O.

REFERENCES

1. Sato, W., Hitaoka, S., Inoue, K., Imai, M., Saio, T., Uchida, T., Shinzawa-Itoh, K., Yoshikawa, S., Yoshizawa, K., Ishimori, K. *J. Biol. Chem.*, **291**, 15320 – 15331 (2016), 10.1074/jbc.M115.708065.



Hemihexaphyrazines. Unusual Coordination Abilities of Six-members Porphyrinoids

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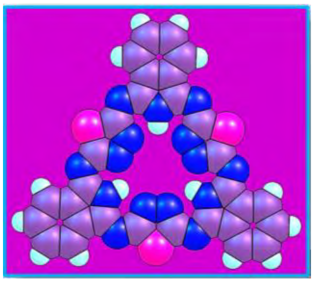
Hemihexaphyrazines (Hhps) are six-members porphyrinoids composed of three thiadiazole and three pyrrole containing subunits unified by an alternating fashion via six aza-bridges. It was established that they are allowed a large structural modification by introductions of functional groups on periphery and by selections of pyrrole bearing moieties. An expanded coordination cavity with 27-members inner macroring bearing 15 nitrogen atoms assumes an enormous potential in coordination chemistry. Inner cavity can be divided on three chelate like sites containing one N-H group and two nitrogen atoms of adjacent thidiazole moieties. Due to that Hhps are able to hold 3 atoms of d-metals within inner cavity to form 3:1 clusters that was confirmed by STM method [1]. Moreover due to presence of six nitrogen atoms of thiadiazole rings at the central part, a reduced H_3Hhp is able to form with potassium a double-decker structure similar to aza-crown ether complexes [2].



Synthesis, structures of various architectures, optical and magnetic properties of the Hhps metal complexes in ground states and reduced forms are reviewed [3, 4].

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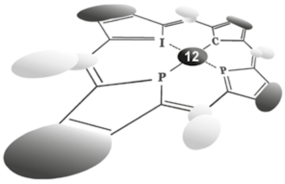
REFERENCES

1. Bacilla Ana C. C., Okada Yusuke, Yoshimoto Soichiro, Islyaikin Mikhail K., Koifman Oskar I. Kobayashi Nagao. *BCSJ.* 2021, Vol.94, No.1, pp. 34 – 43.
2. Dmitri V. Konarev, Salavat S. Khasanov, Mikhail K. Islyaikin, Akihiro Otsuka, Hideki Yamochi, Hiroshi Kitagawa, Rimma N. Lyubovskaya, Evgenii N. Ivanov, Oskar I. Koifman, Yuriy A. Zhabanov. *Chemistry – An Asian Journal.* 2020, 15, 61 – 65.
3. Dmitry I. Nazarov, Salavat S. Khasanov, Ivan A. Rompanen, Evgenii N. Ivanov, Oskar I. Koifman, Mikhail K. Islyaikin, Dmitri V. Konarev. *Polyhedron*. 2021. 202. 115198.
4. Dmitry I. Nazarov, Mikhail K. Islyaikin, Evgenii N. Ivanov, Oskar I. Koifman, Mikhail S. Batov, Leokadiya V. Zorina, Salavat S. Khasanov, Alexander F. Shestakov, Evgeniya I. Yudanova, Yuriy A. Zhabanov, Dmitriy A. Vyalkin, Akihiro Otsuka, Hideki Yamochi, Hiroshi Kitagawa, Tomas Torres, Dmitri V. Konarev. *Inorg. Chem.* 2021, 60, 13, 9857–9868.



De novo designed heme-proteins mimicking both His-coordinated and Cys-coordinated heme enzymes

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The active site of heme-containing enzymes, an Fe^{III} protoporphyrin IX cofactor, is capable of catalyzing a variety of biologically-relevant chemical reactions, such as disproportionation of hydrogen peroxide (catalases[1]), oxidation and haloperoxidation of organic substrates (monofunctional heme peroxidases [2], bi-functional catalase-peroxidases[3]) and oxygenation reactions (cyt P450 monooxygenases and nitric oxide synthases[2]). Such a functional versatility relies upon variations in the heme coordination (*i.e.* His, Tyr, Cys or Met axial ligand(s)), as well as being significantly modulated by the heme environment (2nd coordination sphere and H-bond networks). Studies of heme active sites using mutational analysis, structural biology and molecular spectroscopy provide essential information on the natural systems that delimit the catalytic processes. Yet, the complexity of the natural systems often masks the specific behavior of the metal cofactor. For this reason, smaller artificial proteins capable of binding heme at specified sites are being developed [5, 6]. Our approach is to use α-helical scaffolds to provide ligation to the heme as cofactor to explore heme axial ligand selectivity, specifically hoping to define how one can control the iron coordination geometry when a heme is afforded an opportunity to bind either histidine (imidazole) or cysteine (thiolate) ligands. UV-vis and Electron Paramagnetic Resonance/HYSCORE spectroscopies, as well as redox potentiomery, were applied to characterize heme ligation and differences in heme coordination as a function of pH [7]. We have uncovered an unprecedented pH-dependent switch in the heme binding mode within a single synthetic protein. The resulting miniature protein, that folds as a dimer of antiparallel two-stranded coiled coils upon heme complexation, can catalyze O_2 reduction (as cyt P450 monooxygenases) as well as substrate oxidation (as peroxidases). The further approach of introducing a Trp in order to mimic the concerted reactions of heme&Trp radical as redox cofactors enhancing the catalytic reactivity and mimicking the case of natural heme mono- and bi-functional peroxidases[8, 9] will be discussed.

REFERENCES

1. P. Nicholls, I. Fita, P. C. Loewen, *Adv. Inorg. Chem.* **2000**, *51*, 51-106.
2. T. L. Poulos, *Chem. Rev.* **2014**, *114* (7), 3919-3962.
3. O. J. Njuma, E. N. Ndontsa, D. C Goodwin, *Arch. Biochem. Biophys.* **2014**, *544*, 27-39.
4. G. Smulevich, A. Feis, B. D. Howes, A. Ivancich. Structure-function relationships in heme peroxidases. In Handbook of Porphyrin Science (Kadish, K. M., Smith, K. M., Guilard, R. Eds), vol. 6, chapter 31, pp 367-453, World Scientific, Hackensack, NJ; **2010**.
5. I. Korendovych, W. DeGrado, *Q. Rev. Biophys.* **2020**, *53*, e3
6. F.Nastri, M.Chino, O.Maglio, A.Bhagi-Damodaran, Y.Lu, A.Lombardi, *Chem. Soc. Rev.* **2016**, *45*, 5020-5054.
7. K. J. Koebke, T. Kühl, E. Lojou, B. Demeler, B. Schoepp-Cothenet, O. Iranzo, V. L. Pecoraro, A. Ivancich *Angew. Chem. Int. Ed.* **2021**, *60*, 3974-3978.
8. J. Colin, B. Wiseman, J. Switala, P. C. Loewen, A. Ivancich. *J. Am. Chem. Soc*. **2009**, 131, 8557-8563
9. A. T. Smith, W. A. Doyle, P. Dorlet, A. Ivancich *Proc. Natl. Acad. Sci. USA* **2009**, 106, 16084-16089.

Supramolecular assembly formed by porphyrin derivatives based on multiple hydrogen bonding interaction

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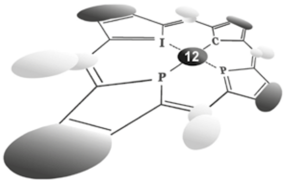
Porphyrins are essential pigments in biological systems. Porphyrins and chlorophylls are often self-assembled into nanoscale superstructures to perform many essential functions, such as light harvesting and electron transport. The crystal structure of the light-harvesting antenna complexes in purple photosynthetic bacteria shows the presence of a highly symmetric wheel-like supramolecular architecture involving a large number of bacteriochlorophyll pigments. From the inspiration of the natural light harvesting systems, a variety of porphyrin-based nanoarchitectures, such as nanofibers, nanosheets, nanoparticles, and nanorings have been fabricated for applications in various research fields including photonics, catalysis, and electronics. On the other hand, molecular recognition is a fundamental and significantly important process in nature that provides the ability to organize biomacromolecules such as proteins and DNA into uniform quaternary and double helical structures, respectively. Moreover, the precisely controlled three-dimensional (3D) molecular structure of biomacromolecules enables molecular recognition of other chemicals to perform sophisticated biological functions. From the inspiration of biosystems, the morphological control of supramolecular assemblies from mixtures of various components through self-sorting phenomena become emerging topics in supramolecular chemistry because it would be helpful to understand naturally occurring self-sorting behaviors as well as contribute to develop novel functional materials. However, the design and control of artificial system having self-sorting behavior is not simple because the molecular building blocks should include topologically organized molecular binding sites, such as geometrical complementarity in size, shape, and hydrogen-bonding sites to recognize each other. The formation of coordination spheres and charge transfer complexes are also used as driving forces for the formation of self-sorted supramolecular assemblies. These interactions are working in the form of an ensemble during the self-sorting process. Although numbers of excellent examples of self-sorted supramolecular assemblies have been reported, in most cases, molecular building blocks have relatively large structural differences because the topological selections are needed for self-sorting. Here we report a series of porphyrin dyads showing large morphological changes in molecular assemblies due to minimal structural differences of molecular building blocks. Moreover, we discovered self-sorting phenomena from the mixture of PDs that have atomic-level differences in porphyrin building blocks.

REFERENCES

1. J. M. Park, K-I. Hong, H. Lee, W-D. Jang, *Acc. Chem. Res.*, **2021**, *54*, 2249.
2. H. Lee, D. Lee, I. Kim, E. Lee, W.-D. Jang, *Macromolecules,* **2020**, *53*, 8060.
3. I. Oh, H. Lee, T. W. Kim, C. W. Kim, S. Jun, C. Kim, E. H. Choi, Y. M. Rhee, J. Kim, W.-D. Jang, H. Lhee, *Adv. Sci*, **2020**, *7*, 2001623.
4. J. M. Park, J. H. Lee, W.-D. Jang, *Coord. Chem. Rew.*, **2020**, *407*, 213157.
5. H. Lee, K.-H. Hong, W.-D. Jang, *Coord. Chem. Rew.*, **2018**, 354, 46.
6. J. Li, D. Yim, W.-D. Jang, J. Yoon, *Chem. Soc. Rev.* **2017**, *46*, 2437.



DNA-Fluorophore Conjugates: G-Quadruplex Based FRET Antenna Systems and Biomolecule Sensors

Janarthanan Jayawickramarajah*[a], **Mohammed Amin Zarandi**[a]
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Building on our recent work on porphyrinoid appended DNA sequences that can form homomeric G-quadruplexes [1-2], this talk will focus on the synthesis and characterization of heteromeric G-quadruplex nanostructures bearing multiple antenna fluorophores. Our self-assembly based approach enables the number of donor fluorophores and their relative distances to be precisely modulated. Due to the heteromeric nature of the G-quadruplexes, these nanostructures contain a single toehold region that enable further decoration of the antenna systems with bridge and/or acceptor fluorophores, *via* Watson-Crick-Franklin based DNA duplex formation. In addition to a host of structural characterization data, we will disclose the photonic FRET antenna properties (including FRET efficiency, antenna effect and effective absorption coefficient) of the ensembles as judged by fluorescence measurements. In the second portion of the seminar, we detail how DNA-small molecule conjugates appended with fluorophores, hydrophobic guests, and cucurbituril hosts, can be used to build dynamic DNA nanostructures capable of sensing key biomacromolecules.

REFERENCES

1. Pathak, P.; Yao, W.; Hook, K. D.; Vik, R.; Winnerdy, F. R.; Brown, J. Q.; Gibb, B. C.; Pursell, Z F.; Phan, A. T.; Jayawickramarajah, J. *Bright G-quadruplex nanostructures functionalized with porphyrin lanterns.* ***J. Am. Chem. Soc. 2019****, 141*, 12582-12591.
2. Pathak, P.; Zarandi, M. A.; Zhou, X.; Jayawickramarajah, J. *Synthesis and applications of porphyrin-biomacromolecule conjugates*. ***Front. Chem. 2021****, 9*, 764137.

Electronic Modulation *via* Peripheral Functionalization of Corroles

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Corroles have been known as interesting molecular platforms to study the peculiar coordination chemistry of metals in higher oxidation states and for catalytic applications. Recently, these macrocycles also have attracted the attention of materials science community due to their inherent photophysical and redox characteristics. The interesting properties arise from the tuneable electronic nature of the π-system present in corroles that can be exploited to suit appropriate application. In this direction, the electronic perturbation effected on the corroles is most often through the meso-substituents. However, the β-positions of the corroles hold huge potential for wide range of easier functionalization. Further, these β-functionalization have also been observed to result in significant modulation of the π-electron delocalization in corroles and thereby alter their photophysical and redox characteristics. Our group has been working in this direction to alter the delocalization in corroles by π-extension and π-expansion to achieve molecules with interesting optoelectronic properties. In this lecture, our recent success in developing new corrole derivatives with striking photophysical and electrochemical properties will be discussed.

REFERENCES

1. J. F. B. Barata,† M. G. P. M. S. Neves, M. A. F. Faustino, A. C. Tome, and J. S. Cavaleiro, *Chem. Rev.* **2017**, *117*, 3192-3253.
2. B. Basumatary, R. V. R. Reddy, Rahul and J. Sankar, Angew. Chem. Int. Ed. 2018, 57, 5052-5056.
3. S. Sujesh and J. Sankar, Unpublished results.

Nanographene-fused porphyrins

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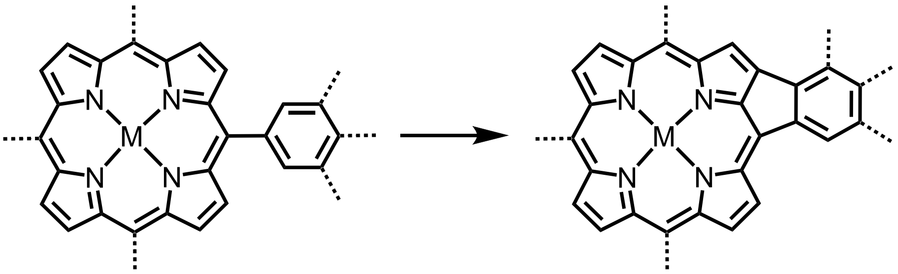
The conjugation of porphyrins with various arenes is an excellent strategy to expand the π-system of the porphyrin [1-2]. Thus, new chromophores are obtained which possess, among others, red-shifted UV/vis absorptions.



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

REFERENCES

1. Roznyatovskiy VV, Leeb CH and Sessler JL. *Chem. Soc. Rev.* 2013; **42**: 1921-1933.
2. Lewtak JP and Gryko, DT. *Chem. Commun.* 2012; **48**: 10069-10086.
3. Martin MM, Oleszak C, Hampel F and, Jux N. *Eur. J. Org. Chem.* 2020; **40**: 6578-6762.
4. Oleszak C and Jux N. Manuscript in preparation.

Electrochemistry of Metallocorroles and Metallodipyrrin-bisphenols

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Our laboratories have long been interested in the redox properties of four-, five- and six-coordinate metallocorroles (Chart 1) with different donor axial ligands and a variety of peripheral corrole substituents. One goal of these studies has been to examine how axial ligand binding, solvent and functionalization of the corrole periphery can influence the redox potentials but also modulate the innocence of the tetrapyrrole complex. In this talk, we describe and compare our most recent results on different transition metal derivatives with a variety of neutral and anionic axial ligands and the data, in some cases, are compared to analogous trianionic dipyrrin bisphenol (DPP) complexes (Chart 1).

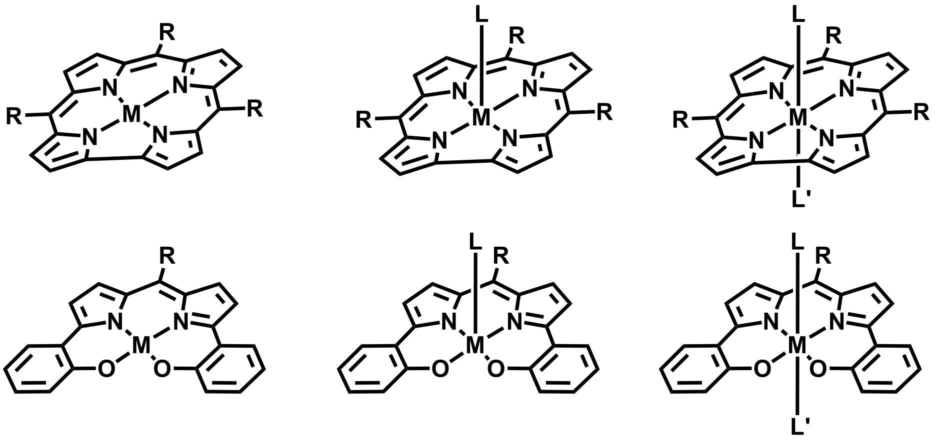

Chart 1. General structures of four-, five- and six-coordinate metallocorroles and metallodipyrrin-bisphenols (DPP).

Modulations of a Metal–Ligand Interaction and Photophysical Behaviors by Hückel–Möbius Aromatic Switching

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In organometallic complexes containing π-conjugated macrocyclic chelate ligands, conformational change significantly affects metal-ligand electronic interactions, hence tuning properties of the complexes.[1] In this regard, we investigated the metal–ligand interactions in hexaphyrin mono-Pd(II) complexes **Pd[28]M** and **Pd[26]H**, which exhibits a redox-induced switching of Hückel–Möbius aromaticity and subsequent molecular conformation, and their effect on the electronic structure and photophysical behaviors. In Möbius aromatic **Pd[28]M**, the weak metal–ligand interaction leads to that the π electronic structure of the hexaphyrin ligand remains almost intact, which undergoes efficient intersystem crossing (ISC) assisted by the heavy-atom effect of Pd metal.[2] In Hückel aromatic **Pd[26]H**, the significant metal-ligand interaction results in ligand-to-metal charge-transfer (LMCT) in the excited-state dynamics.[3] These contrasting metal-ligand electronic interactions have been revealed by time-resolved electronic and vibrational spectroscopies and time-dependent DFT calculations. This work indicates that the conspicuous modulation of metal-ligand interaction by Hückel–Möbius aromaticity switching is an appealing approach to manipulate molecular properties of metal complexes, and further enabling the fine-tuning of metal–ligand interactions and the novel design of functional organometallic materials.

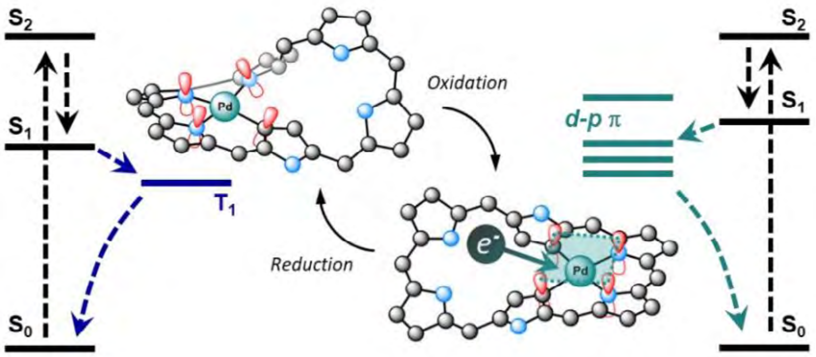

Figure 1. The contrating ISC and LMCT behaviors of redox-switchable **Pd[28]H** and **Pd[26]**

REFERENCES

1. J. Oh, Y. M. Sung, Y. Hong, D. Kim, *Acc. Chem. Res.* **2018**, *51*, 1349–1358.
2. Y. M. Sung, M.-C. Yoon, J. M. Lim, H. Rath, K. Naoda, A. Osuka, D. Kim, *Nat. Chem.* **2015**, *7*, 418–422.
3. J. Kim, J. Oh, T. Soya, T. Yoneda, S. Park, M. Lim, A. Osuka, D. Kim, *Angew. Chem.* **2020**, *132*, 5167–5172; *Angew. Chem. Int. Ed.* **2020**, *59*, 5129–5134.

Molecular Design and Synthesis of Porphyrin Sensitizers for Superior Performance Dye-Sensitized Solar Cells

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Dye-sensitized solar cells (DSSCs) have been regarded as one of the most prospective solar cells, due to low-cost, flexibility, simple device fabrication and high conversion efficiency, in comparison to the conventional photovoltaic devices. However, the unit costs, long-term device stability and PCE must be further improved for real-life applications. D-π-A porphyrin sensitizers offer wide possibilities for rational designing and structural modification and this is vital towards achieving efficient light harvesting. Push–pull structured (D–π–A) Zn(II)–porphyrin sensitizers, containing various electron donor and acceptor groups, for the enhancement of the light-harvesting ability within the expanded absorption region and efficient prevention of undesirable charge recombination of the sensitising dyes in dye-sensitized solar cells (DSSCs) were newly designed and synthesised through molecular engineering. We investigated the effect of bulky donor groups in the D-π-A structured porphyrins on retarded charge recombination between the electrolytes and TiO_2 surface and enhanced power-conversion efficiency (PCE).

The photovoltaic (PV) performance of the **SGT** sensitizer-based DSSCs, employing cobalt redox couples, were systematically evaluated in a thorough comparison with **SM315** as a world champion reference sensitizer. Also, the structure-performance relationship between donor group and cell performance in the platform of porphyrin sensitizers based on porphyrin-triple bond-BTD-acceptor in **SM315** was established. By introducing a more bulky fluorene unit containing alkoxyphenyl unit to the amine donor group in the world champion **SM315** porphyrin dye, for efficient prevention of undesirable charge recombination, the PCE was remarkably enhanced. To further improve the maximum efficiency of the DSSCs, we have also developed a new series of 4-hexyl-4H-thieno[3,2-b]indole (Hx-TI) based organic chromophores by structural engineering. Compared to a biphenylamine based donor (SGT-137), the incorporation with fluorene based donor (**SGT-149**) red-shifted the absorption band and upshifted the highest occupied molecular orbital (HOMO) energy level.

Notably, by utilizing co-sensitization with SGT-149 and porphyrin based **SGT-021** dye, the PCEs of 14.2% for co-sensitization cells are reached and considered as a major breakthrough in the development of DSSCs. In this presentation, the molecular design and synthesis of Zn-Porphyrin sensitizers for superior performance dye-sensitized solar cells will be described through the donor and acceptor structural engineering.

Single-molecule spectroscopy using localized surface plasmon

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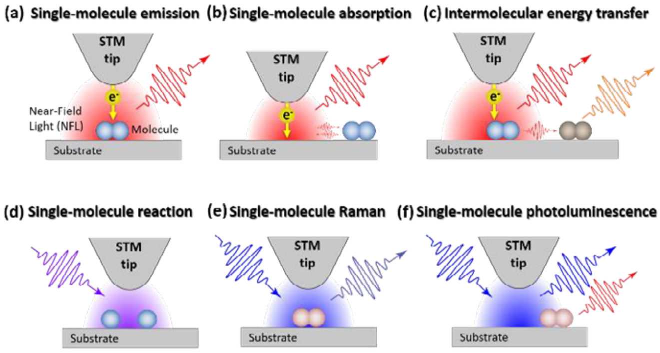
Irradiation of light to the metallic nanostructure causes collective vibration of free electrons (plasmon), followed by the creation of electromagnetic field, i.e., localized surface plasmon (LSP). The LSP has a characteristic interaction with matter, especially a single molecule. The study of single molecules provides deep insights into a bonding nature and underlying quantum mechanics concerning the chemical and physical properties. The scanning tunneling microscope (STM) is a versatile and powerful tool for investigating and controlling the chemistry of individual molecules on solid surfaces. We have developed an optical STM technology that combines the STM with light irradiation and detection technologies for our own purpose [1]. Since the STM has an extremely high (sub-atomic) spatial resolution, it allows us to achieve pioneering research of single-molecule chemistry and spectroscopy using LSP localized at the STM-tip junction.

In recent years, we have applied the LSP to exploring novel chemical reactions and spectroscopy based on the interaction between the LSP and electronic/vibrational quantum states of a single molecule at the STM junction. We have developed single-molecule emission (Fig. 1(a)) and absorption (Fig. 1(b)) spectroscopy [1] using the interaction between the LSP and a molecule, in which the LSP participates in the exciton formation in a target molecule [2,3]. Combining the emission and absorption spectroscopies, we visualized fluorescence resonance energy transfer between two different molecules (Fig. 1(c)) [4]. We have also explored the detailed mechanism of single-molecule chemical dynamics induced by the LSP (Fig. 1(d)) [5]. We also applied the LSP to measure tip-enhanced resonance Raman spectra of a single molecule (Fig. 1(e)) [6]. Furthermore, we achieved an ultrahigh-energy resolution photoluminescence measurement of a single molecule using a tunable excitation laser (Fig. 1(f)) [7]. In this talk, I will discuss recent issues focusing on single-molecule spectroscopy based on the molecular excitation by localized surface plasmon at the STM junction, which has been applied to exploring quantum states of a phthalocyanine and its derivatives.


(a) Single-molecule emission (b) Single-molecule absorption (c) Intermolecular energy transfer

(d) Single-molecule reaction (e) Single-molecule Raman (f) Single-molecule photoluminescence

Fig. 1.Schematics of single-molecule chemistry and spectroscopy using localized surface plasmon at the STM tip junction

REFERENCES

1. H. Imada et al., Physical Review Letters, 119 (2017) 013901, 1-6
2. K. Miwa et al., Nano Letters, 19 (2019) 2803-2811.
3. K. Kimura et al., Nature, 570 (2019) 210-213.
4. H. Imada et al., Nature, 538 (2016) 364-367.
5. E. Kazuma et al., Science, 360 (2018) 521-526.
6. R.B. Jaculbia et al., Nature Nanotechnology, 15 (2020) 105-110.
7. H. Imada et al., Science, 373 (2021) 95-98.

Spectroscopic and Magnetic Studies of Spin-Dependent Excited State Processes

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Spin-bearing Donor-Acceptor and Donor-*Bridge*-Acceptor ligands and molecules have been used to control spin-dependent excited state processes that include non-radiative lifetimes,[1] magnetooptical activity,[2] and ground state spin polarization.[3, 4] As such, our efforts continue to focus on the use of synthetic design principles to create new molecules that promote long-range electronic coupling and electron correlation,[2, 5] and develop new platforms for spin control of excited state processes.[1-4] We present here our latest 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]

REFERENCES

1. Tichnell, C. R.; Daley, D. R.; Stein, B. W.; Shultz, D. A.; Kirk, M. L.; Danilov, E. O., Wave Function Control of Charge-Separated Excited-State Lifetimes. *J. Am. Chem. Soc.* **2019,** *141* (9), 3986-3992.
2. Stein, B. W.; Tichnell, C. R.; Chen, J.; Shultz, D. A.; Kirk, M. L., Excited State Magnetic Exchange Interactions Enable Large Spin Polarization Effects. *J. Am. Chem. Soc.* **2018,** *140* (6), 2221-2228.
3. Kirk, M. L.; Shultz, D. A.; Hewitt, P.; Stasiw, D. E.; Chen, J.; van der Est, A., Chromophore-radical excited state antiferromagnetic exchange controls the sign of photoinduced ground state spin polarization. *Chemical Science* **2021,** *12* (41).
4. Kirk, M. L.; Shultz, D. A.; Chen, J.; Hewitt, P.; Daley, D.; Paudel, S.; van der Est, A., Metal Ion Control of Photoinduced Electron Spin Polarization in Electronic Ground States. *J. Am. Chem. Soc.* **2021,** *143* (28), 10519-10523.
5. Stein, B. W.; Dickie, D. A.; Nedungadi, S.; Brook, D. J. R.; Shultz, D. A.; Kirk, M. L., Long-range spin dependent delocalization promoted by the pseudo Jahn-Teller effect. *J. Chem. Phys.* **2019,** *151* (20).
6. Wasielewski, M. R.; Forbes, M. D. E.; Frank, N. L.; Kowalski, K.; Scholes, G. D.; Yuen-Zhou, J.; Baldo, M. A.; Freedman, D. E.; Goldsmith, R. H.; Goodson, T.; Kirk, M. L.; McCusker, J. K.; Ogilvie, J. P.; Shultz, D. A.; Stoll, S.; Whaley, K. B., Exploiting chemistry and molecular systems for quantum information science. *Nature Reviews Chemistry* **2020,** *4* (9), 490-504.

Adjustment of the Q band position, intensity and shape of $(4n+2)\pi$ type (aza)porphyrinoids

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The Q band is generally the absorption band located at the longest wavelength of the absorption spectra of $(4n+2)\pi$ type (aza)porphyrinoids, although in some metalloporphyrins, CT bands may exist beyond this band. The adjustment of the position, intensity, and shape of the Q band is important, since this affects the colour of compounds and the various properties they may have. The Q-band positions can be tuned by the size and symmetry of the π-system, while its shape is governed by the shape or symmetry of the molecules. Its intensity is mainly affected by the energy difference between the LUMO and LUMO+1 when the HOMO and HOMO-1 energy is close, or by that between the HOMO and HOMO-1 when the LUMO and LUMO+1 energy is close or degenerate [1]. The extent of the shift of the Q band that occurs when D_{4h} type (aza)porphyrinoids are radially expanded by fusion of four benzene molecules to form tetrabenzoporphyrins (TBPs) or phthalocyanines (Pcs) can be set at unity, and by the fusion of the next four benzene to form tetranaphthaloporphyrin (TNP) or naphthalocyanine (Nc) can be reduced to ca. 0.7, and finally by a further four benzene is reduced to ca. 0.5. This indicates that the effect of fusion becomes smaller for more extended site [2]. When one to four aromatic molecules are fused to D_{4h} type porphyrinoids at the β positions of the pyrrole rings, the Q band shifts to longer wavelength and this shift is proportional to the number of fused rings. The Q band splits into two peaks when one or three aromatic molecules are fused, while when two aromatic molecules are fused, it split into two peaks only when they are fused at opposite side of D_{4h} type porphyrinoids [3]. The effect of fusion at non-radial position is much less than that of radial-fusion (we don't discuss the fusion between pyrrole β-positions and *meso*-positions). The effect of alkyl groups on the substituent positions can also be determined for Pcs by using electron-donating and -withdrawing groups [4]. When electron-donating groups are linked to what we call α- or β-positions, the Q band shifts to longer or shorter wavelengths, respectively. If we set the shift by the first four alkyl groups at α-positions at unity, the shift by the second four groups at the next four α-positions becomes ca. 2.6-2.7. The effect at β-positions is generally smaller than that at the α-positions and the shift due to electron-withdrawing groups is just opposite of electron-donating groups [4]. The Q band intensity generally increases with increasing molecular size. Thus, on going from tetraazaporphyrin (TAP) to Pc, Nc, and further to anthracocyanine (Ac), it intensifies [2]. Also, so long as the molecules are nearly flat, it intensifies with increasing number of constituting units such as pyrrole or isoindole due to the increase of energy difference between the HOMO and HOMO-1 or that between the LUMO and LUMO+1 [1,5]. The Q band can be shifted to longer wavelength by using the central metal with highly positive charge [6]. The rationale for this phenomenon will be presented in the talk.

REFERENCES

1. Gouterman, M. *J. Chem. Phys*. 1959, 30, 1139−1161.
2. Kobayashi, N., Nakajima, S., Ogata, H., Fukuda, T. *Chem. Eur. J.* 2004, 10, 6294-6312.
3. Kobayashi, N., Konami, H. In *"Phthalocyanines-Properties and Applications"*, Ed by Leznoff, C. C., B. Lever, A. B. P. Vol. IV, Chapter 6 (pp. 343-404), VCH, New York, Weinheim, Cambridge, 1996.
4. Kobayashi, N., Ogata, H., Nonaka, N., Luk'yanets, E. A. *Chem. Eur. J.* 2003, 9, 5123-5134.
5. Okujima, T., Ando, C., Agrawal, S., Matsumoto, H., Mori, S., Ohara, K., Hisaki, I., Nakae, T., Takase, M., Uno, H., Kobayashi. N. *J. Am. Chem. Soc*. 2016, 138, 7540-7543.
6. Furuyama, T., Satoh, K., Kushiya, T., Kobayashi, N. *J. Am. Chem. Soc*. 2014, 136, 765-776.

Cobalt–carbon bond formation reaction *via* the ligand reduction of cobalt porphycene

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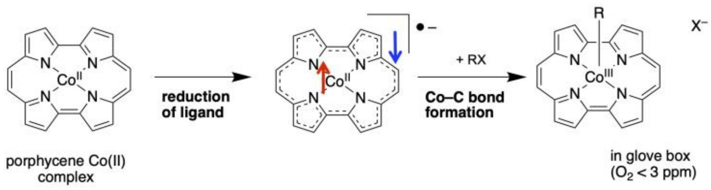
Cobalt–carbon (Co–C) bond formation is a key step of the enzymatic reaction in nature. For instance, vitamin B_{12} is known to play variety of roles such as dehalogenation or methyl group rearrangement reaction. By mimicking such natural reactions, study of cobalt complex coordinated by cyclic tetrapyrrole-based ligand have been carried out. We also reported the Co–C bond formation reaction by using hydrophobic vitamin B_{12} derivatives, which was initiated by the reduction of cobalt center from Co(II) to supernucleophilic Co(I).[1] Aiming for further improvement, it is necessary to control the valence of cobalt center, depending on the substrate. Porphycene, a tetrapyrrolic macrocycle and one of the structural isomer of porphyrin, have been attracted increasing attention because of its intriguing properties such as low energy absorption, small HOMO-LUMO gap, strong emission, as well as rich coordination chemistry and their catalytic activity[2].

The redox properties and reactivity of metalloporphycene have been studied for decades; however, the detailed experimental investigation on the reactivity and reaction mechanism under inert condition combined with theoretical calculations had not been performed so far. In this study, we found the Co–C bond formation between cobalt porphycene complex and organic halides under reductive condition. The reaction was initiated by reduction of the complex, which was proceeded not at the cobalt ion but at the ligand. Radical anion of Co(II) porphycene complex was formed and reacted with alkyl halide. Generated Co(III)–alkyl complexes were purified and characterized by ESI-TOF mass and NMR spectra. From both experimental and theoretical result, a novel reaction mechanism that porphycene works as a non-innocent ligand and is related to the change of electron density of the transition state and formation of Co–C bond was revealed (**Figure 1**) [3]. Co(II) porphycene was regenerated by irradiation of visible light, causing homolytic bond cleavage. The catalytic reaction using this reactivity was also investigated.



REFERENCES

1. H. Shimakoshi, Z. Luo, T. Inaba, Y. Hisaeda, *Dalton Trans*. 2016, 45, 10173.
2. T. Hayashi, K.Okazaki, N. Urakawa, H. Shimakoshi, J. L. Sessler, E. Vogel, Y. Hisaeda, *Organometallics* 2001, 20, 3074.
3. T. Koide, I. Aritome, T. Saeki, Y. Morita, Y. Shiota, K. Yoshizawa, H. Shimakoshi, Y. Hisaeda, *ACS Omega* **2018**, *3*, 4027.

Highly efficient photocatalytic H_2 evolution using a diprotonated porphyrin as a NIR photosensitizer

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Photocatalytic hydrogen evolution is one of important strategies toward establishing a sustainable society based on efficient solar energy utilization. UV- and visible-light-driven photocatalytic H2 evolution has been developed using molecular catalysts and semiconductors to gain considerable achievements toward the goal [1]. In light of the solar energy distribution, however, we have to consider seriously the efficient utilization of near-infrared lights that occupies almost half of the sunlight. Among numerous photocatalytic H2 evolution systems, only limited numbers of examples have been reported to be valid under NIR irradiation and the quantum yield of the catalysis should be improved [2-4].

So far, we have been working on saddle-distorted porphyrins as redox-active and photoresponsive components of catalytic reactions [5-7]. Herein, we would like to describe NIR-light-driven efficient photocatalytic H2 evolution using the diprotonated form of dodecaphenylporphyrin (H4DPP2+), which shows the broad Q band reaching to the NIR region [8], as a photosensitizer (PS) and platinum nanoparticles (PtNPs) as H2-evolving catalysts [9].

We performed photocatalytic H2 evolution using (H4DPP)Cl2 as PS, PtNPs as catalysts, and 10-methyl-9,10-dihydroacridane (AcrH2) as an electron source in CH3CN/CH3OH (1:1 v/v) in the presence of p-toluenesulfonic acid (TsOH) and trifluoroacetic acid (TFA) as a proton source under photoirradiation at 710 nm at 298 K (Figure 1). Catalytic turnover number of H2 evolution reached to 1500 for 3 h and the quantum yield was 17%, which was the highest value for H2 evolution using the NIR light.

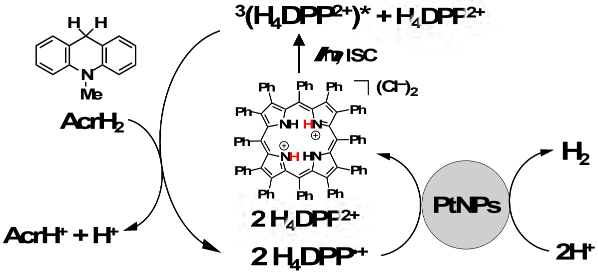
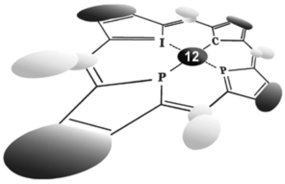


Figure 1. Photocatalytic H_2 evolution using H_4DPP^{2+} as a photosensitizer.

Mechanistic insights into the reaction were gained using various techniques. Dependence of H2 evolution rate on the concentration of (H4DPP)Cl2, AcrH2, PtNPs, TsOH or TFA was scrutinized to reveal that photoinduced electron transfer from AcrH2 to H4DPP2+ to produce H4DPP•+, which injects electron to PtNPs, is involved in the rate determining step. Together with the results of nano-second laser flash photolysis, a proposed mechanism of the photocatalytic H2 evolution will be discussed. Further development of the quantum yield of H2 evolution will be also presented.

REFERENCES

1. A. J. Esswein, D. G. Nocera, *Chem. Rev.* **2007**, *107*, 4022.
2. T. J. Whittemore *et al.*, *Nat. Chem.* **2020**, *12*, 180
3. Y. Tsuji *et al.*, *Angew. Chem. Int. Ed.* **2018**, *57*, 208.
4. Z. Lian *et al.*, *J. Am. Chem. Soc.* **2019**, *141*, 2446.
5. T. Ishizuka *et al.*, *Green Chem.* **2018**, *20*, 1975.
6. E. Aoki *et al.*, *Chem. Commun.* **2019**, *55*, 4925.
7. W. Suzuki *et al.*, *Chem. Eur. J.* **2020**, *26*, 10480.
8. S. Fukuzumi, T. Honda, T. Kojima, *Coord. Chem. Rev.* **2012**, *256*, 2488.
9. H. Kotani *et al.*, *ACS Appl. Energy Mater.* **2020**, *3*, 3193.



Atomic-Scale Analysis of Spin State of Single Molecule Magnet Bis(phthalocyaninato)terbium(III) (TbPc$_2$) Adsorbed on Superconductor Surface

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The application of magnetic molecules to the materials of the devices for the quantum information process attracts attentions. It is critical to make the sharp spin state of the molecule coupled efficiently with the electric current and substrate. The double-decker phthalocyanine complex of bis(phthalocyaninato)terbium(III) (TbPc$_2$) molecule shows intriguing single molecule magnet (SMM) behavior. It was reported to maintain the magnetic property when transferred onto the substrates Au(111) [1], Ag(111) [2]. For SMM application to the quantum computing material, however, the interaction between the molecule spin and the substrate conduction electron has to be suppressed to maintain the directional and phase information of the molecule spin. In this sense, using the superconductor (SC) as the electrode is a crucial technology since the spin state of the SC material is locked by the Cooper pair and does not disturb the molecule spin. At the same time, developing advanced detection methods of the molecule spin, which can replace conventional ESR/NMR methods and enable a single molecule spin analysis. For this purpose, the technique to read/write molecule spin state using a tunneling electron is promising. The sharp electronic state of the superconducting material, which has a high sensitivity to the presence of the magnetic field as already known by the SQUID experiment, should be utilized for this purpose. Here, we studied the TbPc$_2$ molecule adsorbed on the superconducting substrate of NbSe$_2$, in order to demonstrate of the use of the mix states between the SMM spins and the superconducting state.

Experimentally, we show the scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) studies at the sample temperature of 400 mK (Unisoku, Japan) for the system of TbPc$_2$ molecules

In the first part, we show the TbPc moiety adsorbed on NbSe$_2$ surface. TbPc$_2$ has a two spin system; J=6 at Tb atom and S=1/2 at the Pc ligand. The interaction between the two through exchange interaction(J) is critical in controlling the blocking temperature. We successfully detected the exchange energy by using the inelastic component in the tunneling spectroscopy as the excitation from the anti-parallel to the parallel coupling between the two.

Second, we show the development of the ESR/NMR detection by using tunneling spectroscopy. For this purpose, we combine the TbPc$_2$/NbSe$_2$ system with the RF wave injection and magnetic field application. We detected the variation of the electronic state formed in the SC gap by the molecule spin in a resonant manner with the combination of the magnetic field and the RF frequency. The successful detection will open the possibility for the single-molecule ESR/NMR.

REFERENCES

1. Komeda, T.; Isshiki, H.; Liu, J.; Zhang, Y.-F.; Lorente, N.; Katoh, K.; Breedlove, B. K.; Yamashita, M. Observation and electric current control of a local spin in a single-molecule magnet. Nat. Comm. 2011, 2, 217.
2. Ara, F.; Qi, Z. K.; Hou, J.; Komeda, T.; Katoh, K.; Yamashita, M. A scanning tunneling microscopy study of the electronic and spin states of bis(phthalocyaninato)terbium(III) (TbPc2) molecules on Ag(111). Dalton Trans. 2016, 45, 16644-16652.

Radical Anion Metal-free and Metal-containing Porphyrins, Phthalocyanines and Trithiadodecaazahexaphyrins

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Metallophthalocyanines (Pc) and porphyrins (P) and their analogs can be perspective components in the design of conducting and magnetic compounds.They can be obtained under reduction of metallomacrocycles when unpaired spins appear on them. We developed universal methods for preparation of reduced mono- and double-decker phthalocyanines in form of single crystals. Series of salts with radical anions and dianions of fluorenated coppper(II) phthalocyanines is also presented. Spin state of copper(II) is preserved under reduction and it is centered on the macrocycles exclusively [1]. Reduction of copper(II) and nickel(II) tetraphenylporphyrinates showed preservation of Cu^{II} under reduction to form the $\{Cu^{II}(TPP^{4-})\}^{2-}$ dianions, whereas Ni^{II} transfers to paramagnetic nickel(I) in the $\{Ni^{I}(TPP^{2-})\}^{-}$ monoanions. Transtion from low- to high spin state of $\{Ni^{I}(TPP^{2-})\}^{-}$ is explained by thermoinduced charge transfer from nickel(I) to TPP^{2-} to form high spin Ni^{II} ($S = 1$) and $TPP^{\bullet 3-}$ ($S = 1/2$) [2]. Large trithiadodecaazahexaphyrins contain three Ni^{II} or Cu^{II} ions in bonded into the triangles through central oxygen atom. Their reduction yields the $\{Cu^{II}_3O(Hhp^{\bullet 6-})\}^{2-}$ and $\{Ni^{II}_2Ni^{I}O(Hhp^{5-})\}^{2-}$ dianions in which we observed strong magnetic exchange between Cu^{II}_3O ($S = 1/2$) and $Hhp^{\bullet 6-}$ ($S = 1/2$) as well as unusual transtion from singlet to quartet state assotiated with thermal population of excited triplet state of Hhp^{5-} [4]. This work was supported by the Ministry of Science and Higher education (task AAAA-A19-119092390079-8).

REFERENCES

1. D. V. Konarev, M. A. Faraonov, M. S. Batov, M. G. Andronov, A. V. Kuzmin, S. S. Khasanov, A. Otsuka, H. Yamochi, H. Kitagawa, R. N. Lyubovskaya, *Dalton Trans.,* 2020, 49, 16821–16829.
2. D. I. Nazarov, M. G. Andronov, S. S. Khasanov, E. I. Yudanova, A. F. Shestakov, A. Otsuka, H. Yamochi, H. Kitagawa, D.V. Konarev, *Dalton Trans*., 2021, 50, 15620–15632.
3. D. I. Nazarov, M. K. Islyaikin, E. N. Ivanov, O. I. Koifman, M. S. Batov, L. V. Zorina, S. S. Khasanov, A. F. Shestakov, E. I. Yudanova, Y. A. Zhabanov, D. A. Vyalkin, A. Otsuka, H. Yamochi, H. Kitagawa, T. Torres, D. V. Konarev. *Inorg. Chem*. 2021, 60, 9857–9868.

Synthesis, Chemistry and Chemical Biology of Transition Metal Analogues of the Natural B_{12}-Derivatives

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The natural vitamin B_{12} derivatives represent fascinatingly complex, ring-contracted, helical corrins in an exclusive combination with cobalt ions.[1] The intriguing preeminent biological use of cobalt in the B_{12}-cofactors [2] has stimulated the quest for understanding the particular biological selection of cobalt and for finding ways of replacing this transition metal by other ones.[3] The recent availability of well characterized metal analogues of the B_{12}-cofactors has provided deep insights into their structures and valuable applications in chemical biology.[4]
Crucial advances with bioengineered B_{12}-biosynthesis [5, 6] have laid the groundwork for a preparative access to the metal-free corrinoid hydrogenobyric acid (Hby),[7] a rational starting material for the synthesis of B_{12} metal-analogues, Rh(III), Zn(II) and Ni(II)corrins, such as chlororhodibalamin,[8] zincobalamin [9] and nibalamin.[10]
This lecture presents synthetic roads to metal complexes of the natural corrinoids, insights into their structures and their use as structural mimics of natural vitamin B_{12} derivatives.[11] Among such metal analogues are effective ‘antivitamins B_{12}’,[12] promising candidates for interesting biological / biomedical applications.[13]

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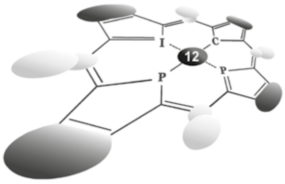
REFERENCES

1. A. Eschenmoser, *Angew. Chem. Int. Ed*., 27 (1988) 5-39.
2. J.M. Pratt, Inorganic Chemistry of Vitamin B12, *Academic Press, New York*, 1972.
3. V.B. Koppenhagen, Metal-Free Corrinoids and Metal Insertion, in: D. Dolphin (Ed.) B12, *John Wiley & Sons*, 1982, pp. 105-150.
4. F.J. Widner, A.D. Lawrence, E. Deery, D. Heldt, S. Frank, K. Gruber, K. Wurst, M.J. Warren, B. Kräutler, *Angew. Chem. Int. Ed*., 55 (2016) 11281-11286.
5. D.A. Bryant, C.N. Hunter, M.J. Warren, J. *Biol. Chem*., 295 (2020) 6888-6925.
6. E. Deery, S. Schroeder, A.D. Lawrence, S.L. Taylor, A. Seyedarabi, J. Waterman, K.S. Wilson, D. Brown, M.A. Geeves, M.J. Howard, R.W. Pickersgill, M.J. Warren, *Nat. Chem. Biol*., 8 (2012) 933-940.
7. C. Kieninger, E. Deery, A.D. Lawrence, M. Podewitz, K. Wurst, E. Nemoto-Smith, F.J. Widner, J.A. Baker, S. Jockusch, C.R. Kreutz, K.R. Liedl, K. Gruber, M.J. Warren, B. Kräutler, *Angew. Chem. Int. Ed*. 58 (2019) 10756-10760.
8. F.J. Widner, C. Kieninger, K. Wurst, E. Deery, M.J. Warren, B. Kräutler, *Synthesis 53* (2021) 332–337.
9. C. Kieninger, J.A. Baker, M. Podewitz, K. Wurst, S. Jockusch, A.D. Lawrence, E. Deery, K. Gruber, K.R. Liedl, M.J. Warren, B. Kräutler, *Angew. Chem. Int. Ed.,* 58 (2019) 14568-14572.
10. C. Kieninger, K. Wurst, M. Podewitz, M. Stanley, E. Deery, A.D. Lawrence, K.R. Liedl, M.J. Warren, B. Kräutler, *Angew. Chem. Int. Ed*., 59 (2020) 20129-20136.
11. B. Kräutler, *Chem. Eur. J.,* 21 (2015) 11280-11287.
12. B. Kräutler, *Chem. Eur. J.,* 26 (2020) 15438-15445.
13. F. Zelder, M. Sonnay, L. Prieto, *ChemBioChem*, 16 (2015) 1264-1278.



Structure and properties of Cu-phthalocyanine-based molecular solids from first principles

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Cu-phthalocyanine based molecular solids are widely used in various areas, from paints to optoelectronics. While much theoretical effort has been directed at the Cu-phthalocyanine molecule and its derivatives, molecular solids have not been studied in as much detail. Here, we present a first principles study, based on advanced approaches within density functional theory, that considers the structure of various Cu-phthalocyanine polymorphs and assesses the ensuing electronic structure.

Prochiral Solvating Agents (*pro*-CSA): NMR Detection of Enantiomeric Excess without Formation of Diastereomers

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Chirality is a key feature in many biological events and is especially important in the development of new pharmaceuticals where the pharmacological effect depends on the identity of enantiomer (e.g. ibuprofen, atropine, thalidomide, etc.). There are three standard protocols of enantiomeric excess (*ee*) measurements using nuclear magnetic resonance (NMR) spectroscopy. However, these are always based on formation of diastereomers in solution. We have developed NMR sensing method utilizing prochiral porphyrin derivatives (example can be seen in Fig. 1a) as detectors of analytes's *ee*. In this method, the formation of diastereomers is not required (Fig. 1b), and the *ee* is obtained from the detector's NMR spectrum as the magnitude of splitting Δ*δ* of reporting group (Fig. 1c), which has a fundamental linear dependence on *ee* (Fig. 1d) [1-5]. Based on symmetry requirements, we also tested the pro-CSA mechanism on small systems, such as benzylamine (prochiral detector) with 2-phenoxylpropionic acid (analyte) [6] or salen-Zn$_2$ coordination complex (prochiral detector) with 2-phenoxylpropionic acid (analyte) [7]. The mechanism, drawbacks and potential applications of pro-CSA sensing method will be discussed.

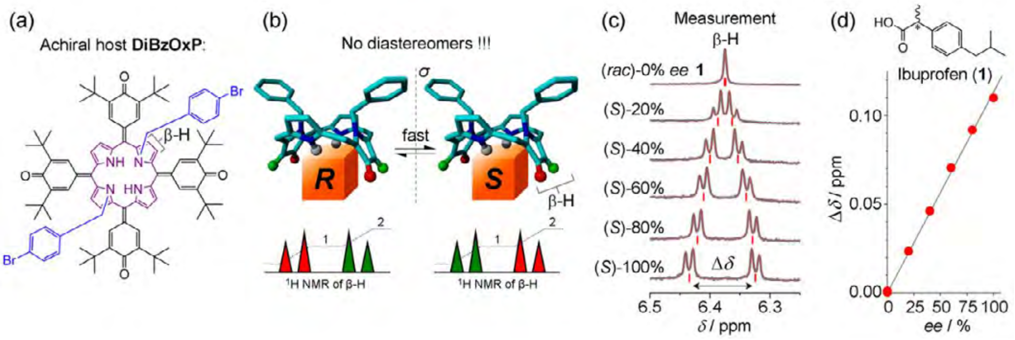

Figure. 1. (a) Structure of prochiral porphyrin derivative **DiBzOxP**. (b) Schematic illustration of sensing mechanism. (c) NMR spectra of porphyrin β-H reporting group in the presence of various *ee* of ibuprofen (**1**) analyte. (d) Fundamental linear relationship between induced chemical shift non-equivalency Δ*δ* and *ee* as obtained from (c).

REFERENCES

1. A. Shundo, J. Labuta, J. P. Hill, S. Ishihara and K. Ariga. *J. Am. Chem. Soc.* **2009**, *131*, 9494.
2. J. Labuta, S. Ishihara, A. Shundo, S. Arai, S. Takeoka, K. Ariga and J. P. Hill. *Chem. Eur. J.* **2011**, *17*, 3558.
3. J. Labuta, S. Ishihara, T. Šikorský, Z. Futera, A. Shundo, L. Hanyková, J. V. Burda, K. Ariga and J. P. Hill. *Nat. Commun.* **2013**, *4*, 2188.
4. J. Labuta, J. P. Hill, S. Ishihara, L. Hanyková, K. Ariga. *Acc. Chem. Res.* **2015**, *48*, 521**.**
5. J. Labuta, S. Ishihara, J. P. Hill. *J. Porphyrins Phthalocyanines* **2020**, *24*, 320.
6. S. Ishihara, J. Labuta, Z. Futera, S. Mori, H. Sato, K. Ariga, J. P. Hill. *J. Phys. Chem. B* **2018**, *122*, 5114.

Self-Assembly-Directed Organization of a Fullerene-Bisporphyrin into Supramolecular Giant Donut Structures

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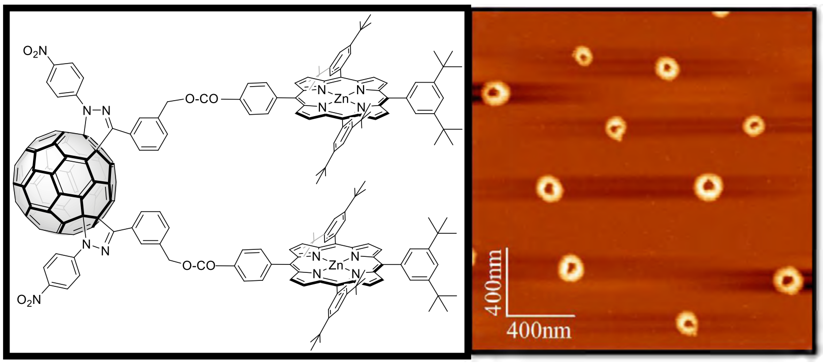
Supramolecular polymers with incorporated fullerene and porphyrin have attracted interest in construction of functionalized supramolecular polymers or oligomers, due to their unique physical and chemical properties.
In the other hand, functional materials comprised of spontaneously self-assembled electron donor and acceptor entities capable of generating long-lived charge-separated states upon photo-illumination are in great demand as they are key in building the next generation of light energy harvesting devices. However, creating such well-defined architectures is challenging due to the intricate molecular design, multi-step synthesis, and issues associated in demonstrating long-lived electron transfer.
Here, we have newly synthesized, by tether-directed functionalization, a [60]fullerene *e*-bisadduct carrying two Zn-porphyrins (Figure), and demonstrate supramolecular organization and photophysical events. Remarkably, the supramolecular assembly of the present bisporphyrin-C_{60} forms donut-shape aggregates, primarily via π-π type charge transfer interactions. Upon photoexcitation, the supramolecular assembly generates long-lived charge-separated states of ≈1−40 μs lifetime due to electron/hole delocalization within the supramolecular structure.



REFERENCES

1. R. Caballero, M. Barrejón, J. Cerdá, J. Aragó, S. Seetharaman, P. de la Cruz, E. Ortí, F. D'Souza, F. Langa. *J. Am. Chem. Soc.* **2021**, *143*, 11199.

How far can the dynamic chirality of Möbius hexaphyrins be controlled?

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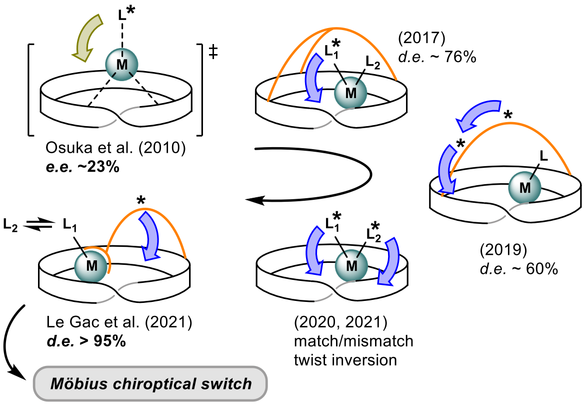
Among various types of chirality, that inherent to the Möbius topology has remained underexplored, partly due to the difficult access to Möbius compounds [1]. In particular, the asymmetric preparation of molecular Möbius rings is a challenge [2], requiring a fine understanding of the transfers of chirality at work. Focusing on the Möbius [28]hexaphyrin scaffold, our group has investigated an original approach taking advantage of its conformational flexibility (dynamic Möbius chirality) [3]. This feature enables chirality induction under thermodynamic control, which is attractive to design innovative responsive systems including Möbius metallo-receptors. Owing to a remarkable interplay between aromaticity, guest recognition, and chirality transfer, Möbius Zn(II)-hexaphyrins sustain remarkable stereoselectivities and tunable chiroptical properties under the influence of one or several stereogenic sources (exo or endogenous). Recently, our dynamic approach has been extended to a situation where a source of fix chirality is part of a covalently linked coordinating arm [3e], leading to the following main findings: (i) both *P* and *M* Möbius configurations are reached *in-situ* by simple addition of suitable achiral effectors, tuning the way a fix stereogenic moiety interacts with the ring. Impressive stereoselectivities (diast. excess > 95%) highlight the most efficient transfer of chirality to a Möbius ring reported so far; (ii) these achiral effectors generate distinct chiroptical signatures, and switching between two chiral states was successfully achieved with high robustness (10 cycles) owing to ligand exchange. These results stimulate the further development of Möbius porphyrinoids as switchable chiral platforms.



REFERENCES

1. a) H. S. Rzepa, *Chem. Rev.* **2005**, *105*, 3697-3715; b) R. Herges, *Chem. Rev.* **2006**, *106*, 4820-4842.
2. a) T. Tanaka, T. Sugita, S. Tokuji, S. Saito, A. Osuka, *Angew. Chem. Int. Ed.* **2010**, *49*, 6619-6621; b) S. Nishigaki, Y. Shibata, A. Nakajima, H. Okajima, Y. Masumoto, T. Osawa, A. Muranaka, H. Sugiyama, A. Horikawa, H. Uekusa, H. Koshino, M. Uchiyama, A. Sakamoto, K. Tanaka, *J. Am. Chem. Soc.* **2019**, *141*, 14955-14960.
3. a) H. Ruffin, G. Nyame Mendendy Boussambe, T. Roisnel, V. Dorcet, B. Boitrel, S. Le Gac, *J. Am. Chem. Soc.* **2017**, *139*, 13847-13857; b) R. Benchouaia, N. Cissé, B. Boitrel, M. Sollogoub, S. Le Gac, M. Ménand, *J. Am. Chem. Soc.* **2019**, *141*, 11583-11593; c) B. Boitrel, S. Le Gac, *Chem. Commun.* **2020**, *56*, 9166-9169; d) B. Boitrel, S. Le Gac, *Chem. Commun.* **2021**, *57*, 3559-3562; e) H. Ruffin, A. Fihey, B. Boitrel, S. Le Gac, *Angew. Chem. Int. Ed.* 10.1002/anie.202113844.

Synthesis and Properties of Core Modified Corrole Analogues and anti-Aromatic Hexaphyrins

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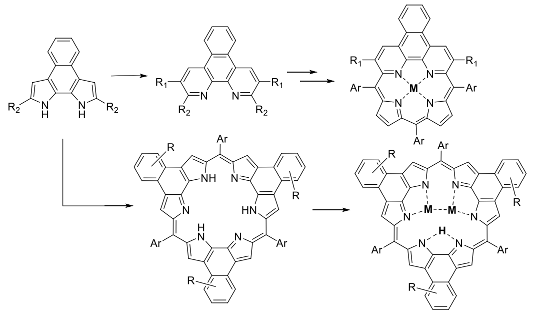
Hexapyrins are family of cross conjugated hexapyrrolic macrocycles and many isomeric, planar or non-plannar analogues have been well documented. Among them, the anti-aromatic hexapyrrolic macrocycles with (1,0,1,0,1,0) macrocyclic ring connections are rare class of compounds. These system are called rosarrin and could exist as non-aromatic, aromatic or anti-aromatic. Along with these line of research, we have been interested in the synthesis of the anti-aromatic systems and in studying their redox chemistry. We have demonstrated the full redox cycle of this system and characterize the 25π electron cation-radical species using single crystal X-ray crystallography. These intriguing properties motivate us to pursue the synthesis of the new systems possessing substituents on the periphery or meso-positions. With these regards, we developed a synthetic method of the key building blocks that can lead to the various peripherally substituted naphthorosarrins. Electrochemical and photophysical properties of the newly synthesized compounds were studied in detail. The redox chemistry and protonation behaviour of the new derivatives showed substituents dependent changes in aromaticity. We will also present the finding associated with one carbon insertion reaction of naphthobipyrrole. The double, successive one carbon insertion reaction of naphthobipyrrole resulted in the formation of corresponding naphthobipyridine (diazatriphenylene derivative). The naphthobipyridines are versatile building blocks for the synthesis of pyridine containing corrole analogues. Since this new bipyridine containing corroloids are mono anionic ligand and thus they can be stabilized various oxidation states of the metalion. The properties of the metal complexes will be discussed in detail.



REFERENCES

1. Trapping of Stable [4n+1] π-Electron Species from Peripherally Substituted, Conformationally Rigid, Antiaromatic Hexaphyrins, Dikhi Firmansyah, Seong-Jin Hong, Ranjan Dutta, Qing He, Jinhee Bae, Hongil Jo, Hakwon Kim, Kang Min OK, Vincent M. Lynch, Hye Ryung Byon, Jonathan L. Sessler and Chang-Hee Lee*,* *Chem. Eur. J.* **2019**, *25*, 3525.
2. Structural, Photophysical, and Magnetic Circular Dichroism Stud-ies of Three Rigidified meso-Pentafluorophenyl-substituted Hex-aphyrin Analogues, Masatoshi Ishida, Taniyuki Furuyama, Jong Min Lim, Sangsu Lee, Zhan Zhang, Sudip K. Ghosh, Vincent M. Lynch, Chang-Hee Lee, Nagao Kobayashi, Dongho Kim and Jonathan L. Sessler, *Chem. Eur. J.* **2017**, 23, 6682.
3. Protonation-coupled redox reaction in planar antiaromatic *meso*-pentafluorophenyl-substituted phenylene bridged annulated rosarins. Masatoshi Ishida, Soo-Jin Kim, Christian Preihs, Kei Ohkubo, Jong Min Lim, Byung Sun Lee, Vincent M. Lynch, Vladimir V. Roznyatovskiy, Pradeepta K. Panda, Chang-Hee Lee, Shunichi Fukuzumi, Dongho Kim, Jonathan L Sessler, *Nature Chemistry*, **2013**, 5, 15.

Synthetic Model Systems for Bacterial Nitric Oxide Reductase

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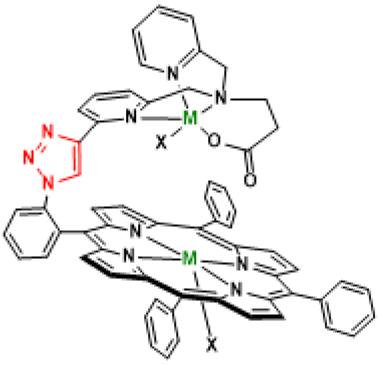
The nitrogen cycle is one of the most important biogeochemical cycles on earth, as nitrogen is an essential element to all forms of life. Denitrification is a major pathway in the nitrogen cycle where microbes utilize nitrite and nitrate as electron acceptors for anaerobic respiration. A key step in denitrification is the two-electron reduction of nitric oxide (NO) to nitrous oxide (N_2O), which is catalyzed by respiratory NO reductases (NORs).[1] Bacterial NOR (NorBC or *c*NOR) is a membrane-bound enzyme found in denitrifying bacteria that has an unusual diiron heme b_3/non-heme Fe_B active site. The mechanism under which NorBC operates is only ill defined, due to the fact that the protein is difficult to work with and the lack of any experimentally observed intermediates.[1] In the $Fe^{III}Fe^{III}$ resting state, the heme b_3 is ligated by a proximal His, and the non-heme Fe center is coordinated by three His residues and a Glu. Also, an oxo bridge connects the two metal centers, making the Fe-Fe distance only 3.5 Å.[2] Synthetic model systems provide the opportunity to add insight into the mechanism of action of this enzyme, by investigating structural and electronic factors that contribute to the observed reactivity. We have developed a synthetic model system of NorBC, consisting of a tetraphenylporphyrin-derivative clicked to a modified BMPA-Pr^- ligand,[3] as shown in the figure below.[4] This complex has been characterized by EPR, NMR and UV-Vis spectroscopy, and mass spectrometry. Armed with this synthetic model, we then investigated the interaction of this complex and related derivatives with NO.



REFERENCES

1. Lehnert, N.; Kim, E.; Dong, H. T.; Harland, J. B.; Hunt, A. P.; Manickas, E. C.; Oakley, K. M.; Pham, J.; Reed, G. C.; Sosa Alfaro, V. The Biologically Relevant Coordination Chemistry of Iron and Nitric Oxide: Electronic Structure and Reactivity. *Chem. Rev.* **2021**, *121*, 14682-14905.
2. Hino, T.; Matsumoto, Y.; Nagano, S.; Sugimoto, H.; Fukumori, Y.; Murata, T.; Iwata, S.; Shiro, Y. Structural Basis of Biological N_2O Generation by Bacterial Nitric Oxide Reductase. *Science* **2010**, *330*, 1666-1670.
3. Berto, T. C.; Hoffman, M. B.; Murata, Y.; Landenberger, K. B.; Alp, E. E.; Zhao, J.; Lehnert, N. Structural and Electronic Characterization of Non-Heme Fe(II)-Nitrosyls as Biomimetic Models of the Fe_B Center of Bacterial Nitric Oxide Reductase (NorBC). *J. Am. Chem. Soc.* **2011**, *133*, 16714–16717.
4. Harland, J. B.; Samanta, S.; Lehnert, N. Rigid Bacterial Nitric Oxide Reductase (NorBC) Models Employing Click Chemistry. Manuscript in preparation.

Silicon Phthalocyanines for Organic Photovoltaics and Organic Thin Film Transistors

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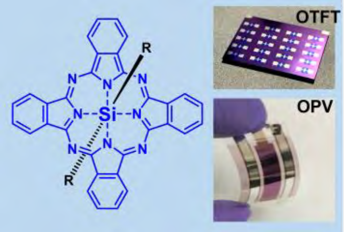
Silicon phthalocyanines are emerging n-type semiconductors for use in organic photovoltaics (OPVs) and organic thin-film transistors (OTFTs).[1] Their low synthetic complexity paired with their versatile axial group facilitates the fine-tuning of their chemical properties, solution properties and processing characteristics without significantly affecting their frontier orbital levels or their absorption properties. The crystal engineering and film forming characteristics of silicon phthalocyanine semiconductors can be tuned through appropriate axial group functionalization, therefore facilitating their integration into both OTFTs and OPVs by solution processing or vapor deposition.



In OPVs: Silicon Phthalocyanines have proven to be effective ternary additives leading to 20% increase in power conversion efficiency of poly(3-hexylthiophene):phenyl-C61-butyric acid methyl ester (P3HT:PC61BM) bulk heterojunction (BHJ) OPVs by increasing the photogeneration at 685 nm. Recently, we demonstrated that SiPcs are effective ternary additives with other conjugated polymer systems including PCDTBT and that the optimal amount of SiPc changes when scaling from spin coating on glass to blade coating on PET substrates.[2] We have also shown that SiPcs can replace the fullerenes all together and provide low cost OPVs when paired with P3HT with power conversion efficiency > 4%.[3] When paired with PBDB-T we obtain high high open circuit voltages approaching 1.1 V.[4]

In OTFTs: We were the first to integrate SiPcs into OTFTs, and unlike the majority of phthalocyanines, SiPcs are inherently better electron transporting materials then hole transport materials. We demonstrated n-type mobilities on the order of 0.5 cm^2/Vs which is among the best of all phthalocyanines.[5] Through axial functionalization we reported that changes in the electron withdrawing character of the axial group lead to predictable drops in device threshold voltage from 45 V to 5 V.[6] The axial group can also be used to improve the SiPc solubility leading to solution processable OTFTs where the choice of axial group also dictates the thin film morphology an ultimately the resulting device performance.[7] GIWAXS studies show that processing conditions and choice of axial groups leads to changes in molecular alignment at the interface providing critical insight into device optimization.

REFERENCES

1. *ACS Applied Materials & Interfaces*. **2021**, 13, 31321-31330
2. *Solar RRL*. **2021**, 5, 2100432
3. *Materials Advances*. **2021**, 2, 2594-2599
4. *Organic Electronics*. **2020**, 87, 105976
5. *Advanced Electronic Materials*. **2019**, 5, 1900087
6. *ACS Appl. Electron. Mater.* **2021**, 3, 5, 2212–2223
7. *ACS Applied Materials & Interfaces*. **2020**, 13, 1008-1020

Phthalocyanines with non-traditional Early Transition-Metals

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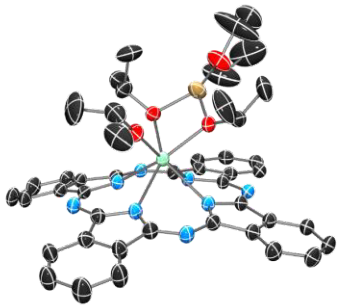
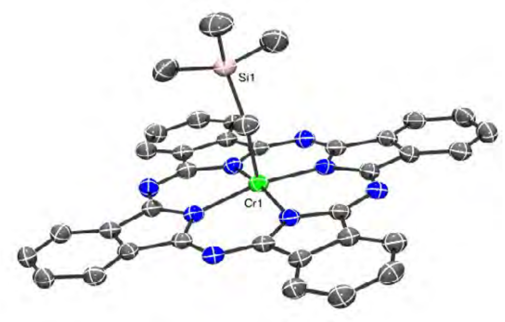
The spectroscopic and redox properties of metallophthalocyanines (PcM) are active areas of research. PcM complexes can be successively reduced using chemical, electrochemical, or photochemical methods to give rise to species containing reduced Pc(3-) to Pc(5-) ligands or oxidized to Pc(-1) and Pc(0). These species are usually generated and characterized *in situ* and have only recently begun to be isolated and structurally characterized. In particular, there are few examples of phthalocyanines with early-transition and f-block metals - despite the rich organometallic-type reactivity of these metals - and thus we targeted new PcM complexes in this underdeveloped area of the periodic table. Given their larger ionic size, the unusual structural feature of the metal centre protruding far out of the Pc cavity is often prevalent. Hence, the exposure of the coordination sphere of these Lewis-acidic (often d0) metals makes these PcM complexes attractive catalysts; this cis-oriented axial ligation also drastically improves the solubility, despite the Pc-ring remaining unsubstituted.

In this presentation the isolation and structural characterization of new PcM materials with M=chromium, zirconium, niobium and molybdenum will be described, along with rare structurally characterized examples of their reduced Pc(4-) and Pc(3-) complexes. Their electronic structure will be discussed using a combination of spectroscopic and structural techniques. Their reactivity with a series of small molecules and ability to catalytically polymerize lactide will be presented. Time permitting, our related work on organometallic PcLn-based complexes will also be described.



Na(THF)PcZr(OiPr)$_3$ ate complex



Organometallic PcCr-CH$_2$SiMe$_3$

REFERENCES

1. W. Zhou, D.B. Leznoff, *Chem. Commun.*, **2018**, *54*, 1829-1832. W. Zhou, J.R. Thompson, C.C. Leznoff, D.B. Leznoff, *Chem. Eur. J.*, **2017**, *23*, 2323-2331; R. Platel, W. Zhou, T.T. Tasso, T. Furuyama, N. Kobayashi, D.B. Leznoff, *Chem. Commun.,* **2015**, 5986-89; D. McKearney, W. Zhou, V.E. Williams, D.B. Leznoff, *Chem. Commun.*, **2019**, *55*, 6696-6699; Y. Ganga-Sah, E. Tajbakhsh, R.H. Platel, W. Zhou, D.B. Leznoff, *J. Porph. Phthalocyanines*, **2019**, *23*, 1592-1602; W. Zhou, D. McKearney, D.B. Leznoff, *Chem. Eur. J.*, **2020**, *26,* 1027-31.

Quantum chemical modeling of porphyrin ligand based redox catalysis

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Porphyrins are essential ligands for metal cofactors in biology. Due to the high-lying π orbitals and low-lying π* orbitals, porphyrins could be redox non-innocent ligand in the catalytic redox reactions. A well-known elegant example is the critical compound I species found in P450 dependent enzymes, in which the electronic structure of the formally Fe(V)=O species is described as a Fe(IV)=O porphyrin radical cation. The involvement of porphyrin ligands as electron donors and as electron acceptors has been analyzed for oxidation/reduction reactions using density functional methods. Examples of aldoxime dehydration, CO_2 reduction, and O_2 reduction catalyzed by metal porphyrin-based catalysts are presented.

REFERENCES

1. S. Shaik, S. Cohen, Y. Wang, H. Chen, D. Kumar, W. Thiel *Chem. Rev.* **2010**, 110, 2, 949
2. R.-Z. Liao, W. Thiel *J. Phys. Chem. B* 2012, 116, 9396
3. Y.-Q.Zhang, J.-Y. Chen, P. E. M. Siegbahn, R.-Z. Liao *ACS Catal.* **2020**, 10, 6332
4. R.-Z. Liao *unpublished results*.

Toward the *de novo* synthesis of (bacterio)chlorophylls

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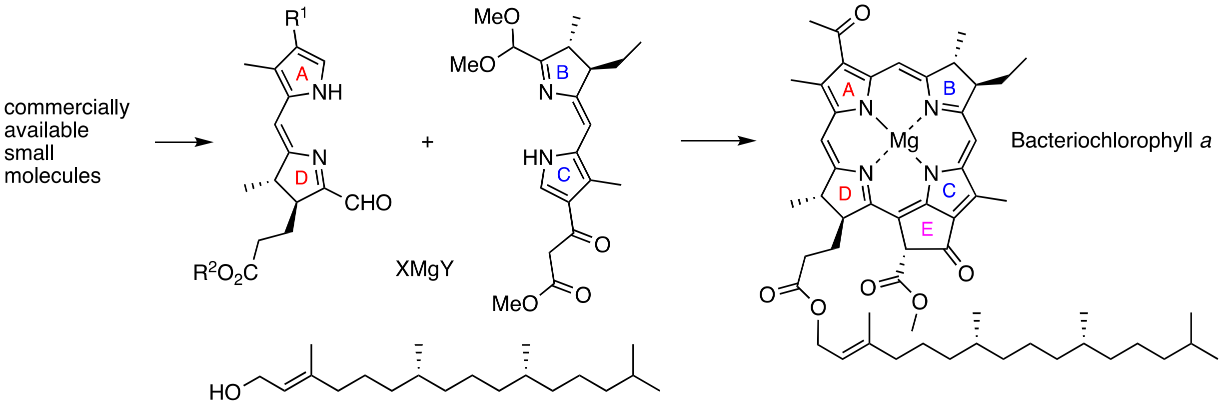
We aspire to develop practical synthetic routes to the native photosynthetic pigments (e.g., chlorophyll *a*, bacteriochlorophyll *a*) and thereby open the door to address physiological, photophysical, ecological, and evolutionary questions in the plant sciences. Sweeping synthetic advances have accrued since Woodward's magisterial campaign toward chlorophyll *a* in 1960 [1]. Our 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 in a stereoselective manner at the outset of the synthesis. To date we have prepared the individual A–D constituents (≥10 mmol each) and have validated the ability to carry stereochemically defined substituents over the entire course of the synthesis [2–5]. A stereoselective synthesis of phytol also is under investigation. This research is supported by the NSF (CHE-2054497).



REFERENCES

1. "Total Synthesis Campaigns Toward Chlorophylls and Related Natural Hydroporphyrins – Diverse Macrocycles, Unrealized Opportunities," Liu, Y.; Zhang, S.; Lindsey, J. S. *Nat. Prod. Rep.* **2018**, *35*, 879–901.
2. "Asymmetric Synthesis of a Bacteriochlorophyll Model Compound Containing *trans*-Dialkyl Substituents in Ring D," Chau Nguyen, K.; Wang, P.; Lindsey, J. S. *J. Org. Chem.* **2020**, *85*, 6605–6619.
3. "Study of Conditions for Streamlined Assembly of a Model Bacteriochlorophyll from Two Dihydrodipyrrin Halves," Chau Nguyen, K.; Wang, P.; Lindsey, J. S. *New J. Chem.* **2021**, *45*, 569–581.
4. "Synthesis of Model Bacteriochlorophylls Containing Substituents of Native Rings A, C and E," Chung, D. T. M.; Tran, P. V.; Chau Nguyen, K.; Wang, P.; Lindsey, J. S. *New J. Chem.* **2021**, *45*, 13302–13316.
5. "Synthesis of AD-Dihydrodipyrrins Equipped with Latent Substituents of Native Chlorophylls and Bacteriochlorophylls," Wang, P.; Lindsey, J. S. *J. Org. Chem.* **2021**, *86*, 11794–11811.

Catalytic promiscuity in iron and manganese porphyrin-containing mini-enzymes

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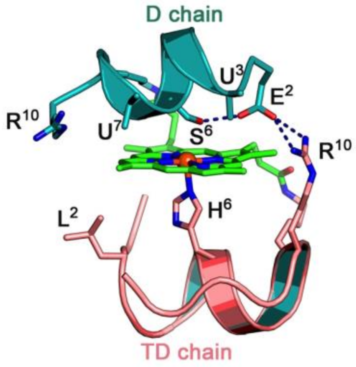
Porphyrin cofactors may be considered as the ideal example for demonstrating how properly built interactions may be terrifically fruitful in specifying their reactivities. Such cofactors are ubiquitous and perform a wide range of crucial functions, such as oxygen transport and storage, electron transfer, oxidation/oxygenation reactions [1]. This spectacular task is possible thanks to the fine-tuning of the cofactor chemical properties, by acting at least at three different levels: (i) nature of the metal center; (ii) cofactor molecular structure; (iii) covalent and non-covalent interactions from the surrounding host. Wise "design" at these three levels affects the cofactor coordination sphere (geometry, metal/ligand affinity, complex stability) and its conformational freedom (in/out-of-plane distortions), electrochemistry (electron transfer, substrate activation) and photochemistry [2].

Inspired by Nature, the scientific community has devoted many efforts to replicate this wise design, with the aim of developing artificial molecules endowed with specific functions [2,3].



*MC6*a designed model*

To this aim, we developed Mimochromes, simple yet functional synthetic models, featuring two helical peptides that are covalently linked to deuteroporphyrin. Either one or both peptide chains contain a His residue acting as axial ligand to the metal ion inserted into the porphyrin ring (see Figure). We have demonstrated that the Mimochome scaffold is well-suited to host a wide set of metal ions, thus enabling to explore a variety of different chemistries and applications. [2,3]. Mimochrome VI*a (MC6*a), the most active analogue, acts as a proficient and promiscuous catalyst as it switches its activity from an efficient peroxidase to peroxygenase and hydrogenase when iron is replaced by manganese or cobalt, respectively [4,5].

Our recent results in the oxidative dehalogenation of halogenated phenols by FeMC6*a and in the selective oxidation of indole at its C3 position by MnMC6*a will be discussed. They confirm that Mimochromes are able to surpass the kinetic parameters of natural peroxidases, providing active and robust bioinspired catalysts. Further, they show excellent tolerance in organic solvents, thereby facilitating their use in aqueous:organic mixtures. All these beneficial features make Mimochromes potential candidates in applicative and industrial processes.

REFERENCES

1. R. A. Baglia, J. P. T. Zaragoza and D. P. Goldberg, *Chem. Rev.* 2017, **117**, 13320–13352
2. L. Leone, M. Chino, F. Nastri, O. Maglio, V. Pavone and A. Lombardi, *Biotechnol. Appl. Biochem.* 2020, **67**, 495–515, and references therein.
3. F. Nastri, D. D'Alonzo, L. Leone, G. Zambrano, V. Pavone and A. Lombardi, *Trends Biochem. Sci.* 2019, **44**, 1022–1040.
4. L. Leone, D. D'Alonzo, O. Maglio, V. Pavone, F. Nastri and A. Lombardi, *ACS Catalysis* 2021, **11**, 9407–9417.
5. V. Firpo, J. M. Le, V. Pavone, A. Lombardi and K. L. Bren, *Chem. Sci.* 2018, **9**, 8582–8589.

BODIPYs: Structure and Excited-State Regulation

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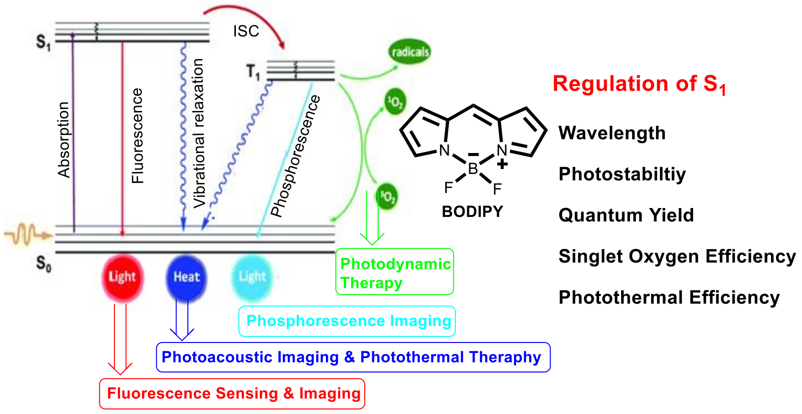
The 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY)-based molecules have emerged as interesting dyes in a multitude of diverse biotechnological fields such as probe for diagnosis by means of bioimaging and photosentitizers in photodynamic and photothermal therapy of cancer [1]. The key of functional design of BODIPY to meet the fundamentals of each application field is the excited-state regulation [2]. In my talk, I will demonstrate how to control the excited-state properties of BODIPYs through molecular structure design to achieve red/NIR absorption, super photostability, metal-free photosensitizer and/or photothermal chromophores [3-6].



REFERENCES

1. Sola-Llano R, and Bañuelos J. BODIPY Dyes-A Privilege Molecular Scaffold with Tunable Properties, Bañuelos-Prieto J, and Sola Llano R, IntechOpen, 2018.
2. Lu H, Mack J, Yang Y, Shen Z. Structural modification strategies for the rational design of red/NIR region BODIPYs. *Chem Soc Rev.* **2014**, *43*, 4778.
3. Xu N, Xiao Y, Ni Z, Gai L, Zhou Z, Lu H. Rationalizing the effect of benzo-fusion at [a] and [b] positions of BODIPY on fluorescence yields. *Phys. Chem. Chem. Phys.* **2021**, *23*, 17402.
4. Feng S, Qu Z, Zhou Z, Chen J, Gai L, Lu H. Si-Bridged annulated BODIPYs: synthesis, unique structure and photophysical properties. *Chem. Commun.* **2021**, *57*, 11689.
5. Lu H, Nakamuro T, Yamashita K, Yanagisawa H, Nureki O, Kikkawa M, et al. B/N-Doped pArylenevinylene Chromophores: Synthesis, Properties, and Microcrystal Electron Crystallographic Study. *J. Am. Chem. Soc.* **2020**, *142*, 18990 .
6. Gai L, Zhang R, Shi X, Zhou Z, Zhang J, Lu H, Guo Z. BOINPYs: rapid access to novel photothermal chromophores, in preparation.

Porous Corrole Framework Materials

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The corrole unit from the porphyrinoid family represents one of the most important ligands in the field of coordination chemistry, which creates a unique environment allowing for the observation of unusual electronic states of bound metal cations and has shown great promise in various applications. Nevertheless, studies that directly and systematically introduce these motifs in porous materials for targeting further functionalizations have been rarely explored. Herein, we demonstrate the employment of corrole as a new class of building block for the construction of functional porous materials including metal-organic framework [1], covalent organic framework [2], and porous organic polymer (POP) [3] as well as the exploration of resultant porous corrole framework materials for applications in heterogeneous catalysis and photodynamic therapy.

REFERENCES

1. "Robust Corrole-Based Metal-Organic Frameworks with Rare 9-Connected Zr/Hf-Oxo Clusters" Zhao, Y.; Qi, S.; Niu, Z.; Peng, Y.; Shan, C.; Verma, G.; Wojtas, L.; Zhang, Z.; Zhang, B.; Feng, Y.; Chen, Y.-S.; Ma, S. *J. Am. Chem. Soc.*, **2019**, *141*, 14443-14450.
2. "A Corrole-Based Covalent Organic Framework Featuring Desymmetric Topology" Zhao, Y.; Dai, W.; Peng, Y.; Niu, Z.; Sun, Q.; Shan, C.; Yang, H.; Wojtas, L.; Yuan, D.; Zhang, Z.; Dong, H.; Zhang, X.; Zhang, B.; Feng, Y.; Ma, S. *Angew Chem. Int. Ed.*, **2020**, *59*, 4354-4359.
3. "Metallocorrole-based porous organic polymers as a heterogeneous catalytic nanoplatform for efficient carbon dioxide conversion" Zhao, Y.; Peng, Y.; Shan, C.; Lu, Z.; Wojtas, L.; Zhang, Z.; Zhang, B.; Feng, Y.; Ma, S. *Nano Res.*, **2021**, *14*, DOI: 10.1007/s12274-021-3617-3.

Rational structural modification of porphyrins: NIR absorbing photosensitizer dyes for biomedical applications

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Over the last three years, considerable progress has been made with a rational structural modification approach [1] guided by TD-DFT calculations and an application of Michl's perimeter model to prepare tetraarylporphyrin 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 [2-9]. Initially, novel corrole [2-4], chlorin [5,6], and N-confused [7] tetraarylporphyrin analogues were prepared along with their Sn(IV) complexes, and the effect of peripheral bromination of the ligand was also explored [8]. *Trans*-axial ligation of a Sn(IV) ion hinders aggregation effects, while the metal ion promotes intersystem crossing resulting in unusually high singlet oxygen quantum yields through a heavy atom effect [2-5,7,8]. Relatively low IC_{50} values were obtained during *in vitro* studies against MCF-7 breast cancer cells for the entire series of tetraarylporphyrin analogues [3-8].

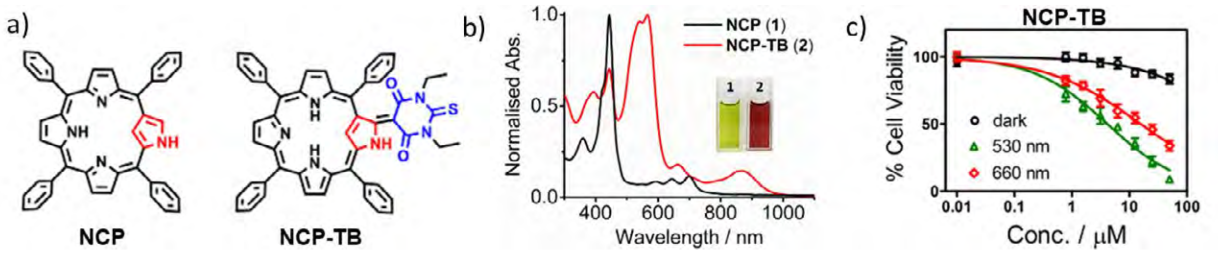

Fig. 1. (a) The N-confused porphyrins (NCPs) studied [9]; (b) UV-vis absorption spectra in DMSO (Inset: Color of the compounds in DMSO); c) Cytotoxicity against MCF-7 cells after 24 h incubation.

More recently (Fig. 1), this approach has progressed to a novel π-extended 1,3-diethyl-2-thiobarbituric-acid-substituted N-confused porphyrin (NCP-TB) [9], which absorbs significantly across the entire therapeutic window (620−850 nm) and exhibits favorable photodynamic activity properties against MCF-7 cancer cells due in part to the presence of a sulfur atom (Φ_Δ = 0.38 in DMSO). Further progress on the preparation of exotic porphyrin analogues and their conjugation to nanomaterials will be described.

REFERENCES

1. Mack J, *Chem. Rev*. 2017; 117: 3444-3478.
2. Babu B, Prinsloo E, Mack J, Nyokong T, New *J. Chem.* 2019, 43, 18805-18812.
3. Dingiswayo S, Babu B, Prinsloo E, Mack J, Nyokong T, *J. Porphyrins Phthalocyanines* 2020, 24, 1138-1145.
4. Soy RC, Babu B, Mack J, Nyokong T, *Dyes Pigments* 2021, 194, 109631.
5. Babu B, Mack J, Nyokong T, *Dalton Trans.* 2021, 50, 2177-2182.
6. Babu B, Sindelo A, Mack J, Nyokong T, *Dyes Pigments* 2021, 185A, 108886.
7. Babu B, Mack J, Nyokong T, *Dalton Trans.* 2020, 49, 15180-15183.
8. Babu B, Mack J, Nyokong T, *Dalton Trans*. 2020, 49, 9568-9573.
9. Babu B, Mack J, Nyokong T, *New J. Chem.* 2021, 45, 5654-5658.

Charged Porphyrins That Provide π-Electronic Ion-Pairing Assemblies

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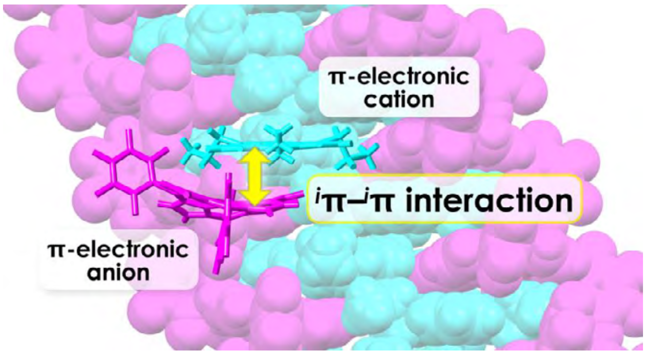
π-Electronic ions with appropriate geometries and peripheral substituents provide assemblies through the interactions between charged building subunits, resulting in fascinating electronic properties. Structures and properties of the assemblies can be controlled by the combined negatively and positively charged species in the assemblies. Thus far, diverse π-electronic ions along with ion-responsive π-electronic systems have afforded dimension-controlled ion-pairing assemblies as crystals, supramolecular gels, and thermotropic liquid crystals [1,2]. Highly ordered arrangement of charged species has been found to be a key factor to exhibit the enhanced performance as fascinating electronic materials. In fact, ion pairs of porphyrin–AuIII complexes as π-electronic cations, prepared with the combination of various anions including π-electronic anions, formed assemblies as crystals and thermotropic liquid crystals, whose ionic components were highly organized by iπ–iπ interactions (mainly electrostatic and dispersion forces) [3]. Furthermore, π-electronic ion pairs comprising porphyrin-based π-electronic anions [4] have exhibited characteristic assembling modes via iπ–iπ 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 [5].



REFERENCES

1. Recent reviews: (a) Haketa, Y. et al. Mol. Syst. Des. Eng. 2020, 5, 757; (b) Yamasumi, K. et al. Bull. Chem. Soc. Jpn. 2021, 94, 2252.
2. Recent reports on dipyrrolydiketone-based π-electronic molecules: (a) Kita, H. et al. Chem. Eur. J. 2020, 26, 340; (b) Watanabe, Y. et al. Chem. Eur. J. 2020, 26, 6767; (c) Haketa, Y. et al. J. Am. Chem. Soc. 2020, 142, 16420.
3. (a) Haketa, H. et al. iScience 2019, 14, 241; (b) Tanaka, H. et al. Chem. Asian J. 2019, 14, 2129; (c) Tanaka, H. et al. Chem. Asian J. 2020, 15, 494; (d) Fumuto, N. et al. Org. Lett. 2021, 23, 3897; (e) Kuno, A. et al. Chem. Eur. J. 2021, 27, 10068.
4. (a) Sasano, Y. et al. Dalton Trans. 2017, 46, 8924. (b) Sasano, Y. et al. Chem. Eur. J. 2019, 25, 6712.
5. Sasano, Y.; Tanaka, H. et al. Chem. Sci. 2021, 12, 9645.

New generation corroles, better suited for serving as drug candidates and catalysts for clean-energy processes

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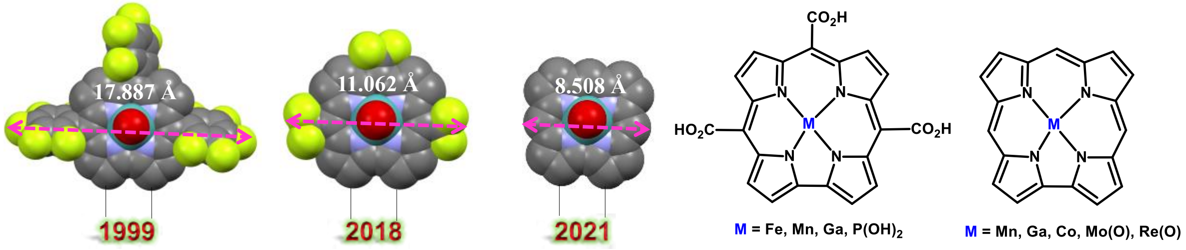
The one-pot synthesis of triarylcorroles in 1999 induced an enormous increase of activity for utilization of corroles and their metal complexes for the benefit of mankind, in terms of new drug candidates for treating various diseases and as catalysts for sustainable energy relevant processes. Still, all reported corrole derivatives do not fulfil the most basic standards expected for oral drug administration: a combination of low molecular weight and water solubility. Regarding electrocatalysis, strong absorbance of triarylcorroles onto electrodes used for heterogenous catalysis might be hampered by the aryls that are perpendicular to the corrole plane. These considerations, as well as pure scientific curiosity, were our motivation for developing synthetic methodologies for gaining access to derivatives that are much smaller in size than triarylcorroles.

We now disclose a very straightforward synthetic method that relies on surprisingly facile trifluoromethyl hydrolysis for gaining access to a new class of corroles that do satisfy all druglikeness criteria, as well as the development of several approaches leading to the metal complexes of the parent (with no substituents whatsoever) corrole [1-3].



REFERENCES

1. P. Yadav, S. Khoury, A. Mahammed, M. Morales, S. C. Virgil, H. B. Gray and Z. Gross “Enhanced Synthetic Access to Tris-CF_3-Substituted Corroles” *Org. Lett.* **2020**, *22*, 3119-3122.
2. P. Yadav, S. Khoury, N. Fridman, V. K. Sharma, A. Kumar, M. Majdoub, A. Kumar, Y. Diskin-Posner, A. Mahammed and Z. Gross “Trifluoromethyl Hydrolysis En Route to Corroles with Increased Druglikeness” *Angew. Chem. Int. Ed.* **2021**, *60*, 12829 –12834.
3. A. Kumar, P. Yadav, M. Majdoub, I. Saltsman, N. Fridman, S. Kumar, A. Kumar, A. Mahammed and Z. Gross “Corroles: The Hitherto Elusive Parent Macrocycle and its Metal Complexes” *Angew. Chem. Int. Ed.* **2021**, *60*, 25097-25103.

Evaluation of critical structural factors affecting heme degradation catalyzed by a noncanonical heme oxygenase

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Heme degradation is an important physiological process in many eukaryotic and prokaryotic organisms that is catalyzed by heme oxygenase (HO) enzymes. These complex multistep reactions in which the substrate acts as a prosthetic group are the subject of many studies and their mechanistic details have been heavily debated for a few decades, with new reactive pathways being just recently proposed. Mycobacterium heme utilization degrader (MhuD) is a noncanonical HO protein that plays a crucial role in the heme uptake pathway in *Mycobacterium tuberculosis* [1]. MhuD is distinguished from canonical HO enzymes by its heme degradation products, releasing mycobilins and ferrous iron without generating carbon monoxide [2]. Interestingly, MhuD can bind one or two heme molecules in the same active site. Although it was initially proposed that monoheme MhuD is enzymatically active and diheme is inactive [1], our recent work actually showed that both forms can effectively degrade heme [3]. It has been proposed that the first step of MhuD heme degradation is monooxygenation of heme to hydroxyheme, which is mediated by the Fe-OOH intermediate analogous to canonical HOs, though the hydroxylation takes place at the β- or δ-meso carbon atoms [4]. In this work we generated the oxygenated forms of mono- and diheme MhuD samples and characterized them using resonance Raman (rR) spectroscopy. These relatively stable oxy adducts were then cryogenically exposed to gamma irradiation to generate and stabilize reactive intermediate states, such as Fe-O-O(H)/Fe=O species. In order to facilitate reliable identification of these intermediates, the oxygenated MhuD samples were prepared in H_2O and D_2O buffers using $^{16}O_2$ and $^{18}O_2$ gas isotopes. The combination of rR spectroscopy and cryoradiolysis presented here provides for the first time direct experimental characterization of these fleeting intermediates that dictate the reactivity of MhuD.

REFERENCES

1. Chim N, Iniguez A, Nguyen TQ, Goulding CW. *J. Mol. Biol.* 2010, 395, 595-609.
2. Wilks A, Heinzl G. *Arch. Biochem. Biophys*. 2014, 544, 87-95.
3. Snyder SN, Mak PJ. *J Biol. Chem.* 2021, in press, DOI: 10.1016/j.jbc.2021.101475.
4. Matsui T, Nambu S, Goulding CW, Takahashi S, Fujii H. Ikeda-Saito, M. *Proc. Natl. Acad. Sci. U.S.A*. 2016, 113, 3779-3784.

Novel Phthalocyanine-Biomolecules Conjugates; Highly Potential Activity Assessed In Vitro PDT Efficacy

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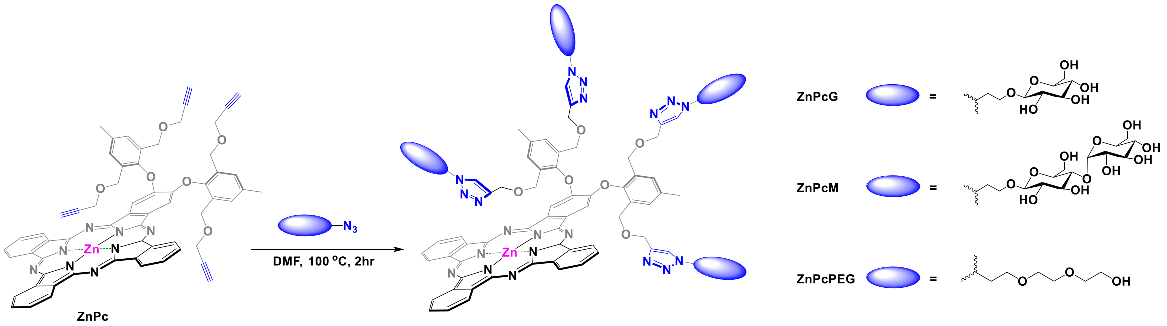
Asymmetrical zinc (II) phthalocyanine (Pc) bearing four terminal alkyne moieties was successfully prepared as a novel macrocyclic scaffold.[1, 2] Subsequently, this promising non-aggregated molecular platform was conjugated with a range of biomolecules, such as D-glucose, D-maltose and triethylene glycol by metal-mediated azide-alkyne cyclo-addition reaction. The photophysical/photochemical properties of these newly prepared Pc-biomolecule conjugates (ZnPcG, ZnPcM, and ZnPcPEG) were performed and found to efficiently generating singlet oxygen in both DMF and water. Consequently, such bioconjugate complexes represent promising photosensitisers in PDT and their photocytotoxicity and cellular uptakes capability have been investigated.



Scheme 1. Synthesis of water-soluble zinc (II) phthalocyanines **ZnPcG**, **ZnPcM** and **ZnPcPEG**

REFERENCES

1. Husain A, Ganesan A, Ghazal B, Durmuş M, Zhang X-F, Makhseed S. Dual-directional alkyne-terminated macrocycles: Enroute to non-aggregating molecular platforms. Organic Chemistry Frontiers. 2019;6(18):3192-204.
2. Husain A, Ganesan A, Ghazal B, Makhseed S. Multivalent Allyl-Substituted Macrocycles as Nonaggregating Building Blocks. The Journal of Organic Chemistry. 2020;85(12):8055-61.

Functional Reprogramming in Heme Enzymes

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The cytochrome P450 (CYP) OleT initiates the decarboxylation of fatty acids using the high-valent iron-oxo intermediate known as Compound I. This reaction significantly deviates from the canonical oxygen rebound chemistry that typifies most CYPs. Continuing work with a suite of OleT orthologs and the variable metabolic profiles with different chain length substrates has suggested a fine interplay between the distal pocket and substrate identity for determining reaction trajectory in this class of enzymes. Here, we have utilized substrate and cofactor "mutagenesis" to further refine the role of substrate-positioning and heme redox properties for mediating both the C-H abstraction and oxygen rebound steps. In the former approach, fatty acid derivatives containing substituents at the C2 position (OH or CH_3) show an array of different enzymatic activities - decarboxylation, desaturation, and hydroxylation – that most likely arise from altered presentation of the scissile C-H bond to the oxo-fragment. The ease of preparing high-valent intermediates in OleT has allowed for a thorough thermodynamic description of these critical steps in catalysis and strategy to thwart radical recombination.

Synthesis and studies of Porphyrin Isomers

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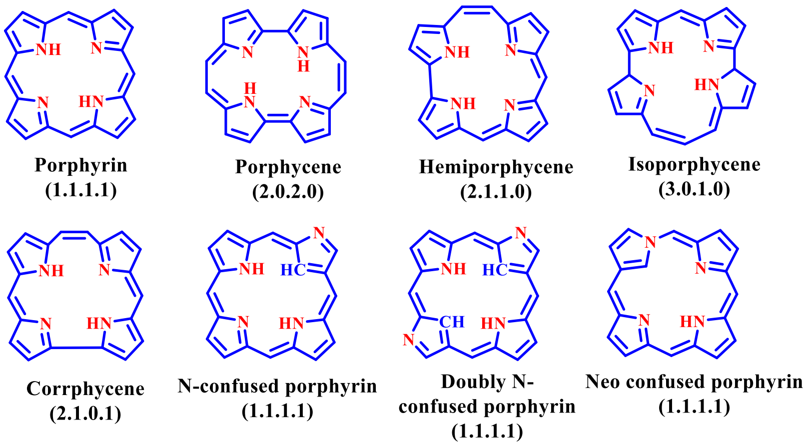
Porphyrins are tetrapyrrolic macrocycles in which the four pyrroles are connected by four meso-carbon atoms and represented as porphyrin (1.1.1.1). The four pyrroles and four methine carbons can be arranged in different possible ways to form tetrapyrrolic constitutional isomers of porphyrins. Thus, different structural isomers of porphyrin(1.1.1.1) such as porphycene(2.0.2.0), hemiporphycene(2.1.1.0), corrphycene (2.1.0.1), isoporphycene(3.0.1.0), N-confused porphyrin((1.1.1.1), doubly N-confused porphyrin(1.1.1.1) and neoporphyrin(1.1.1.1) have been known in the literature (Chart 1). Furthermore, porphyrin isomers differ from each other significantly in terms of their stability, structure, spectral, redox and coordination properties. Our group is involved in synthesis of core-modified porphyrins which are resulted by replacing one or two pyrrole rings with other heterocycles/carbacycles. In this presentation, I will share our successful results on some of these porphyrin isomers specially on porphycene, hemiporphycene and neo-porphyrinoids.1-3



Porphyrin (1.1.1.1) **Porphycene (2.0.2.0)** **Hemiporphycene (2.1.1.0)** **Isoporphycene (3.0.1.0)**

Corrphycene (2.1.0.1) **N-confused porphyrin (1.1.1.1)** **Doubly N-confused porphyrin (1.1.1.1)** **Neo confused porphyrin (1.1.1.1)**

Chart 1. Molecular structures of porphyrin and its constitutional isomers.

REFERENCES

1. E. Ganapathi, T. Chatterjee and M. Ravikanth, *Eur. J. Org. Chem*. 30, 6701-6706 (**2014**),
2. K. G. Thorat and M. Ravikanth, *Chem. Asian J.* 13, 3040-3050 (**2018**),
3. P. Poornenth and M. Ravikanth, *Topics in Current Chem. 379:26,* 1-42 (**2021).**

Porphyrins as Scaffolds for Multivalent Presentation of Glycofullerenes

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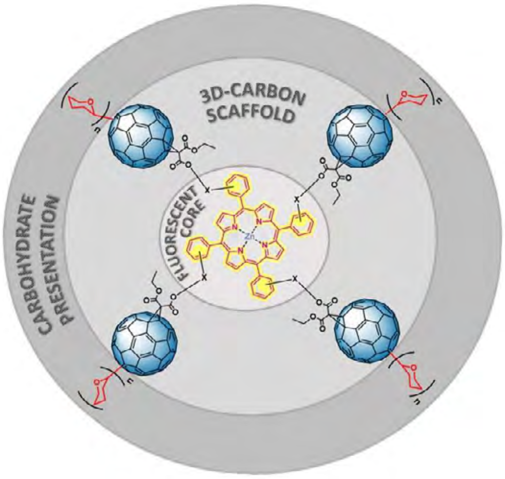
The supramolecular interaction carbohydrate-protein is ubiquitous in a large variety of biological processes. In order to design multivalent peripheral ligands with glycomimetic properties that structurally can attach to the receptor sites of complex biological structures, a broad variety of "artificial glycoforms" have been created with the aim of understanding the mechanisms involved in multivalent binding interactions. In this regard, we have shown that hexakis-adducts of [60]fullerene endowed with 12, 24 or 36 mannoses, act as strong inhibitors for DC-SIGN in an Ebola infection assay model [1]. Furthermore, a drastic increase in the inhibition process at the subnanomolar scale has been observed when the size and mannoses´ number are increased in the firstly reported tridecafullerenes endowed with 120 mannose units decorating the periphery of the molecule [2].



The efficiency to block DC-SIGN mediated viral infection by an artificial Ebola virus has been tested in a cellular experimental assay finding that, these systems are potent inhibitors of viral infection. Actually, a variety of carbon nanostructures endowed with sugars (sugar-balls) have shown their effect for inhibiting infection by emergent viruses, namely Ebola, Zika and Dengue [3] and, by modifying the organic addend molecules at the periphery, to other viruses like VIH [4].

In this presentation, we will show the first examples where the glycofullerenes are covalently linked to a porphyrin acting as central core. The aim of these new compounds is to gather the properties of glycofullerenes to those of the porphyrins in order to validate the multivalence character of the ZnP as a new scaffold endowed with amazing photophysical properties.

REFERENCES

1. B. M. Illescas, J. Rojo, R. Delgado, N. Martín, J. Am. Chem. Soc., 2017, 139, 6018−6025.
2. A. Muñoz, D. Sigwalt, B. M. Illescas, J. Luczkowiak, L. Rodríguez, I. Nierengarten, M. Holler, J.-S. Remy, K. Buffet, S. P. Vincent, J. Rojo, R. Delgado, J.-F. Nierengarten, N. Martín, Nature Chem., 2016, 8, 50-57.
3. a) J. Ramos-Soriano, J. J. Reina, B. M. Illescas, N. de la Cruz, L. Rodríguez-Pérez, F. Lasala, J. Rojo, R. Delgado, N. Martín, J. Am. Chem. Soc., 2019, 141, 15403−15412; b) L. Rodríguez-Perez, J. Ramos-Soriano, A. Perez-Sánchez, B. M. Illescas, A. Muñoz, J. Luczkowiak, F. Lasala, J. Rojo, R. Delgado, N. Martín, J. Am. Chem. Soc., 2018, 140, 9891−9898.
4. M. Ruiz-Santaquiteria, B. M. Illescas, J. Neyts, R. Abdelnabi, D. Schols, A. Boonen, S. Noppen, O. Martí-Marí, A. Mills, F. Gago, A. San-Félix, M. J. Camarasa, N. Martín, Chem. Eur. J. 2021, 27, 10700-10710.

Annulative π-Extension of Subphthalocyanines

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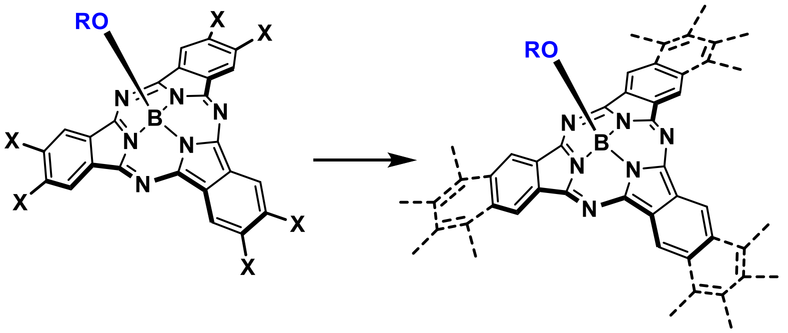
Organic synthesis in solution has provided efficient methods to prepare polycyclic aromatic hydrocarbons (PAHs), aiming to obtain nanographene derivatives by a bottom-up approach. More recently, research has focused on the incorporation of different hetereoatoms (or heterocycle subunits) into the PAHs skeleton as a powerful strategy to modulate the physicochemical properties of nanographenes.

The introduction of peripheral π-extended conjugated substituents has proven to be the most successful method to shift the Q band absorption of SubPc towards the near-IR region, which is desirable for many applications. [1] Peripheral annelation represents a less explored approach to modify SubPc structure, permitting the extension of its π-conjugated system and, therefore, the modulation of the macrocycle properties. Among the few examples, SubNcs are the best known benzoannulated SubPc derivatives that have found a relevant role in photovoltaic devices, owing to their red-shifted absorption [2].

In most cases, these SubPcs have been prepared by conventional cyclotrimerization of the corresponding annulated-phthalotriles, leading to different synthetic problems and low reaction yields. Considering the high impact of merging SubPcs and polycyclic aromatic hydrocarbons (PAHs), the development of new efficient synthetic approaches for the preparation of π-extended PAH-fused SubPc derivatives, based on the post-functionalization of easily prepared preformed SubPcs, is important. We are presenting here our efforts in this direction [3].



REFERENCES

1. Claessens, C. G.; González-Rodríguez, D.; Rodríguez-Morgade, M. S.; Medina, A.; Torres, T. Chem. Rev. 2014, 114, 2192.
2. Josey, D.S.; Ingram, G.L.; Garner, R.K.; Wang, J.M.; Evans, G.J.; Lu, Z.-H.; Bender, T.P. ACS Appl. Energy Mater. 2019, 2, 979.
3. Tejerina, L.; Martinez-Diaz, M.V.; Torres, T. Org. Lett. 2019, 21, 2908.

Heteroleptic lanthanide trisphthalocyaninate scaffold as a multi-tool to study molecular magnetism

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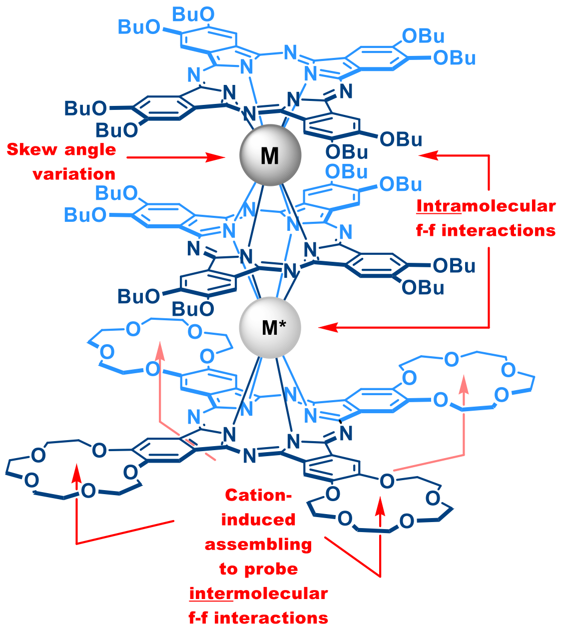

Since the discovery of single molecule magnetism in lanthanide complexes on the example of Tb(Pc)$_2$, sandwich phthalocyaninates have become attractive objects to study the influence of structural and electronic effects on their magnetic properties. In our work, we focus on the combination of static and dynamic factors that can control the behavior of SMM. Among the dynamic factors, we focus on supramolecular assembly, which can be induced by the interaction of crown-substituted sandwiches with alkali metal ions [1,2]. To broaden the range of possible effects under study, we developed triple-decker complexes containing one terminal tetra-15-crown-5-substituted ligand and two octa-n-butoxy-substituted phthalocyanine ligands, [(BuO)$_8$Pc]M[(BuO)$_8$Pc]M*[(15C5)$_4$Pc]. A convenient synthesis ensured by the stabilization of the complexes with electron-donor substituents and an easy chromatographic purification provided by the high solubility of the complexes made it possible to obtain a series of homo- and heteronuclear compounds, where M and M* = Tb and/or Y. Varying the metal centers in such triple-deckers can be used to study relatively strong intramolecular f-f interactions at distances Ln...Ln ca. 3.5 Å, while supramolecular assembly can be used to study weaker f-f interactions in the range of distances from 6.2 to 13.1 Å. In addition, the synthesized complexes are interesting objects for NMR studies of correlations between the conformational state of the sandwiches and their magnetic properties. We have shown that changing the solvent used for such studies can switch the coordination polyhedron of the metal "M" center from square-antiprismatic in toluene to distorted prismatic in chloroform. This switch manifests itself in an increase in the axial component of the magnetic susceptibility tensor, which leads to an increase in the lanthanide-induced shifts in the NMR spectra. Thus, the chosen molecular architecture of the complexes allows advanced studies of structural and supramolecular effects in SMM, including aggregation and solvation.

Acknowledgement: this work was supported by Russian Science Foundation (grant 18-73-10174_P).

REFERENCES

1. A. G. Martynov et al., *Inorg. Chem.*, **2020**, 59, 9424–9433.
2. A. G. Martynov et al., *Inorg. Chem.*, **2021**, 60, 9110–9121.

Aromaticity and Antiaromaticity of Redox-Switchable 5,10,15,20-Tetraaryl-5,15-diazaporphyrinoids

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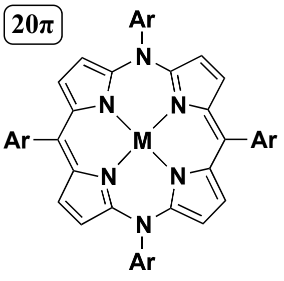
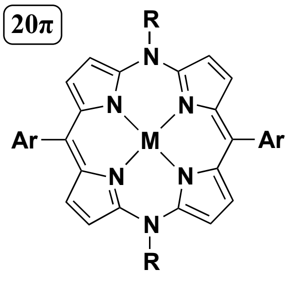
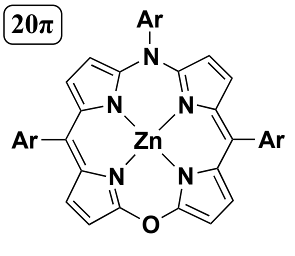
Porphyrins in the doubly reduced oxidation state (20π porphyrins) have received significant attention because of their diverse antiaromatic characters and unique optical and redox properties [1]. However, the 20π porphyrin dianions are intrinsically unstable under ambient conditions and readily undergo oxidation back to the parent 18π porphyrins to acquire aromatic stabilization energies. To date, various approaches have been reported to increase the stability of 20π porphyrins [2]. Recently, we have established a new approach, *meso*-modification with nitrogen atoms, to stabilize 20π porphyrins; we have reported 5,10,15,20-tetraaryl-5,15-diazaporphyrinoids (Ar_4DAP) **1M**,[3] 5,15-dialkyl-10,20-diaryl-5,15-diazaporphyrinoids (Ar_2R_2DAP) **2M**,[4] and 5,10,20-triaryl-5-aza-15-oxaporphyrinoids (Ar_3AOP) **3M**,[5] which are neutral and antiaromatic. The chemical and electrochemical oxidation reactions of **1M** produced the corresponding 18π dications **4M** through the 19π radical cations. Most importantly, these diazaporphyrinoids have highly flat π-planes and can be used as platforms for evaluating the aromatic and antiaromatic characters by simply switching their oxidation states. The diatropic and paratropic ring-current effects induced by the DAP rings of the alkyl-chain-strapped derivatives of **1M**/**4M** were evaluated using NMR spectroscopy and DFT calculations [6]. In this presentation, the synthesis and aromaticity of new *meso*-modified azaporphyrinoids are also reported.



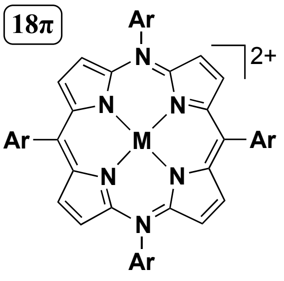
Ar_4DAP **1M**



Ar_2R_2DAP **2M**



Ar_3AOP **3M**



Ar_4DAP^{2+} **4M**

Ar = aryl, R = alkyl; M = Ni, Cu, Zn

REFERENCES

1. For example, see: R. Cosmo, C. Kautz, K. Meerholz, J. Heinze, K. Müllen, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 604.
2. For example, see: K. Reddy, A. Basavarajappa, M. D. Ambhore, V. G. Anand, *Chem. Rev.* **2017**, *117*, 3420.
3. a) T. Satoh, M. Minoura, H. Nakano, K. Furukawa, Y. Matano, *Angew. Chem. Int. Ed.* **2016**, *55*, 2235. b) K. Sudoh, T. Satoh, T. Amaya, K. Furukawa, M. Minoura, H. Nakano, Y. Matano, *Chem. Eur. J.* **2017**, *23*, 16364. c) Y. Satoh, Y. Fujita, N. Muramatsu, K. Furukawa, T. Ikoma, M. Minoura, H. Nakano, Y. Matano, *ChemPlusChem* **2021**, *25*, 1476.
4. M. Mutoh, K. Sudoh, K. Furukawa, M. Minoura, H. Nakano, Y. Matano, *Asian J. Org. Chem.* **2019**, *8*, 352.
5. K. Sudoh, K. Furukawa, H. Nakano, S. Shimizu, Y. Matano, *Heteroatom Chem.* **2018**, *29*, e21456.
6. H. Ochiai, K. Furukawa, H. Nakano, Y. Matano, *J. Org. Chem.* **2021**, *86*, 2283.

How Aromatic Are Large Molecular Nanorings? The Role of Electron Delocalization

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Large conjugated rings with persistent currents are novel promising structures in molecular-scale electronics. A six-porphyrin nanoring structure that allegedly sustained an aromatic ring current involving 78 electrons was recently synthesized [1]. We provide here compelling evidence that this molecule is not aromatic, contrary to what was inferred from the analysis of 1H-NMR data and computational calculations. The electron delocalization error –a common feature of density functional approximations with a low percentage of Hartree-Fock exchange– is responsible for the overestimation of aromaticity [2-6]. The main reason behind the absence of an aromatic ring current in these nanorings is the low delocalization in the transition from the porphyrins to the bridging butadiyne linkers, which disrupts the overall conjugated circuit [6]. These results highlight the importance of choosing a suitable computational method to study large conjugated molecules and the appropriate aromaticity descriptors to identify the part of the molecule responsible for the loss of aromaticity [6].

REFERENCES

1. M. D. Peeks, T. D. Claridge, H. L. Anderson, *Nature* **2017**, 541, 200 – 205
2. I. Casademont-Reig, E. Ramos-Cordoba, M. Torrent-Sucarrat, E. Matito, *Molecules* **2020**, 25, 711
3. I. Casademont-Reig, E. Ramos-Cordoba, M. Torrent-Sucarrat, E. Matito, *Aromaticity : Modern Computational Methods and Applications Aromaticity descriptors based on electron delocalization*, Elsevier, Amsterdam, **2021**, pp. 235 – 258.
4. I. Casademont-Reig, T. Woller, J. Contreras-García, M. Alonso, M. Torrent-Sucarrat, E. Matito, *Phys. Chem. Chem. Phys.* **2018**, 20, 2787 – 2796
5. M. Torrent-Sucarrat, S. Navarro, F. P. Cossío, J. M. Anglada, J. M. Luis, *J. Comput. Chem.* **2017**, 38, 2819 – 282
6. I. Casademont-Reig, R. Guerrero-Avilés, E. Ramos-Cordoba, M. Torrent-Sucarrat, E. Matito, *Angew. Chem. Int. Ed.* **2021**, 60, 24080–24088

Photosensitising Nanoassemblies based on Cyclodextrin/Porphyrinoid Complexes with Antimicrobial Photodynamic Action

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New broad-spectrum antimicrobial strategies, alternative to antibiotics and able to efficiently inactivate pathogens without inducing resistance, is one of the main objectives in public health. Antimicrobial photodynamic therapy (aPDT), based on the light-induced production of reactive oxygen species from photosensitizers (PS), is attracting growing interest to infection treatment, also including biofilm destruction. Due to partial photostability of free PS, delivery systems fabricated with carriers and PS are highly required to decrease PS photodegradation, thus improving the therapeutic efficacy and to reduce collateral effect on unaffected tissues. Here we will discuss different PS releasing systems studied in our research labs ranging between eluting fabrics based on the anionic porphyrin (tetrakis(4-sulfonatophenyl)-21H,23H-porphine (TPPS)) and a polymeric cyclodextrin [1] and nanoconstructs in aqueous dispersions based on the cationic porphyrin (N-methyl- 4-pyridyl)-21H,23H-porphyrin (TMPyP)) assembled with two different cyclodextrins (CDs), namely the trade sulfobutylether-beta-cyclodextrin (CAPTISOL®) and CD nanosponge (CDNS) [2,3]. Dynamic Light Scattering (DLS) and ζ-potential pointed out the complexation between PS and CDs. Nanoassemblies with photodynamic features exhibited photo-antimicrobial activity on Gram-negative and Gram-positive bacteria, in addition to generally sustained release properties and a higher photostability. Moreover, preliminary results of TMPyP/CAPTISOL® and CAPTISOL® alone against biofilms from *P. aeruginosa* reveal that i) CAPTISOL® alone inhibits biofilm formation and ii) TMPyP/CAPTISOL® nanoassembly significantly increases biofilm degradation respect to TMPyP alone. Altogether in vitro photo-antibactericidal studies elucidated the aPDT efficacy of our photosensitizing nanosystems based on CD.

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REFERENCES

1 M. A. Castriciano, R. Zagami, M. P. Casaletto, B. Martel, M. Trapani, A. Romeo, V. Villari, M. T. Sciortino, L. Grasso, S. Gugliemino, L. Monsù Scolaro, A. Mazzaglia (2017). Poly(carboxylic acid)-Cyclodextrin/Anionic Porphyrin Finished Fabrics as Photosensitizer Releasers for Antimicrobial Photodynamic Therapy. *Biomacromolecules*, *18*, 1134-1144.

2 R. Zagami, D. Franco, J.D. Pipkin, V. Antle, L. De Plano, S. Patanè, S. Guglielmino, L. Monsù Scolaro, A. Mazzaglia (2020). Sulfobutylether-β-cyclodextrin/5,10,15,20-tetrakis (1-methylpyridinium-4-yl)porphine nanoassemblies with sustained antimicrobial phototherapeutic action *Int. J. Pharm., 585*, 119487

3 F. Caldera, M. Tannous, R. Cavalli, M. Zanetti, F. Trotta (2017). Evolution of Cyclodextrin Nanosponges. *Int. J. Pharm*, *531(2)*, 470-479, 2017

Systemic protein-corrole bioparticles cross multiple biological barriers to target metastatic tumors

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Triple negative breast cancer (TNBC) is among the most aggressive, recurrent and highly metastatic of breast tumors with a worse clinical outcome compared to other breast cancer subtypes. Metastatic breast cancer predicts a 2-5 year average survival whereas metastatic TNBC predicts ~1 year overall survival from the time of treatment due in part to early distant site metastasis.[1] Sulfonated metallated corroles have shown promise as multifunctional agents for biomedicine as these compounds can bear imaging, therapeutic, and diagnostic capabilities. While the sulfonates prevent unintended penetration into healthy tissue, delivery by targeted biological particles enables transport into specific sites in the body to act as targeted "theranostics".[2] We have shown the utility of sulfonated corroles in targeting resistant and metastatic tumors through their self-assembly with our bioengineered tumor-invading protein, HerPBK10 (HPK). HPK is a chimeric biocarrier that uses the human epidermal growth factor receptor 3 (HER3/ErbB3) to penetrate metastatic and resistant tumors due to the increased cell surface HER3 on such tumors.[3] We show here that HPK can self-assemble with sulfonated corroles, forming serum-stable nano-capsids (NCs) that evade immune-inhibition and bypass tumor barriers by mimicking an essential ligand that enters tumor cells through HER3. Systemic NCs in preclinical breast cancer models show preferential accumulation in secondary tumors due to the increased HER3 associated with metastasis. Systemic NCs can also cross the blood-brain barrier and accumulate in intracranial TNBC tumors using HER3 to mediate both routes. We have observed differentially metallated corroles exhibiting selective impact on tumor vs non-tumor tissue that includes modulating mitochondrial transporters and redox enzymes in tumor cells, and reducing oxidative damage in non-tumor tissue. We are leveraging these findings to refine protein-corrole bioparticles with both targeted tumoricidal activity and cytoprotection of non-tumor tissue. As a growing number of metastatic and resistant tumor types show increased HER3, these studies could eventually offer improved options for patients, especially those with brain-metastatic and brain-localized tumors.

REFERENCES

1. Yao, Y., Chu, Y., Xu, B., Hu, Q., Song, Q. Bioscience Reports 2019, 39 (6).
2. Teh, J., Kauwe, L. M. Magnetic Resonance Contrast Enhancement and Therapeutic Properties of Corrole Nanoparticles, Astrid, S.; Eva, F.; Roland, K. O. S., Eds. De Gruyter: 2021; pp 299-314.
3. Alonso-Valenteen, F., Pacheco, S., Srinivas, D., Rentsendorj, A., Chu, D., Lubow, J., Sims, J., Miao, T., Mikhael, S., Hwang, J. Y., Abrol, R., Medina Kauwe, L. K. Nucleic acids research 2019, 47 (21), 11020-11043.

Polar Assemblies of Subphthalocyanines and their Unique Properties

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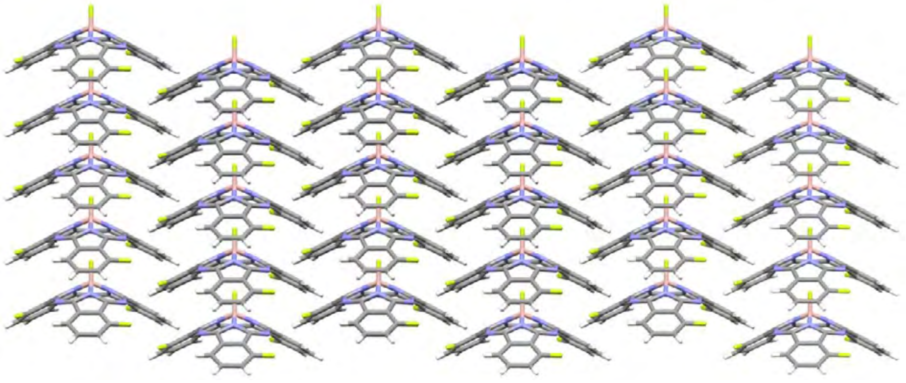
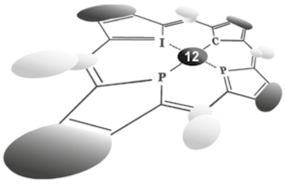
Polar materials attract wide research interest due to their unique properties, such as ferroelectricity and the bulk photovoltaic effect (BPVE)[1], which are not accessible with nonpolar materials. However, in general, rationally designing polar materials is difficult because nonpolar materials are more favorable in terms of dipole-dipole interactions. On the other hand, we recently developed a rational strategy to form polar assemblies with bowl-shaped π-conjugated molecules such as subphthalocyanines (SubPcs).[2] We revealed that polar assemblies are surely formed if one-dimensional columns of SubPcs are assembled into trigonal lattices. In this previous study, we reported only polar assemblies with SubPcs having fluorine substitutions. As a follow-up study, we further developed polar assemblies with various SubPcs including chiral ones.[3] In this presentation, the details of our strategy to form polar assemblies as well as the bulk photovoltaic effects of the obtained polar crystals will be discussed.



REFERENCES

1. C. Zhang, K. Nakano, M. Nakamura, F. Araoka, K. Tajima, D. Miyajima, *J. Am. Chem. Soc.*, **142**, 3326–3330, 2020.
2. C. Zhang, Y. Guo, D. He, J. Komiya, G. Watanabe, T. Ogaki, C. Wang, A. Nihonyanagi, H. Inuzuka, H. Gong, Y. Yi, K. Takimiya, D. Hashizume, D. Miyajima, *Angew. Chem. Int. Ed.*, **60**, 3261, 2021.
3. To be submitted.



Resonance Raman Study of the Mechanism of Heme Extraction from Human Hemoglobin by the Staphylococcus aureus Receptor IsdH

Pierre Moënne-Loccoz[a], **Therese Albert**[a], **Robert T. Clubb**[b], **Kat Ellis-Guardiola**[b]

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Staphylococcus aureus is an opportunistic bacterial pathogen that relies on an iron-regulated surface determinant (Isd) system to acquire iron from human hemoglobin (Hb) [1]. IsdH is a cell-wall associated receptor that contains three NEAT (NEAr iron Transporter) domains and is believed to trigger hemin release from Hb through distortion of helix F which carries the proximal His87 [2]. While the second NEAT domain (N2) of IsdH binds Hb with high-affinity, the third NEAT domain (N3) contains the hemin binding pocket with Tyr642 which coordinates the Fe(III) after dissociation from Hb. The N2 and N3 domains are connected by a short flexible tether and a helical linker domain that restricts inter-domain motions in the highly dynamic IsdH:Hb complex. To delineate the mechanism of hemin extraction from Hb by IsdH, the Clubb's lab has engineered IsdH constructs with surface mutations at the N2 domain to produce specificity to the α-subunits of Hb, and Y642F substitution in the N3 domain to preclude the final step of hemin transfer. These constructs have allowed detailed NMR, stopped-flow UV-vis, and ITC binding analyses [3], but these IsdH:Hb complexes had yet to be probed by resonance Raman spectroscopy. Changes in porphyrin skeletal vibrations upon exposure of Hb to a range of IsdH constructs provide us with a sensitive and direct handle on perturbations of hemin coordination that supplement and refine prior mechanistic models of the Hb destabilization process by IsdH.

REFERENCES

1. Grigg, J. C., Ukpabi, G., Gaudin, C. F. M. Murphy, M. E. P. (2010) Structural biology of heme binding in the *Staphylococcus aureus* Isd system. *J. Inorg. Biochem. 104*, 341-348.
2. Dickson C. F., Kumar K. K., Jacques, D. A., Malmirchegini, G. R., Spirig, T., Mackay, J. P., Clubb, R. T., Guss, J. M., Gell, D. A. (2014) Structure of the hemoglobin-IsdH complex reveals the molecular basis of iron capture by *Staphylococcus aureus*. *J. Biol. Chem. 289*, 6728–6738
3. Sjodt, M., Macdonald, R., Marshall, J. D., Clayton, J., Olson, J. S., Phillips. M., Gell, D. A., Wereszczynski, J., Clubb, R. T. (2018) Energetics underlying hemin extraction from human hemoglobin by *Staphylococcus aureus*. *J. Biol. Chem. 293*, 6942–6957.

The Rich Chemistry of Hydroporphyrins

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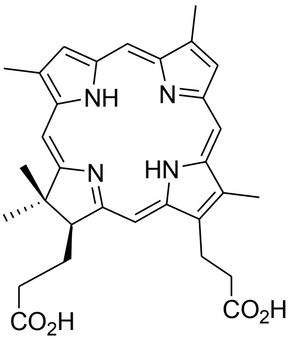
Since the discovery of the vital pigments heme, chlorophyll and vitamin B_{12} legions of researchers were attracted by structure elucidation, synthesis, biosynthesis, biochemistry, properties and function of naturally occurring porphyrinoids and their unnatural congeners. During the last four decades porphyrin research in particular in the synthesis field was coined by two main streams. The first line comprises chemistry of isomeric, contracted and expanded porphyrins. The second main stream is characterized by discovery, chemistry and biochemistry of less common natural hydroporphyrins and their unnatural congeners. Bonellin **1** and heme d_1 **2** are typical naturally occurring representatives of this class of compounds. The chlorin framework present in bonellin but also in chlorophylls influenced search for novel synthesis strategies for construction of this structural type. Synthesis strategies to achieve naturally occurring and artificial isobacteriochlorins were strongly influenced by methods investigated in the field of synthesis of vitamin B_{12} and artificial corrins.



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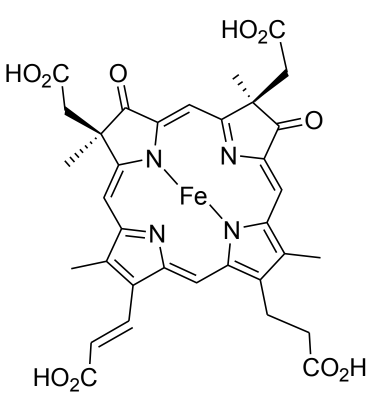

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REFERENCES

1. Montforts F-P, Gerlach B, Hoeper F, *Chem. Rev.* **1994**, *94*, 327- 347.
2. Montforts F-P, Glasenapp-Breiling M, In *Progress in the Chemistry of Organic Natural Products*, Herz W, Falk H, Eds, Springer: Vienna 2002, *84*, 1-52.
3. Lindsey J S, *Chem. Rev*. **2015**, *115*, 6534-6620
4. Jacobi P A, Brielmann H L, Chiu M, Ghosh I, Hauck S I, Lanz S, Leung S, Li Y, Liu H, Loewer F, O´Neal W G, Pippin D, Pollina E, Pratt B A, Robert F, Roberts W P, Tassa C, Wang H, *Heterocycles* **2011**, *82*, 1029-1081.

Kinetic Investigations on Hydrogen Atom Abstraction by a Compound I Model Complex from Alkane Derivatives

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Oxido-iron(IV) porphyrin π-radical cation species, so-called compound I, are involved in various heme-containing enzymes, such as cytochrome P450 and peroxidase, responsible for the metabolism of aliphatic substrates. This reactive species has attracted considerable attention due to its biological importance and characteristic oxidation states consisting of the high-valent iron centre and the π-conjugated ligand. Many kinetic studies are conducted on the reaction of compound I with substrates to elucidate its mechanism and key factor determining its great reactivity. However, the short lifetime of the complex due to its high reactivity has restricted the experimental conditions. Low-temperature conditions (e.g., –80 °C) for the observation of compound I have limited the substrate to those with weak C–H bonds. We have reported remarkable lifetime elongation of Fe^{IV}(TMP$^{+•}$)(O)(Cl) (TMP: 5,10,15,20-tetramesitylporphyrin dianion) in a fluorocarbon solvent.[1] This solvent system enables us to examine the oxidation of normal alkane, cycloalkane, and branched alkane substrates by compound I directly. We herein report the effect of electron-withdrawing and donating substituents on the reaction rate.

UV-vis spectrum of Fe^{III}(TDCPP)(Cl) (**1**) (TDCPP: tetrakis-2,6-dichlorophenyl-porphyrin) immediately disappeared by the–reaction with ozone gas to give an absorption band at 690 nm, which is almost identical to that of Fe^{IV}(O)(TDCPP$^{•+}$)(Cl) **2** in CH_2Cl_2. Electron paramagnetic resonance (EPR) spectrum of the generated species also endorsed the formation of **2**. The absorption band of **2** gradually decayed to form the starting iron(III) complex **1** (self-decay). Upon adding an excess amount of a substrate into the reaction solution, pseudo-first-order rate constants (k_{obs}) of the decay process increased, showing linear dependence on the concentration of the added substrate. The second-order rate constant of the reaction was determined from the slope of the plot of k_{obs} vs [substrate]. As the substrate having electron-withdrawing substituents, dichloromethane, chloroform, acetonitrile, and nitromethane were employed. Tetrahydrofuran, tetrahydropyran, and 1,4-dioxane were employed as the substrates containing electron-donating ether group. The substrates with electron-withdrawing substituents tend to show smaller reaction rate constants than those of non-substituted alkane substrates even though the bond dissociation energies of the C–H bonds are similar. Electron donating substituents facilitated reactions. In this presentation, the effects of the substituents of alkane substrate are quantitatively analyzed.

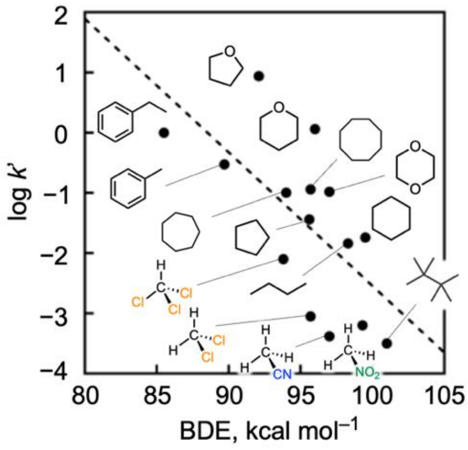
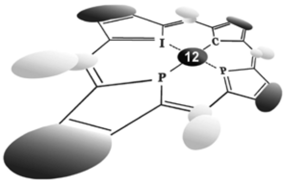


Figure 1. Logarithms of second-order late constants normalized by the number of equivalent C–H bonds (log *k*') plotted against bond dissociation energy of the C–H bonds (BDE).

REFERENCES

1. Y. Morimoto, Y. Shimaoka, Y. Ishimizu, H. Fujii, and S. Itoh, *Angew. Chem., Int. Ed.* **2019**, *58*, 10863–10866.



Ligand and on-surface chemistry as a strategy to tune charge and spin interactions at surfaces

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Interfacing materials with different functionalities is an efficient way to manipulate their respective properties and promote the emergence of novel phenomena. Controlling interfacial interactions is however a complicated task in most cases. In that respect, the tunability offered by ligand chemistry in organic materials is an interesting asset that can be exploited at hybrid interfaces. Here I will present two examples where the molecular strategy is employed to tune the interactions of single transition metal ions with underlying spin-degenerated electrons in non-magnetic metals, and with spin-textured electrons in topological insulators. In both cases, we obtain a comprehensive picture of the phenomenology by combining scanning tunnelling microscopy/spectroscopy, atomic manipulation, X-ray absorption and photoelectron spectroscopy, and ab-initio calculations.

On our systematic study of transition metal phthalocyanines on noble metals we show how the interaction with the substrate can be mediated by the metal ion or the organic ligand and how, depending on this, the molecular magnetic moment can either be quenched or enhanced [1,2]. The molecular spin and charge can be further manipulated by doping with alkalis atom by atom [3,4]. By moving from phthalocyanines to porphyrine single molecules, and then to on-surface synthesized covalent networks, we will see that the interaction with substrate can be exquisitely fine-tuned by the conformational differences between the systems.

For molecular films on topological insulators, the tunability of ligands is exploited to tune the interaction of Co ions with the underlying topological surface state (TSS), going from the strongly interacting regime where the TSS is quenched in the first quintuple layer [5], to the weakly interacting regime where both the TSS and the Co magnetic moment are preserved [6].

REFERENCES

1. A. Mugarza et al., *Phys. Rev. B* 85, 155437 (2012).
2. A. Mugarza et al., *Nature Comm.* 2:490 (2011).
3. C. Krull et al., *Nature Mater.* 12, 337 (2013).
4. S. Stepanow et al., *J. Am. Chem. Soc.* 136, 5451 (2014).
5. M. Caputo et al., *Nano Letters,* 16, 3409 (2016).
6. M. G. Cuxart et al, *ACS Nano.* 14, 6285–6294 (2020).

Synthesis and Chiroptical Properties of Helical Open-Ring Hemiporphyrazines

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Hemiporphyrazines are low-symmetry phthalocyanine analogues in which two oppositely facing isoindoline units are replaced by other aromatic units [1]. Because of their 20π-electron structure, hemiporphyrazines have a large transition magnetic dipole moment ($\boldsymbol{m}$) for the lowest energy electronic transition [2]. We previously reported that $\boldsymbol{m}$ is still large even in helical open-ring hemiporphyrazines ($\mathbf{1}_{\mathbf{M}}$) and that the optically-resolved $\mathbf{1}_{\mathbf{Zn}}$ exhibits intense circularly polarized luminescence (CPL) [3]. Although its luminescence dissymmetry factor (g_{lum}, ±0.021) is quite high as compared with those of related small organic molecules, the CPL signal is only observed at –20 °C due to the facile interconversion of helical structures. Herein we report novel open-ring hemiporphyrazines ($\mathbf{2}_{\mathbf{M}}$) whose helical structure is fixed by an optically-active binaphthyl unit (Figure 1a). It was found that when using the (*S*)-binaphthyl unit, $\mathbf{2}_{\mathbf{2H}}$ exclusively adopts a left-handed helical structure. (*S*)-$\mathbf{2}_{\mathbf{2H}}$ exhibited an intense negative CPL signal at room temperature and its g_{lum} (–0.028) was 1.3 times larger than that of $\mathbf{1}_{\mathbf{Zn}}$ (Figure 1b). Effects of the central metal ion on the chiroptical properties will be discussed in the presentation.

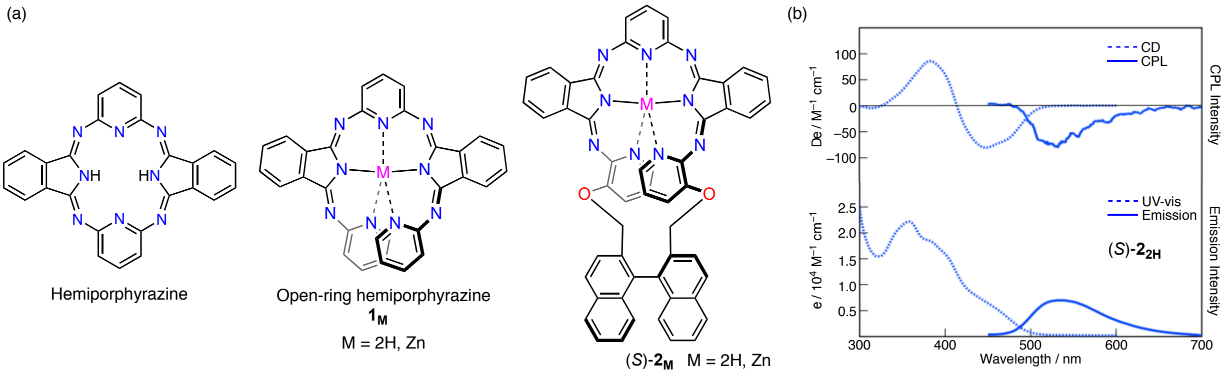
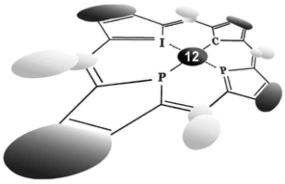


Figure 1. (a) Chemical structures of hemiporphyrazine and helical open-ring hemiporphyrazines. (b) Optical and chiroptical properties of (*S*)-$\mathbf{2}_{\mathbf{2H}}$ in ethylene glycol at room temperature.

REFERENCES

1. Fernández-Lázaro, F.; Torres, T.; Hauschel, B.; Hanack, M. *Chem. Rev.* **1998**, *98*, 563.
2. (a) Fleischhauer, J.; Höweler, U.; Michl, J. *J. Phy. Chem. A* **2000**, *104*, 7762. (b) Muranaka, A.; Ohira, S.; Toriumi, N.; Hirayama, M.; Kyotani, F.; Mori, Y.; Hashizume, D.; Uchiyama, M. *J. Phys. Chem. A* **2014**, *118*, 4415.
3. Tanaka, Y.; Murayama, T.; Muranaka, A.; Imai, E.; Uchiyama, M. *Chem. Eur. J.* **2020**, *26*, 1768.



Spin Transport through Chiral Systems

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Spin based properties, applications, and devices are commonly related to magnetic effects and to magnetic materials. However, we found that chiral molecules, crystals, and films act as spin filters for photoelectrons transmission, in electron transfer, and in electron transport.

The new effect, termed Chiral Induced Spin Selectivity (CISS),[1] was found, among others, in bio-molecules and in bio-systems as well as in chiral oxides and in chiral perovskites. It has interesting implications for the production of new types of spintronics devices, [2] in controlling magnetization,[3] and on electron transfer and conduction. It also enables the introduction of new type of catalysts, especially for oxygen related processes. We also found that charge polarization in chiral molecules is accompanied by spin polarization. This finding shed new light on spin dependent interaction between chiral molecules and be-tween them and magnetic surfaces.[4]

REFERENCES

1. R. Naaman, Y. Paltiel, D,H, Waldeck*, J. Phys. Chem. Lett.,* 11 (2020) 3660.
2. K. Michaeli, V. Varade, R. Naaman, D. A Waldeck, *J. of Physics: Condensed Matter.* 29 (2017) 103002.
3. E. Z. B. Smolinsky et al. *J. Phys. Chem. Lett.* 10 (2019) 1139.
4. K. Banerjee-Ghosh, et al., *Science 360* (2018) 1331.

Structural basis of metabolic detoxification of α-tomatine by various 2-oxoglutarete-depedent dioxygenases

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The eggplant family contains toxic steroidal glycoalkaloids, such as α-tomatine found in the unripe fruits of the tomato plant [1, 2]. Several metabolic pathways detoxify α-tomatine, and the primary reactions of these metabolic processes are carried out by 2-oxoglutarate-dependent dioxygenases (2OGDs), which contain a non-heme iron at the active site [3, 4]. Habrochaitoside synthase converts α-tomatine to habrochaitoside A, which has an expanded F-ring, and C23 atom of α-tomatine is hydroxylated by a C23-hydroxylase. Although these two enzymes are highly homologous, they contribute to the different regiospecific metabolism of α-tomatine. The substrate-bound crystal structure of habrochaitoside synthase and the QM/MM calculations of α-tomatine and Fe(IV)=O species, which is a reactive oxygen intermediate of 2OGDs, suggest the occurrence of a dehydrogenation reaction at the C20 position of α-tomatine and the subsequent ring expansion of the F-ring. For crystallization of the substrate-bound C23-hydroxylase, the enzyme was mixed with α-tomatine and the co-crystals were grown with sitting drop vapor diffusion method. Surprisingly, not α-tomatine but isotomatine, which has the F-ring of α-tomatine inverted, was found in the co-crystal structure, and the C23 atom was pointed toward the metal center. Isomerization of the F-ring is considered to occur after the hydroxylation of α-tomatine by the C23-hydroxylase to form the isotomatine skeleton [4]. However, the co-crystal structure suggests that the C23-hydroxylase selectively binds and hydroxylates isotomatin, thus apparently functioning as an isomerase and promoting α-tomatine metabolism.

REFERENCES

1. Petersen, H. W., Mølgaard, P., Nyman, U., Olsen, C. E., *Biochem. Syst. Ecol.,* **21**, 629-644, 91993.
2. D. M. Harrison, *Nat. Prod. Rep*., **7**, 139-147, 1990
3. Akiyama, R., Watanabe, B., Nakayasu, M., Lee, H. J., Kato, J., Umemoto, N., Muranaka, T., Saito, K., Sugimoto, Y., Mizutani, M., *Nat. Commun*. **12**, 1300, 2021
4. Nakayasu, M., Akiyama, R., Kobayashi, M., Lee, H. J., Kawasaki, T., Watanabe, B., Urakawa, S., Kato, J., Sugimoto, Y., Iijima, Y., Saito, K., Muranaka, T., Umemoto, N., Mizutani, M., *Plant Cell. Physiol.* **61**, 21-28., 2020

Highly Reactive Manganese(IV)-Oxo Complexes in C-H bond Activation Reactions

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We report that Mn(IV)-oxo porphyrin complexes, Mn^{IV}(O)(TMP) (**1**) and Mn^{IV}(O)(TDCPP) (**2**), are capable of activating the C-H bonds of hydrocarbons, including unactivated alkanes such as cyclohexane, via an oxygen non-rebound mechanism. Interestingly, **1** with an electron-rich porphyrin is more reactive than **2** with an electron-deficient porphyrin at a high temperature (e.g., 273 K). However, at a low temperature (e.g., 233 K), the reactivity of **1** and **2** is reversed, showing that **2** is more reactive than **1**. To the best of our knowledge, the present study reports the first example of highly reactive Mn(IV)-oxo porphyrins and their temperature-dependent reactivity in C-H bond activation reactions. Other mechanistic aspects, such as the oxygen non-rebound mechanism in Mn(IV)-oxo porphyrin system, are discussed as well.

Aryl and Alkyl Corroles: “brothers” with different characters

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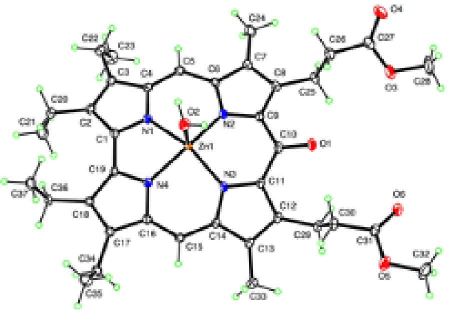
The multifaceted properties of corrole make this macrocycle different from the parent porphyrins and consequently interesting for both theoretical and practical studies [1]. The coordination chemistry of corrole is a perfect example of these studies because the correct interpretation of the electronic structures of metal complexes of corrole is often challenging [2, 3].

Their low oxidation potentials and strong σ-donor character make easy ligand-to-metal electron transfer and result in the non-innocent character of corrole as ligand, which often complicates the elucidation of the electronic structure of the resulting complexes.

Despite these difficulties, a great development of the Periodic Table of Metallocorrolates has been achieved, but zinc ion, widely present in the porphyrin field, has been poorly studied in the case of corrole. The mismatch among the divalent charge of the metal ion and the trianionic character of corrole probably caused this disinterest, but there is no shortage of Zn metalation examples [4]. In 2015 Broring’s group [5] obtained the formation of the first example of zinc aryl corrole complex as a derivative of the corrole π-radical cation, but a complete description of the coordinative behavior of these species has not yet been reported. For this reason, we focused on the study of the synthetic pathways and the spectroscopic characterization of the products obtained from the reaction of both aryl- and alkylcorroles with zinc salts, pointing out their differences in terms of reactivity and obtained compounds.



REFERENCES

1. Paolesse, R.; Erben, C.; Will, S.; Kadish, K. M. In The Porphyrin Handbook Volume 2 / Heteroporphyrins, Expanded Porphyrins and Related Macrocycles; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: **2002**, p. 201-295.
2. Nardis, S.; Mandoj, F.; Stefanelli, M.; Roberto, P. *Coord. Chem. Rev*. **2019**, *388*, 360.
3. Ghosh, A. *Chem. Rev.* **2017**, *117*, 3798.
4. Paolesse, R.; Licoccia, S.; Boschi, T. *Inorganica Chim. Acta*, **1990**, *178*, 9.
5. Schweyen, P.; Brandhorst, K.; Wicht, R.; Wolfram, B.; Bröring, M. *Angew. Chem. Int. Ed*. **2015**, *54*, 8213.

Creating new types of scalable, aza-BODIPY like chromophores: from electron-deficient MB-DIPYs to aza-DIPY-isoindigo hybrids

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We have developed synthetic protocols for the preparation of two new classes of aza-BODIPY like chromophore systems: (i) electron-deficient MB-DIPY chromophores and (ii) hybrid aza-DIIPY-isoindigo systems (Figure 1). Two series of chromophores and their metal complexes were characterized by UV-Vis-NIR, NMR, HRMS, and X-ray crystallography, while their redox properties were investigated by electrochemical and spectro-electrochemical methods as well as by the chemical reduction approach. Single- and double-electron reduced forms of MB-DIPYs were characterized by UV-Vis-NIR spectroscopy. The photophysical properties of new systems were investigated using steady-state fluorescence and transient absorption spectroscopy. The experimental electronic, spectroscopic, and geometric parameters of the MB-DIPYs and hybrid aza-DIPY-isoindigo chromophores were correlated with their electronic structures elucidated by DFT and TDDFT calculations.

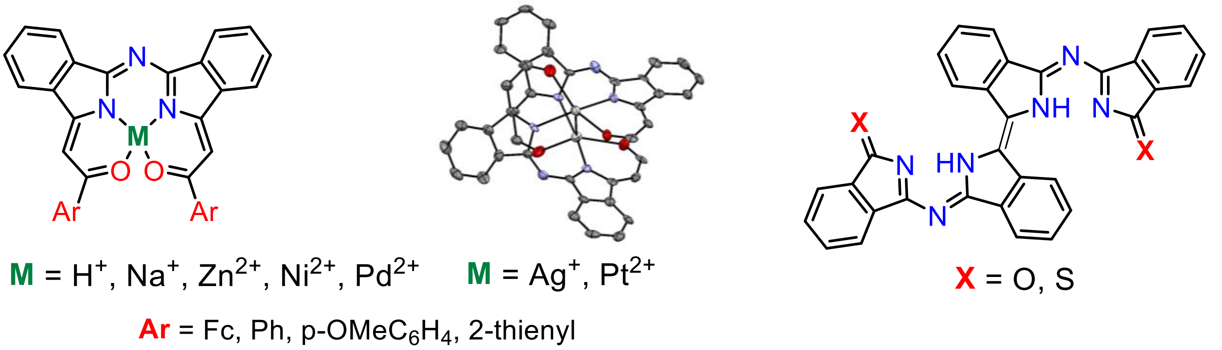

Figure. 1. Representative examples of MB-DIPYs and hybrid aza-DIPY-isoindigo systems.

REFERENCES

1. Nemykin, V. N.; Zatsikha, Y. V.; Shamova, L. I.; Herbert, D. *Angew. Chem. Int. Ed.* **2021**, *60*, 12304-12307.
2. Zatsikha, Y. V.; Shamova, L. I.; Nemykin, V. N. *J. Org. Chem.* **2021**, *86*, 4733-4746.
3. Zatsikha, Y. V.; Shamova, L. I.; Schaffner, J. W.; Healy, A. T.; Blesener, T. S.; Cohen, G.; Wozniak, B.; Blank, D. A.; Nemykin, V. N. *ACS Omega* **2020**, *5*, 28656-28662.
4. Zatsikha, Y. V.; Shamova, L. I.; Blesener, T.; Herbert, D. E.; Nemykin, V. N. Dalton Trans. 2020, 49, 5034-5038.
5. Y. V. Zatsikha, L. I. Shamova, T. S. Blesener, I. A. Kuzmin, Y. V. Germanov, D. E. Herbert, V. N. Nemykin *J. Org. Chem.* **2019**, *84*, 14540-14557.

Molecular Dyad Systems Based on Boron Subphthalocyanine

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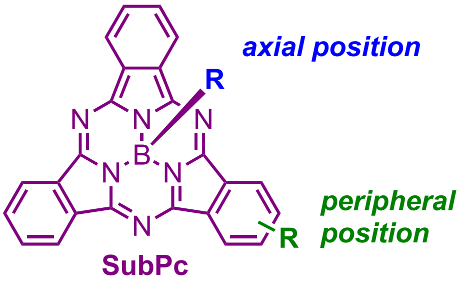
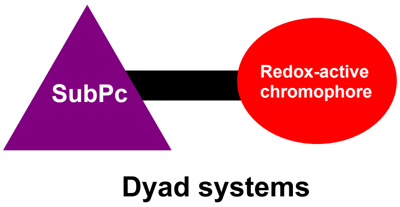
Boron subphthalocyanines (SubPcs) are cone-shaped molecules comprised of three isoindole units bridged by aza-linkages and with a central boron atom containing an axial substituent. They are attractive units in for example organic photovoltaics owing to their optical and redox properties.[1-4] Here, I will show our work on combining the SubPc unit with other functional units using acetylenic coupling reactions as the major synthetic tool.[5-7] Thus, a variety of dyad systems will be presented. The influence on the connectivity between the two units was studied, that is, how optical and redox properties depend on whether the two functional units are connected via the axial position of the SubPc or via a peripheral position of the SubPc. Experimentally determined redox potentials were compared to theoretically calculated ones, allowing us to move forward a reliable theoretical method for predicting redox properties.





REFERENCES

1. C. G. Claessens, D. González-Rodriguez, M. S. Rodríguez-Morgade, A. Medina, T. Torres, *Chem. Rev.* **2014**, *114*, 2192-2277.
2. T. M. Grant, D. S. Josey, K. L. Sampson, T. Mudigonda, T. P. Bender, B. H. Lessard, *Chem. Rec.* **2019**, *19*, 1093-1112.
3. G. Bottari, G. de la Torre, D. M. Guldi, T. Torres, *Coord. Chem. Rev.* **2021**, *428*, 213605.
4. M. Dowds, M. B. Nielsen, *Mol. Syst. Des. Eng.* **2021**, *6*, 6-24.
5. H. Gotfredsen, T. Holmstrøm, A. V. Munoz, F. E. Storm, C. G. Tortzen, A. Kadziola, K. V. Mikkelsen, O. Hammerich, M. B. Nielsen, *Org. Lett.* **2018**, *20*, 5821-5825.
6. H. Gotfredsen, T. Neumann, F. E. Storm, A. V. Munoz, M. Jevric, O. Hammerich, K. V. Mikkelsen, M. Freitag, G. Boschloo, M. B. Nielsen, *ChemPhotoChem* **2018**, *2*, 976-985.
7. M. G. Rasmussen, M. F. Jespersen, O. Blacque, K. V. Mikkelsen, M. Juríček, M. B. Nielsen, *Energy Sc. Eng.*, In revision.

Synthesis of Molecular Motor-functionalized Porphyrin Macrocycles

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As part of our program aimed at the encoding of digital information into polymers in the form of chiral epoxide functions (*R*,*R*-epoxide = digit 0, *S*,*S*-epoxide = digit 1) with chiral catalytic machines (Figure 1a) we report the synthesis of two motor-functionalized porphyrin macrocycles (Figure 1b, **1** and **2**). These compounds display helical, planar and point chirality, and are mixtures of enantiomers and diastereomers, which differ in the relative orientation of the motor and macrocyclic components. They are light-switchable and have been separated by (chiral) chromatography. Fluorescence, UV-vis, and ^{1}H-NMR studies reveal that the motor-functionalized macrocycles can bind and thread viologen guest molecules, including one-side blocked polymers of 30 repeat units. The latter feature indicates that the new motor systems can find the open end of a polymer chain, thread on it, and move along the chain to eventually bind at the viologen trap, opening possibilities for light-switchable catalytic writing on single polymer chains via chemical routes.

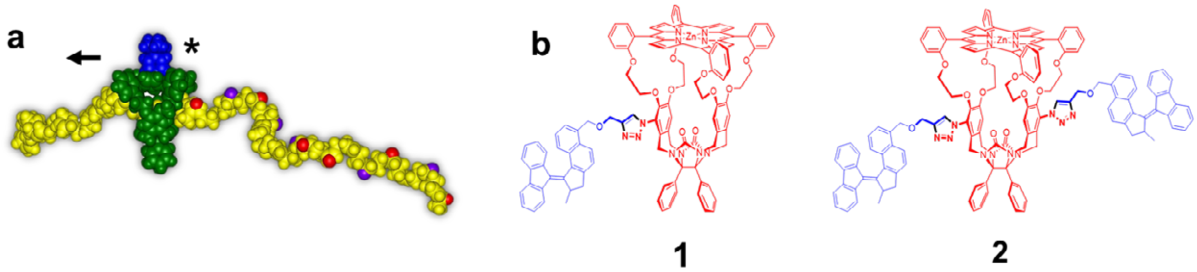

Figure 1 : (a) Encoding information into a polymer chain (yellow) with a chiral catalytic machine (green and blue). Red and purple balls represent enantiomeric epoxides (digits 0 and 1). (b) Chiral motor-functionalized porphyrin macrocycles **1** and **2**.

REFERENCES

1. M.G.T.A. Rutten, F.W. Vaandrager, J.A.A.W. Elemans, and R.J.M. Nolte, Encoding information into polymers. *Nature Revs. Chem.,* **2**, 365-381 (2018).
2. P.J. Gilissen, P.B. White, J.A. Berrocal, N. Vanthuyne, F.P.J.T. Rutjes, B.L. Feringa, J.A.A.W. Elemans, and R.J.M. Nolte, Molecular motor-functionalized porphyrin macrocycles, *Nature Commun.,* **11** Article Number: 5291 (2020).
3. P.J. Gilissen, N. Vanthuyne, B.L. Feringa, J.A.A.W. Elemans, and R.J.M. Nolte, Light-gated binding in double-motorized porphyrin cages, *Natural Sciences*, in press (2021).

Targeted Porphycenes for Photodynamic Therapy Applications

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Porphycenes are structural isomers of porphyrins that are promising photosensitising candidates thanks to their high singlet oxygen photoproduction efficiency and their broad and strong absorption in the red/near-IR spectral region. Despite these desirable optical properties, their aggregation in water detracts from their photosensitising activity. Conjugation of porphycenes to hydrophilic targeting entities may thus enhance both their solubility and selectivity for the target cells. Herein, we present the conjugation of 2,7,12,17-tetramethoxyethyl-9-isothiocyanato porphycene to two hydrophilic entities, gentamicin as an antibiotic and triphenylphosphonium as a lipophilic cation. The synthesis, photophysical, and photochemical characterization of the compounds is reported, as well as their *in vitro* photodynamic activity against Gram+ and Gram- bacteria, yeasts, and cancer cells. The conjugates presented high absorption coefficients in the red/near-IR and tautomerism between two different photoactive species, together with large singlet oxygen quantum yields. The gentamicin conjugate was particularly apt to inactivate *S. aureus*, *E. coli* and *C. albicans* in the submicromolar range. The triphenylphosphonium conjugate showed less activity against microorganisms than the previous conjugate, but higher for HeLa cells. Mechanistic studies using fluorescence correlation spectroscopy, confocal and STED super resolution microscopy, and femtosecond transient absorption shed light on the underlying processes.

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REFERENCES

1. Vogel, E.; Köcher, M.; Schmickler, H.; Lex J. Porphycene - a Novel Porphin Isomer. *Angew. Chemie Int. Ed.* 1986, 25 (3), 257–259
2. Planas, O.; Fernández-Llaneza, D.; Nieves, I.; Ruiz-González, R.; Lemp, E.; Zanocco, A.; Nonell, S. Acid- and Hydrogen-Bonding-Induced Switching between 22-π and 18-π Electron Conjugations in 2-Aminothiazolo[4,5-c]Porphycenes. *Phys. Chem. Chem. Phys.* 2017, 19 (37), 25537–25543
3. Cahan, R.; Swissa, N.; Gellerman G.; Nitzan, Y. Photosensitizer-Antibiotic Conjugates: A Novel Class of Antibacterial Molecules. *Photochem. Photobiol*. 2010, 86 (2), 418–425
4. Malatesti, N.; Munitic, I. ; Jurak, I. Porphyrin-Based Cationic Amphiphilic Photosensitisers as Potential Anticancer, Antimicrobial and Immunosuppressive Agents. *Biophys. Rev.* 2017, 9 (2), 149–168
5. Nieves, I.; Hally, C.; Viappiani, C.; Agut, M.; Nonell, S. A porphycene-gentamicin conjugate for enhanced photodynamic inactivation of bacteria, *Bioorg. Chem.* 2020, 97, 103661

DFT calculated Pathways of Electrons, Protons, and Oxygen derived Species in a bacterial cytochrome c oxidase: Comparisons with Experimental Spectroscopies and Structures

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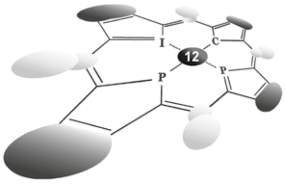
Using DFT Methods, we present calculations of geometries, relative energies, and spectroscopic properties over the catalytic reaction cycle of a bacterial ba3 type cytochrome c oxidase (CcO) compared to available experimental structures and spectroscopic parameters. In particular, calculated Fe-O vibrational frequencies will be emphasized over the catalytic cycle and compared with those found by Resonance Raman spectroscopy.[1-2] In addition, we explore comparisons and contrasts between ba3 Class CcO enzymes and aa3 Class enzymes.

REFERENCES

1. L. Noodleman, W.-G. Han Du, D. McRee, Y. Chen, T. Goh, A.W. Goetz *Phys.Chem. Chem.Phys.* 2020, **22.** 26652.
2. W.-G. Han Du, A.W. Goetz, L. Noodleman. *Inorg. Chem.* 2019, **58**, 13933.



Design of Phthalocyanines for Photoinactivation of Multidrug Resistance Bacteria

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Metallophthalocyanines (MPcs) have attracted the attention of many researchers due to their numerous applications including in non-linear optics, photodynamic therapy, and photodynamic antimicrobial chemotherapy (PACT). For these applications, high triplet state quantum yields and long triplet lifetimes as well as large singlet oxygen quantum yields are required. These parameters can be improved by introduction of heavy centrals in the center of the phthalocyanine ring, changes in the ring substituents, symmetry, or by linking to nanoparticles. The different methods of improving these parameters will be discussed together with the use of the conjugates for PACT on biofilms and planktonic cells. PACT is an alternative method to deal with bacterial and fungal infections, which requires a photosensitizer that can be illuminated with light to cause the oxidative destruction of microbial pathogens.

Nanometric chiral platform for the induction of chiral properties to porphyrin derivatives – towards enantioselective sensors

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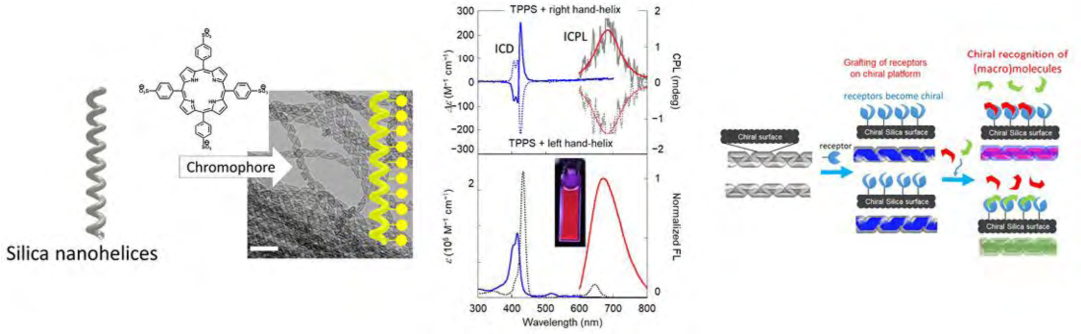
Nanometric helices with controllable pitches are attractive nanoobjects for a wide range of applications in materials sciences, chemical and biomaterial sensing, and enantioselective catalysis. We have reported that chiral supramolecular assembly system can be achieved from non-chiral cationic surfactants with chiral counterions [1]. In this talk, I show how such structures can be used as scaffolds to obtain hybrid organic/inorganic nanohelices [2], which can be used as chiral platform to organize achiral dyes such as porphyrin derivatives in order to induce chiroptical signals from them [3]. I will then discuss how such chiral porphyrin network with induced chirality is used to design enantioselective sensors.



REFERENCES

1. a) Oda, R.; Huc, I.; Schmutz, M.; Candau, S. J.; MacKintosh, F. C. Nature 1999, 399 (6736), 566–569.; b) Brizard, A.; Aimé, C.; Labrot, T.; Huc, I.; Berthier, D.; Artzner, F.; Desbat, B.; Oda, R. J. Am. Chem. Soc. 2007, 129 (12), 3754–3762
2. a) Sugiyasu, K.; Tamaru, S.; Takeuchi, M.; Berthier, D.; Huc, I.; Oda, R.; Shinkai, S. Chem. Commun. 2002, No. 11, 1212–1213.; b) Delclos, T.; Aimé, C.; Pouget, E.; Brizard, A.; Huc, I.; Delville, M.-H.; Oda, R. Nano Lett. 2008, 8 (7), 1929–1935.
3. a) Scalabre, A.; Gutiérrez Vílchez, A. M.; Sastre-Santos, A.; Fernández-Lázaro, F.; Bassani, D. M.; Oda, R. Supramolecular Induction of Topological Chirality from Nanoscale Helical Silica Scaffolds to Achiral Molecular Chromophores. J. Phys. Chem. C 2020. 124, 43, 23839–23843; b) Liu, P.; Chen, W.; Okazaki, Y.; Battie, Y.; Brocard, L.; Decossas, M.; Pouget, E.; Muller-Buschbaum, P.; Kauffmann, B.; Pathan, S.; Sagawa, T.; Oda, R. Nano Lett. **2020**.; c) Liu, P, Battie, Y. Decossas, M. Tan, S. Pouget, E. Okazaki, Y. Sagawa, T. Oda, R. ACS Nano **2021** doi.org/10.1021/acsnano.1c05819.

Immobilization of iron porphyrin on inorganic semiconductor for photocatalytic CO_2 reduction

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Developing efficient solar driven photocatalytic materials for the reduction of CO_2 into fuels or added-values commodities represents a promising strategy to deviate from petrochemical feedstock and to close the carbon cycle. Among molecular CO_2 reduction catalysts, iron tetra-arylporphyrin derivatives and particularly that substituted by four cationic trimethylanilinium groups exhibits the highest activity ever reported even in water.[1] These outstanding performances prompted us to envision the preparation of a graftable version of this catalyst and to investigate its activity upon immobilization on $Cu(In,Ga)Se_2$ (CIGS) electrodes. Indeed, CIGS is a very attractive p-type semiconductor, which proved to be particularly suitable for CO_2 photocatalysis.[2] In this communication, we will report the synthesis of new iron porphyrins functionalized with anchoring group to be grafted on electrode surfaces (Figure). The electrocatalytic and photocatalytic activities in aqueous environment will be also presented.

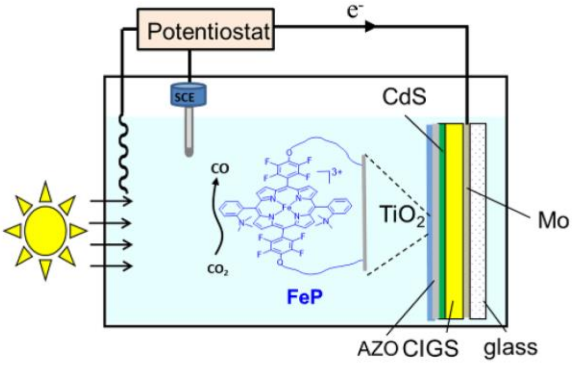

Figure. Schematic representation of the photocathode with a grafted iron porphyrin catalyst.

REFERENCES

1. Azcarate, I.; Costentin, C.; Robert, M.; Savéant, J.-M., *J. Am. Chem. Soc.* **2016**, 138, 16639-16644.
2. Pati, P. B.; Wang, R.; Boutin, E.; Diring, S.; Jobic, S.; Barreau, N.; Odobel, F.; Robert, M., *Nature Commun.* **2020**, 11, 3499.

A New Approach for Peripheral Annelation of Porphyrin: Synthesis of Unusual Phenathrene-fused Porphyrins

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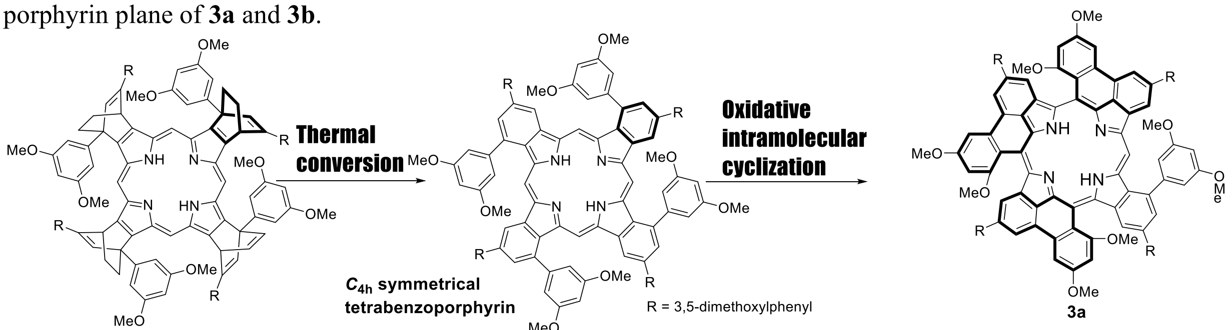
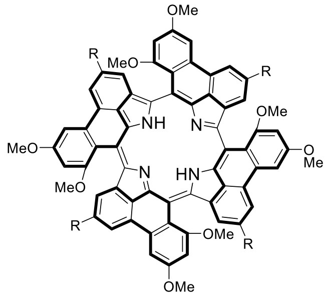
The expansion of the π-systems of porphyrins have been extensively studied for applications such as organic electronic devices and photosensitizers for photodynamic therapy. Peripheral annelation of aromatics is an effective method for modifying the electronic structures and optical properties of porphyrins. The precursor methods for linearly π-extended porphyrins are known as two aromatization-methods: oxidative dehydrogenation of partially saturated rings and retro Diels–Alder reaction of bicyclo[2.2.2]octadiene moieties. These approaches afforded benzo-, [2,3]naphtho-, [2,3]anthra- and benzofluoranthene-fused porphyrins. On the other hand, π-expanded porphyrins at α,β-pyrrolic and *meso*-positions were obtained via intramolecular cyclization at the *meso*-substituent and β-pyrrolic carbon. Similarly, synthesis of unusual phenanthro- and picenoporphyrins was reported via Masamune–Bergman reaction of β-diethynyl-*meso*-tetraphenylporphyrin followed by Pt(II)-catalyzed intramolecular radical cyclization.[1] This strategy afforded the corresponding porphyrins in good yield. However, multiple-phenanthrene-fused poprphyrins could not be obtained by intramolecular cyclization between *meso*-substituent and β-fused benzo moiety.

We herein report another route for peripheral annelation method of porphyrinoid based on stepwise precursor method: the retro Diels–Alder conversion of BCOD-fused porphyrin and the subsequent oxidative intramolecular ring-closure reaction. C_{4h} symmetrical octaaryltetrabenzoporphyrin **2** was synthesized *via* cyclotetramerization and thermal conversion based on retro Diels–Alder reaction.[2] The oxidative intramolecular ring-closure reaction of octaarylTBPs **2** afforded tri- and tetraphenanthroporphyrins. X-ray crystallographic analysis showed a distorted porphyrin plane of **3a** and **3b**.



REFERENCES

1. Nath, M.; Pink, M.; Maleski, J. M. *J. Organomet. Chem.* **2011**, *696*, 4152.
2. (a) Furuyama, T.; Okujima, T.; Muramatsu, K.; Takahashi, Y.; Mikami, H.; Fukumura, T.; Mori, S.; Nake, T.; Takase, M.; Uno, H.; Kobayashi, N. *Eur. J. Org. Chem.* **2019**, 3224. (b) Muramatsu, K.; Okujima, T.; Mori, S.; Takase, M.; Uno, H. *Chem. Lett.* **2021**, *50*, 841.



3b

Reconstituted Myoglobin with Corrole Metal Complexes and its Reactivity toward Hydrogen Peroxide

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In biological systems, various metalloproteins have been found. Especially, a series of hemoprotein demonstrate unique functions such as electron transfer, gas binding and catalysis. In hemoprotein, physicochemical property and reactivity of a common cofactor, heme, is strongly dependent on a protein matrix: protein matrix enables to regulate the function of heme [1]. Our group has focused on this unique system, and expanded the system with artificial heme derivatives. For example, Mn and Fe porphycenes are inserted into apo-form of myoglobin, a simple oxygen-binding hemoprotein, to provide artificial metalloenzymes for C–H bond hydroxylation [2] and olefin cyclopropanation [3], respectively. Similarly, reconstituted myoglobins with Co and Ni tetradehydrocorrins serve as natural enzyme models for methionine-synthase [4] and methyl conenzyme M reductase [5], respectively. In addition to two porphyrinoid metal complexes, we have focused on corrole metal complexes and the investigated the reactions of the reconstituted myoglobins with hydrogen peroxides.

Corrole is a trianionic ligand for metal complex whereas porphyrin is a dianionic ligand. Thus, quite different reactivity for redox reactions is expected. Fe corrole was successfully inserted into apo-form of myoglobin to afford the reconstituted myoglobin. This protein shows much higher peroxidase activity than that of native myoglobin. Two intermediate species were clarified by stopped-flow experiments. Both of the compound I-like two electron oxidized species and compound II-like one-electron oxidized species are related to the catalytic activity. The efficient formation of compound I-like species could contribute the high catalytic activity for peroxygenase reaction. Co corrole also was investigated as an artificial cofactor of myoglobin. The reconstituted myoglobin with Co corrole is reacted with hydrogen peroxide only in the presence of phenol derivatives. The intermediate was not observed, but transiently formed peroxide complex may react with the phenol-type substrate to provide one-electron oxidized Co corrole. In the case of Co corrole without a myoglobin matrix or Co porphyrin-containing myoglobin, this type of reaction does not occur. This finding indicates quite different and unique reactivity of Co corrole relative to other heme derivatives in the myoglobin matrix.

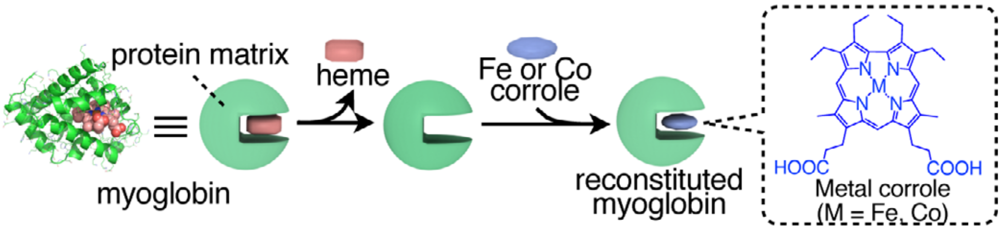

Figure 1. Schematic representation of reconstitution of myoglobin with metal corroles.

REFERENCES

1. K. Oohora, T. Hayashi, *Dalton Trans.* **2021**, *50*, 1940-1949.
2. K. Oohora, H. Meichin, Y. Kihira, H. Sugimoto, Y. Shiro, T. Hayashi, *J. Am. Chem. Soc.* **2017**, *139*, 18460-18463.
3. K. Oohora, H. Meichin, L. Zhao, M. W. Wolf, A. Nakayama, J. Hasegawa, N. Lehnert, T. Hayashi, *J. Am. Chem. Soc.* **2017**, *139*, 17265-17268.
4. Y. Morita, K. Oohora, A. Sawada, T. Kamachi, K. Yoshizawa, T. Hayashi, *Inorg. Chem.* **2017**, *56*, 1950-1955.
5. K. Oohora, Y. Miyazaki, T. Hayashi, *Angew. Chem. Int. Ed.* **2019**, *58*, 13813-13817.

Self-Assembly of Cone-Shaped Subphthalocyanines: A Theoretical Insight

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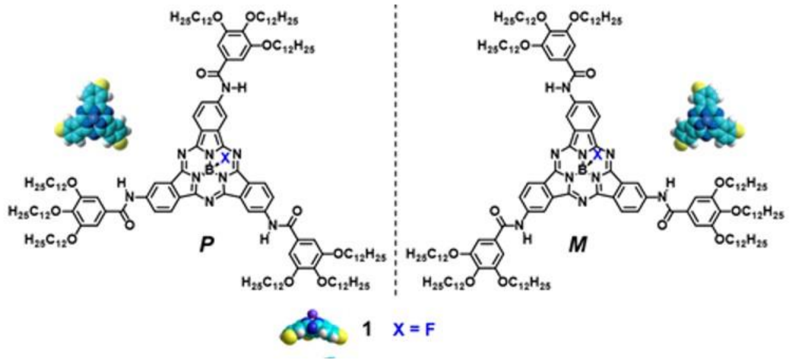
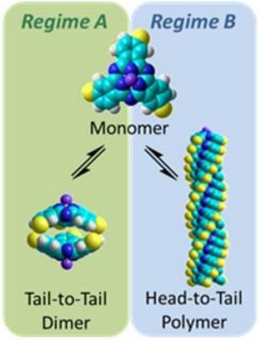
Conic discotic molecules such as subphthalocyanines (SubPcs) present two relevant differences compared to planar discotics: 1) they exhibit axial dipole moments and, if piled up in columns, give rise to polarly ordered materials, and 2) when properly substituted, they become intrinsically chiral. Furthermore, owing to their rigid cone-shaped structure, SubPcs display a convex side (a head) and a concave side (a tail) and their intermolecular stacking interactions may lead to centrosymmetric head-to-head and tail-to-tail and to noncentrosymmetric head-to-tail aggregation geometries.

In this contribution, we perform a theoretical study on the aggregation modes of the C_3-symmetric boron SubPc **1**, in which the central boron is substituted with a small, highly electronegative fluorine atom and the SubPc core is decorated with arilamide groups giving rise to **1*P*** and **1*M*** enantiomers. Depending solely on the solvent nature (aromatic or aliphatic), π-conjugated SubPc **1** can self-assemble either in a tail-to-tail dimer (regime A) or in a head-to-tail columnar stack (regime B), formed via a nucleation-elongation polymerization mechanism [1]. Furthermore, **1*P*** and **1*M*** enantiomers give rise to homochiral assemblies with opposite helicities [2]. Calculations indicate that whereas the SubPc enantiomers socially self-sort in the polymer regime, showing an alternate columnar stacking order, they reveal narcissistic self-sorting in the dimer regime, each enantiomer disclosing a strong preference to associate with itself.





REFERENCES

1. M. J. Mayoral, J. Guilleme, J. Calbo, J. Aragó, F. Aparicio, E. Ortí, T. Torres, D. González-Rodríguez, *J. Am. Chem. Soc.* **2020**, *142*, 21017−21031.
2. J. Guilleme, M. J. Mayoral, J. Calbo, J. Aragó, P. M. Viruela, E. Ortí, T. Torres, D. González-Rodríguez, *Angew. Chem. Int. Ed.* **2015**, *54,* 2543–2547.

Versatile Aromaticities of Expanded Porphyrins

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Since our serendipitous finding of the facile synthesis of a series of *meso*-aryl-substituted expanded porphyrins [1], we have continued to study the versatile aromaticities of the expanded porphyrins [2,3,4]. These studies will be overviewed here. Porphyrins can be delineated as [18]porphyrin(1.1.1.1) possessing a 18π-aromatic circuit over a rigid skeleton. In most cases, their oxidized 16π- and reduced 20π-congeners are not stable. In contrast, *meso*-aryl expanded porphyrins become more conformationally flexible and are allowed to take several stable oxidation states. As similar to the porphyrin case, the overall energetic stabilizations of *meso*-aryl expanded porphyrins are coming mostly from the aromatic stabilization of the constituent pyrroles and the energetic stabilization and destabilization of the global conjugated network are only minor. Therefore, if *meso*-aryl expanded porphyrins take an electronically unstable state, they are often sufficiently stable under ambient conditions. Conformational flexibilities of *meso*-aryl expanded porphyrins offer a chance that they search the most stable conformation depending upon the number of the conjugated π-electrons. When the number of the conjugated π-electrons of *meso*-aryl expanded porphyrin (larger than [26]hexaphyrin(1.1.1.1.1.1) is set *4n*, the expanded porphyrin is so smart to twist its conformation to acquire Möbius aromaticity [5]. Stable Möbius antiaromatic molecules were isolated and characterized to show that aromaticity switch between [4n+2] vs [4n] is also valid for cyclic π-conjugated molecules having a molecular twist.

REFERENCES

1. J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi, A. Osuka, *J. Am. Chem. Soc.,* **123**, 7190-7191 (2001).
2. A. Osuka, S. Saito, *Chem. Commun.*, **47**, 4330-4339 (2011).
3. S. Saito, A. Osuka, *Angew. Chem. Int. Ed*., **50**, 4342-4373 (2011).
4. T. Tanaka, A. Osuka, *Chem. Rev.*, **117**, 2584-2640 (2017).
5. Y. Tanaka, S. Saito, S. Mori, N. Aratani, H. Shinokubo, N. Shibata, Y. Higuchi, Z. S. Yoon, K. S. Kim, S. B. Noh, J. K. Park, D. Kim, and A. Osuka, *Angew. Chem. Int. Ed.*, **47**, 681-684 (2008).
6. T. Higashino, J. M. Kim, T. Miura, S. Saito, J.-Y. Shin, D. Kim, and A. Osuka, *Angew. Chem. Int. Ed.*, **49**, 4950-4954 (2010).

Subtle effects of solvents and cosolvents on the supramolecular polymerization pathways of amide-functional discotics

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The supramolecular polymerization of two different disc-shaped monomers with an extended π-system and amides connecting the core to solubilising side groups is discussed. First, a porphyrin-based monomer comprising 4 amides encoding for helical hydrogen bonds was studied at various concentrations, solvent compositions and temperatures. Monomers aggregate in isodesmic J-aggregates at intermediate solvent quality and temperature, followed by nucleated H-aggregates at lower solvent qualities and temperatures. At increased thermodynamic driving forces, such as high concentration and low temperature, the H-aggregates form hierarchical superhelices as evidenced by AFM measurements. The existence of the isodesmic aggregation buffers the free monomer pool and renders the nucleation of the H-aggregates insensitive to concentration changes in the limit of high concentrations [1].

Interestingly, a similar behaviour is observed in chiral triphenylene-2,6,10-tricarboxamides (TTAs). In addition, the supramolecular polymerization of TTAs was also studied in chiral solvents. Diastereomeric differences in the supramolecular polymerization of enantiomers were revealed in a chiral chlorinated solvent. The competition between the preferences induced by the stereocenters of the assembled monomers and those present in the solvent molecules resulted in unforeseen temperature-dependent solvation effects. When the energetic difference between the P- and M-helical aggregates is close to the energetic contribution of the chiral solvent, the dissymmetry introduced by the solvent was amplified by the additive cooperativity of these effects along the polymer backbone [2].

REFERENCES

1. Mabesoone, M. F. J.; Markvoort, A. J.; Banno, M.; Yamaguchi, T.; Helmich, F.; Naito, Y.; Yashima, E.; Palmans, A. R. A.; Meijer, E. W. Competing Interactions in Hierarchical Porphyrin Self-Assembly Introduce Robustness in Pathway Complexity. *J. Am. Chem. Soc*. 2018, 140, 7810–7819.
2. Ślęczkowski, M. L.; Mabesoone, M. F. J.; Ślęczkowski, P.; Palmans, A. R. A.; Meijer, E. W. Competition between Chiral Solvents and Chiral Monomers in the Helical Bias of Supramolecular Polymers. *Nat. Chem.* 2021, 13, 200–207.

Ethoxycarbonyl-derived B(III)Subchlorins: Direct Synthesis & Photophysical Studies

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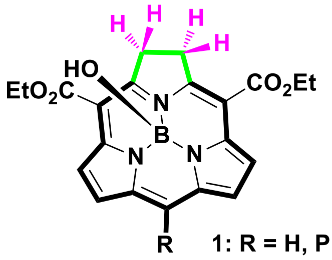
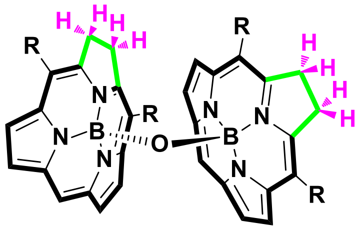
B(III)subporphyrinoids are bowl-shaped 14-π aromatic macrocycles of great promise. Their chemistry emerged with the synthesis of B(III)subphthalocyanines by Meller and Ossko in 1972 [1]. Subsequently, subporphyrin was first reported independently by Osuka's and Kobayashi's groups as its B(III)-complexes [2]. In 2008, Osuka's group reported *meso*-aryl B(III)subchlorins **1** (Scheme 1), the contracted congener of naturally occurring reduced porphyrinoid chlorin [3]. Despite its attractive photophysical properties, there is very little progress noticed in the chemistry of subchlorin. This may be attributed to its not so straightforward synthesis and isolation protocols. Recently, our group demonstrated an exclusive and facile synthetic route towards B(III)subchlorin by the introduction of strong electron-withdrawing substituents like ethoxycarbonyl groups as its diester-derivative **2** [4a]. This subchlorin was found to be quite stable towards oxidation and could only be oxidized to the corresponding subporphyrin analogue by refluxing with DDQ in toluene. In addition, we could also isolate the first subchlorin dimer as the corresponding B(III)-O-B(III) dimer. Further, *meso*-trisubstituted subchlorins revealed easier modulation of their photophysical properties [4b-c]. These subchlorins exhibit intense fluorescence and can be employed for cell imaging and in addition, found to generate singlet oxygen efficiently and kills cancerous cells through photodynamic mechanism only [4d].



1: R = H, Ph, *n*-Pr, COOEt



2: R = H

REFERENCES

1. (a) Claessens, C. G.; Gonzalez-Rodriguez, D.; Rodriguez-Morgade, M. S.; Medina, A.; Torres, T. *Chem. Rev.* **2014**, *114*, 2192−2277. (b) Meller, A.; Ossko, A. *Monatsh. Chem.* **1972**, *103*, 150-155.
2. (a) Inokuma, Y.; Kwon, J. H.; Ahn, T. K.; Yoo, M-C.; Kim, D.; Osuka, A. *Angew. Chem. Int. Ed.* **2006**, *45*, 961-964; (b) Kobayashi, N.; Takeuchi, Y.; Matsuda, A. *Angew. Chem. Int. Ed.* **2007**, *46*, 758-760.
3. Tsurumaki, E.; Saito, S.; Kim, K. S.; Lim, J. M.; Inokuma, Y.; Kim, D.; Osuka, A. *J. Am. Chem. Soc.* **2008**, *130*, 438-439;
4. (a) Chandra, B.; Soman, R.; Sathish Kumar, B.; Jose, K. V. J.; Panda, P. K. *Org. Lett.* **2020**, *22*, 9735-9739. (b) Soman, R.; Chandra, B.; Bhat, I. A.; Sathish Kumar, B.; Hossain, S. S.; Nandy, S.; Jose, K. V. J.; Panda, P. K. *J. Org. Chem.* **2021**, *86*, 10280-10287. (c) Bhat, I. A.; Soman, R.; Chandra, B.; Sahoo, S.; Thaltiri, V.; Panda, P. K. *J. Porphyrins Phthalocyanines* **2021**, *25*, 1015-1021. (d) Soman, R.; Chandra, B.; Ishfaq, A. B.; Raveendra, B. M.; Panda, P. K.; *IN Patent Application No.*: 202041048863; November 09, 2020.

Photodynamic therapy in combination with chemotherapy is superior to monotherapy for the treatment of lung cancer

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For the past several years, one of the objectives of our laboratory has been to develop multi-functional agents for cancer-imaging (PET, MRI, fluorescence alone or in combination) and treatment of cancer by PDT, using a *"See and Treat"* approach. In one of such attempts, we have been able to develop an iodinated PS (methyl-3-(1'-*m*-iodobenzyloxy)ethyl-3-devinylpyropheophorbide-a), which in its radioactive form (^{124}I-) can be used to image a variety of tumors by PET-imaging, and as a non-radioactive analog for NIR fluorescence-imaging and treatment of cancer by PDT. Thus, a single agent (in combination of radioactive + corresponding non-radioactive FIRMS) can be used for imaging (PET, fluorescence) and therapy of cancer This iodinated compound provides a unique opportunity to determine the stage of cancer (localized or metastasized) by PET imaging of the cancer with ^{124}I-labeled agent and could help to select the treatment plan accordingly either by PDT alone (if cancer is localized), or PDT + chemotherapy (if the cancer is metastasized). Therefore, we initially investigated the PET-imaging ability of the ^{124}I-lbeled of this compound (PET-ONCO) in a variety of tumor types, including lung tumors, and excellent results were obtained. This current study presents the utility of a non-radioactive PS for treating lung cancer with and without chemotherapy (doxorubicin or cisplatin) in a variety of lung tumor xenografts derived from lung cancer patients. The advantages of PDT in combination with chemotherapy will be discussed.

REFERENCES

1. Gattamachi A and Johnson J. What are the treatment options for lung cancer. *Medical News Today*, July 28, 2021.
2. Nwogu C., Pera P., Bashara W, Attwood K and Pandey RK. Photodynamic therapy of human lung cancer xenografts in mice. *J. Surg. Res.*, 2016, 200, 8-12.

Supramolecular Porphyrin Aggregates: The Long Road for the Development of Chiral Sensors

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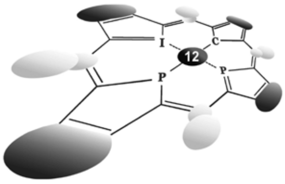
Porphyrins are versatile macrocycles which fulfill vital functions in living systems; the property richness of porphyrins allows their exploitation in different application fields, such as materials science, sensing, photovoltaics or medical treatments. Although it is true that monomeric porphyrins possess valuable properties, such as catalytic or sensitizers for dye-sensitized solar cells (DSCCs), their self-assembly in sophisticated, size and shape-controlled suprastructures often significantly boosts their potentialities, leading to advanced functional materials with improved properties.

Furthermore, the implementation of elements of chirality on such systems widens their applicability in different fields of science and technology, spanning from asymmetric catalysis to chiral sensing. Chiral porphyrin-based architectures can be obtained from either chiral or achiral platforms.

In the last few years, we have been interested in the development of chiral layers based on supramolecular assemblies of porphyrins. The deposition of these layers onto the surface of quartz crystal microbalances (QMB) led to their exploitation for chiral discrimination of enantiomeric pairs of volatile organic compounds (VOC). Promising results have been obtained using hybrid materials, when porphyrin aggregates were combined with different materials.

The latest progress in the development of stereoselective hybrid systems will be presented and discussed.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Harvesting the reactivity of metalloporphyrin pedestals on planar, solid surfaces

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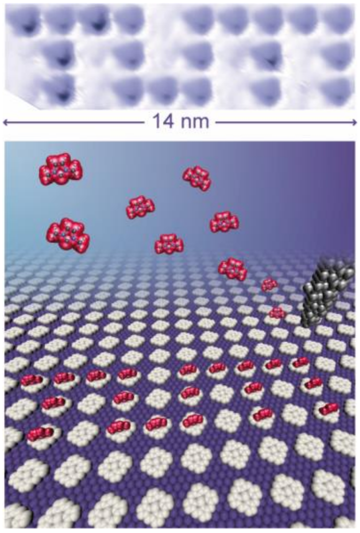
Metal-organic species and nanoarchitectures at well-defined interfaces bear great potential for key technological applications, spanning over the design of single-site heterogeneous catalysts, novel materials for light harvesting, the fabrication of molecular rotors and nanomachines and the advent of molecular spintronics. The high stability, conformational flexibility and ease of chemical functionalisation of porphyrins make them ideal building blocks of such structures. Here we establish a model system of Ru porphyrins on a planar, close-packed silver surface [1]. Our analysis encompasses an integration of microscopy, diffraction, spectroscopy and desorption in ultra-high vacuum combined with theoretical considerations to generate a high degree of precision in the understanding of interfacial processes at the atomic level. By using carbon monoxide (CO) as a probe molecule, crucial differences in the binding to the Ru porphyrin were discovered depending on its conformation: if the central cyclic part of the porphyrin has a saddle-shape, CO can bind; if, instead, the central cyclic part of the molecule is more planar or bowl-shaped, CO does not bind [2]. The surface chemistry of the saddle shape Ru porphyrin was further exploited to control the surface tethering of N-heterocyclic carbenes (NHCs), a current challenge of surface functionalization. The metalloporphyrin acts as a pedestal that orients and defines the lateral arrangement of NHCs on a planar surface by providing single metal atom sites for discrete binding. We deposited NHCs on a self-assembled metalloporphyrin layer and found that they are suitable pillars for the formation of out-of-plane architectures [3]. The resulting modular arrangement of NHCs allows us to individually address the ligands by controlled manipulation with the tip of a scanning tunnelling microscope, creating patterned structures on the nanometer scale (see illustration). Under certain conditions, we also observed a fascinating, dynamic interface rearrangement where the NHC ligand acts as a molecular porter: they transfer metalloporphyrin molecules from the first to the second molecular layer. Harnessing these dynamic events will serve the engineering of atomically precise NHC-containing complex interfaces.



REFERENCES

1. P. Knecht, P. T. P. Ryan, D. A. Duncan, L. Jiang, J. Reichert, P. Deimel, F. Haag, J. Küchle, F. Allegretti, T.-L. Lee, M. Schwarz, M. Garnica, W. Auwärter, A. P. Seitsonen, J. V. Barth, A. C. Papageorgiou *J. Phys. Chem. C* **2021**, *125*, 3215.
2. P. Knecht, J. Reichert, P. S. Deimel, P. Feulner, F. Haag, F. Allegretti, M. Garnica, M. Schwarz, W. Auwärter, P. T. P. Ryan, T.-L. Lee, D. A. Duncan, A. P. Seitsonen, J. V. Barth, A. C. Papageorgiou *Angew. Chem. Int. Edit.* **2021**, 60, 16561.
3. P. Knecht, B. Zhang, J. Reichert, D. A. Duncan, M. Schwarz, F. Haag, P. T. P. Ryan, T.-L. Lee, P. S. Deimel, P. Feulner, F. Allegretti, W. Auwärter, G. Médard, A. P. Seitsonen, J. V. Barth, A. C. Papageorgiou. *J. Am. Chem. Soc.* **2021**, *143*, 4433.

New Porphyrin- and Phthalocyanine-Based Dendrimers for Optics

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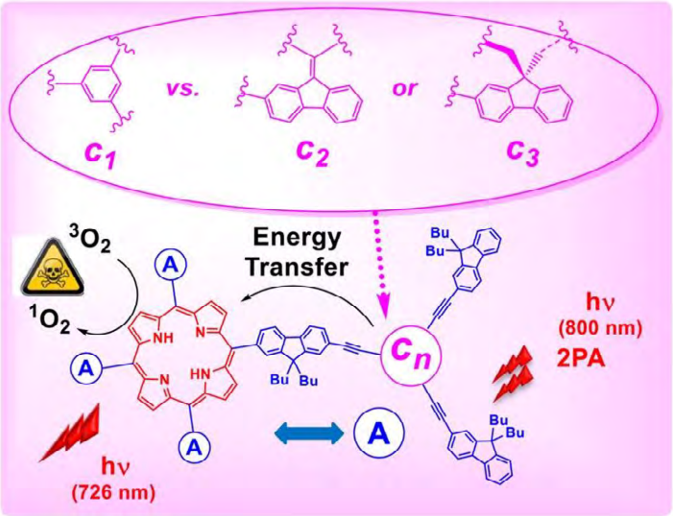

In 2004, we synthesised a porphyrin possessing four fluorenyl arms (**TFP**), with a remarkable high quantum yield (24%), compared to the reference **TPP**, demonstrating the capacity of the fluorenyl units to enhance quantum yields.[1] Then, to exploit this efficiency, a series of **porphyrin dendrimers** based on **TPP porphyrin core** and bearing, in a **non-conjugated** way, fluorenyl dendrons was prepared.[2,3] Different applications were exploited: as the fabrication of red Organic Light Emitting Diodes (OLEDs),[4-6] 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.[9] 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** instead of the more classic 1,3,5-phenylene unit. Their detailed luminescence properties and selected photophysical properties are discussed in the frame of two-photon-induced theranostics.

REFERENCES

1. C. Paul-Roth, G. Williams, J. Letessier, G. Simonneaux *Tetrahedron Lett.* **2007**, 48, 4317.
2. S. Drouet, C. Paul-Roth, G. Simonneaux, *Tetrahedron* **2009**, 65, 2975.
3. S. Drouet, C. O. Paul-Roth, *Tetrahedron* **2009**, 65, 10693.
4. S. Drouet, C. O. Paul-Roth, V. Fattori, M. Cocchi, J. A. G. Williams, *New J. Chem.* **2011**, 35, 438.
5. X. Ren, A. Ren, J. Feng, C. Sun, *Journal of Photochemistry and Photobiology A: Chemistry* **2009**, 203, 92.
6. A. Merhi, S. Drouet, N. Kerisit, C. O. Paul-Roth, *Tetrahedron* **2013**, 69, 7112.
7. S. Drouet, A. Merhi, G. Argouarch, F. Paul, O. Mongin, M. Blanchard-Desce, C. O. Paul-Roth, *Tetrahedron* **2012**, 68, 98.
8. Yao, D.; Hugues, V.; Blanchard-Desce, M.; Mongin, O.; Paul-Roth, C. O.; Paul, F. *New J. Chem.* 2015, 39, 7730; D. Yao, X. Zhang, O. Mongin, F. Paul and C. O. Paul-Roth, *Chem. Eur. J.* **2016**, 22, 5583.
9. D. Yao, X. Zhang, A. Triadon, N. Richy, O. Mongin, M. Blanchard-Desce, F. Paul and C. O. Paul-Roth, *Chem. Eur. J.* **2017**, 23, 2635; D. Yao, X. Zhang, S. Abid, L. Shi, M. Blanchard-Desce, O. Mongin, F. Paul and C. O. Paul-Roth, *New J. Chem.* 2018, 42, **395**.
10. X. Zhang, S. Ben hassine, N. Richy, O. Mongin, M. Blanchard-Desce, F. Paul and C. O. Paul-Roth, *New J. Chem.* **2020**, 44, 4144.

Effect of Molecule-Substrate Interaction on the Adsorption of Meso-Dibenzoporphycene Tautomers Studied by Scanning Probe Microscopy and First-Principles Calculations

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Meso-dibenzoporphycene molecules adsorbed on the Ag(111) surface and on 2-monolayer thick NaCl films were studied using submolecular resolution atomic force microscopy (AFM), scanning tunneling microscopy (STM) and first-principles calculations in order to clarify its stability and tautomerization behavior [1]. We have found that the bonding of the molecules with the surface is determined by the interplay of different contributions, including the interaction of the π-aromatic orbitals of the benzene rings, and the metal-coordination bond of the lone-pair electrons of the imine nitrogen atoms with the metal atoms (Ag, Na) on each substrate. The strength of the latter ultimately governs the molecular adsorption configuration and determines the nature and energy barriers for tautomerization. On Ag(111), the interaction of the imine nitrogen atoms with the Ag atoms deforms the macrocycle of porphycene, leading to a distinct AFM contrast [2] that allows a clear identification of the molecule in its *cis* tautomeric form. In contrast, on NaCl films, the weaker interaction with the Na atoms leads to a flatter geometry and very similar adsorption configurations for the *cis* and *trans*-forms, that cannot be distinguished in AFM experiments. Although weak, the dominant role of this local N-Na interaction, compared to the essentially non-directional dispersive interactions, results in a new type of tautomerization process. In this case, the transfer of the hydrogen atoms within the porphycene cavity is accompanied by a significant displacement of the whole molecule to a new site in order to reach a new minimum energy adsorption configuration. Our theoretical calculations indicate that this lateral translation, rather than the intramolecular H transfer, dominates the activation energy on NaCl. This novel tautomerization behavior, that we have identified on a rather inert ionic surface, might be also present on other weakly interacting substrates.

REFERENCES

1. T. K. Shimizu, et al., *J. Phys. Chem.* C 124 (2020) 26759–26768.
2. M. Ellner, et al., *ACS Nano* 2019, 13, 786–795.

Redox Properties of Bacterial Multiheme Modules Related to Microoxic Respiration

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Multiheme proteins are common in electron-transfer (ET) chains of bacteria, especially those that function at low or no O_2. Cytochrome (cyt) *cbb*$_3$ oxidases catalyze O_2 reduction in microoxic environments. *Cbb*$_3$ oxidase from *Pseudomonas stutzeri* (*Ps*) has a chain of five hemes for ET to the catalytic site and its electron donor cyt *c*$_4$ has two. Cyt *c*$_4$ binds to the diheme periplasmic domain of the CcoP domain (CcoP^{sol}) of *cbb*$_3$ oxidase to inject electrons to the enzyme; both proteins have two *c*-type His/Met-ligated hemes. Studies of redox properties of these modules not only inform on their native ET functions but also provide fundamental understanding of the effects of the protein structure and external perturbations relevant to microoxia, such as reducing environment and rise in NO levels, on redox properties of similar assemblies. By preparing monoheme fragments containing only heme A or heme B as well as bis-His ligated variants of cyt *c*$_4$ and performing activity assays, we have demonstrated that heme A is the site of electron injection to the enzyme. Spectroscopic and stability characterization of monoheme fragments, homodimers, and full-length cyt *c*$_4$ proteins suggest the critical role of the interface between the two heme fragments in tuning reduction potentials of the hemes. Critical in establishing this interface, heme A is hydrogen-bonded to one heme propionate (HP) of heme B. The break-up of this interaction, possibly upon deprotonation of one or both HPs, has been previously suggested may be important for ET. Our photoinduced ET studies of Ru-labeled cyt *c*$_4$ have revealed an increase in interheme rates at lower pH. The ^{13}C NMR titrations have identified two pH-dependent transitions, but with smaller changes in chemical shifts than those expected for deprotonation of HPs. The transitions were the same for both ferric and ferrous proteins, arguing against the proton-coupled ET behavior of cyt *c*$_4$. We conclude that the four HPs in cyt *c*$_4$ maintain their protonation states within the pH range investigated and the observed transitions reflect changes in the protonation state of nearby residues. The robust interface between the two monoheme domains mediated by hydrogen-bonded HPs may be important for structural integrity and redox properties of cyt *c*$_4$. We show that NO binds to the heme in both cyt *c*$_4$ and CcoP^{sol}, replacing the native Met ligand(s), and this modification alters the enzymatic activity of *cbb*$_3$ oxidase. With a series of spectroscopic measurements we rationalize the effects of Met-to-NO ligand substitution on structure and redox properties of cyt *c*$_4$ and CcoP^{sol}, both at the replacement site and beyond.

Group (15) Porphyrin Chemistry

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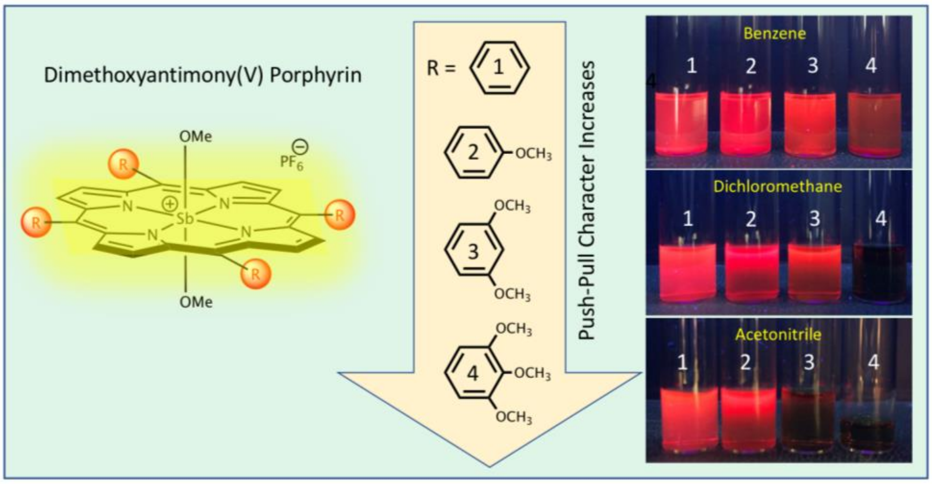
Recently, our research group has been focusing on the main-group porphyrin chemistry consisting of the group(15) elements. A series of phosphorus(V), antimony(V), and bismuth(III) porphyrin derivatives have been synthesized. The meso-positions of porphyrin were substituted with a variety of electron-donating and electron-withdrawing groups. Several interesting features were observed: (i) The resulting porphyrins can form one/two axial bonds with two different/same molecular components through covalent bonds. (ii) The porphyrins hold high oxidation potentials. (iii) The optical properties (absorption and fluorescence) indicate intramolecular charge transfer from the meso-substituted unit to the central porphyrin ring. (iv) Some of the porphyrins showed relatively high phosphorescence quantum yields at room temperature. The study revealed that the redox and optical properties can be tailored either by introducing appropriate substituents in meso-positions of the porphyrin ring or inserting group(15) elements in its cavity. These properties make the group(15) porphyrins excellent candidates for constructing multi-component Donor-Acceptor systems for various applications.



REFERENCES

1. Poddutoori, P. K.; Bayard, B. J.; Holzer, N.; Seetharaman, S.; Zarrabi, N.; Weidner, N.; Karr, P. A.; D'Souza, F. *Inorg. Chem.*, **2021**, *60*, 17952.
2. Holzer, N.; Sharma, J. K.; Peterson, S.; Bayard, B. J.; D'Souza, F. *Manuscript submitted.*

New insight in the chirality of J-aggregates of H_2TPPS

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Chemists have been fascinated by the challenging syntheses of natural complex systems. Porphyrins represent very attractive building blocks for them, but they are not easy to handle. In fact, even if the peripheral charged groups make these macrocycles water-soluble, porphyrins remain mainly hydrophobic, preserving a tendency to self-aggregate. This ''dichotomy'' is worth of special attention because it plays a central role in the non-covalent syntheses of quite complex porphyrin array, such as those formed by meso-tetrakis(4-sulfonatophenyl)porphyrin (H_2TPPS). H_2TPPS becomes zwitterionic when core-protonated (at pH around 5) and in the presence of ionic strength self-assembles forming edge to edge J-aggregates. The chemical-physical properties of these aggregates have been studied by several groups obtaining a control on morphology and chirality [1]. These aggregates are inherently chiral forming for the parity rule a racemic mixture in solution. However, it is possible to induce desired chirality to J-aggregates by using asymmetric physical forces (vortex or magnetic) [2], or chemical chiral matrixes (polymers, polyelectrolytes, etc...) [3]. More challenging is the induction of chirality with monomeric molecules. We have demonstrated that chiral single molecules such as Λ or Δ $[Ru(Phen)_3]^{2+}$, in no-aggregating conditions, are able to control the induced chirality to J-aggregates. Noteworthy this system can work as switch of chirality [4]. Even chiral carbon nanodots provide us another interesting chiral template, indeed also these small nanoparticles (2-4 nm) are able to induce chirality to J-aggregates controlling the size of porphyrin assembly [5]. Finally we tested four amino acids (Lys, Arg, His and Phe) to induce chirality to J-aggregates, analyzing several aspects of these self-assembled systems: *(i)* the chiral transfer process; *(ii)* the hierarchical effects leading to the aggregates formation; and, *(iii)* the influence of the amino acid concentrations on both transferring and storing chiral information [6].

REFERENCES

1. a) Ohno, O.; Kaizu, Y.; Kobayashi, H. *J. Chem. Phys.* **1993**, 99, 4128–4139; b) Koti, A.S.R.; Taneja, J.; Periasamy, N. *Chem. Phys. Lett.* **2003**, 375, 171–176; c) Micali, N.; Mallamace, F.; Romeo, A.; Purrello, R.; Monsù Scolaro, L. *J. Phys. Chem. B* **2000**, 104, 5897–5904; d) Short, J.M.; Berriman, J.A.; Kubel, C.; El-Hachemi, Z.; Naubron, J.-V.; Balaban, T.S. *ChemPhysChem* **2013**, 14, 3209–3214; e) El-Hachemi, Z.; Escudero, C.; Arteaga, O.; Canillas, A.; Crusats, J.; Mancini, G.; Purrello, R.; Sorrenti, A.; D'Urso, A.; Ribo, J.M. *Chirality* **2009**, 21, 408–412.
2. a) D'Urso, A.; Randazzo, R.; Lo Faro, L.; Purrello, R. *Angew. Chem. Int. Ed*. **2010**, 49, 108–112; b) Ribo, J.M.; Crusats, J.; Sague, F.; Claret, J.; Rubires, R. *Science* **2001**, 292, 2063–2066; c) Micali, N.; Engelkamp, H.; van Rhee, P.G.; Christianen, P.C.M.; Monsù Scolaro, L.; Maan, J.C. *Nat. Chem.* **2012**, 4, 201–216.
3. a) Purrello, R.; Bellacchio, E.; Gurrieri, S.; Lauceri, R.; Raudino, A.; Monsù Scolaro, L.; Santoro, A.M. *J. Phys. Chem. B* **1998**, 102, 8852–8857; b) Onouchi, H.; Miyagawa, T.; Morino, K.; Yashima, E. *Angew. Chem. Int. Ed.* **2006**, 45, 2381–2384; c) Gaeta, M.; Raciti, D.; Randazzo, R.; Gangemi, C.M.A.; Raudino, A.; D'Urso, A.; Fragal, M.E.; Purrello, P. *Angew. Chem. Int. Ed.* **2018**, 57, 10656 –10660.
4. Randazzo, R.; Mammana, A.; D'Urso, A.; Lauceri, R.; Purrello, R. *Angew. Chem. Int. Ed.* **2008**, 47, 9879.
5. Dorđević, L.; Arcudi, F.; D'Urso, A.; Cacioppo, M.; Micali, N.; Bürgi, T.; Purrello, R.; Prato, M. *Nat. Comm.* **2018**, 9:3442.
6. Randazzo, R.; Gaeta, M.; Gangemi, C.M.A.; Fragalà, M.E.; Purrello, R.; D'Urso, A. *Molecules* **2019**, 24, 84.

Anion binding in supramolecular hydrogels incorporating porphyrins: from phototoxicity to molecular machines

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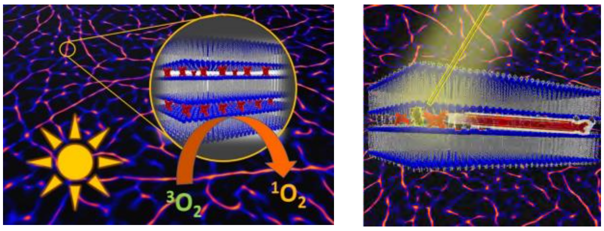
Anion binding [1] can be used as the driving force of functional materials. In the talk we will present our work on the preparation and characterisation of supramolecular hydrogels self-assembled from cationic gemini surfactants, and their ability to encapsulate anionic porphyrins. The resulting hybrid materials show an enhanced singlet oxygen production [2] of interest in photodynamic therapy. When this system is irradiated, light induces motion at the micrometric scale of the porphyrin on the supramolecular fibres, and real-time of the motion in the solvated state has been proved using total internal reflection fluorescence microscopy [3].



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REFERENCES

1. Piepenbrock, M.-O. M.; Lloyd, G. O.; Clarke, N.; Steed, J. W. *Chem. Rev.* **2010**, *110*, 1960–2004.
2. Samperi, M.; Limón, D.; Amabilino, D. B.; Pérez-García, L. *Cell Reports Physical Science*, **2020**, *1*, 100030.
3. Samperi, M.; Bdiri, B.; Sleet, C.D.; Markus, R.; Mallia, A.R.; Pérez-García, L.; Amabilino, D.B. *Nature Chem.*, **DOI:** 10.1038/s41557-021-00791-2.

Tailor-Made Aromatic (antiaromatic) Porphyrinoids with NIR Absorption

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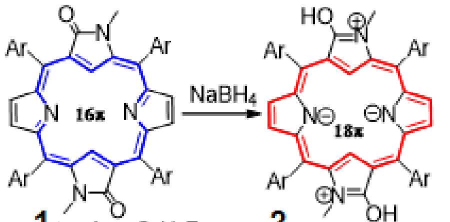
N-confused porphyrinoids happen to be new NIR dyes resulting from incorporation of unconventional pyrrole connectivity into the tetrapyrrolic conjugated core [1]. NCPs are further confused, resulting in doubly N-confused porphyrins (N_2CPs) where two types of isomers of N_2CPs are known in literature [2].

The first part of the scientific talk will be about high yield synthesis, spectroscopic and solid-state structural proof of the lactam embedded smallest ever metal free stable Hückel antiaromatic *trans*-doubly N-confused [16] porphyrins **1** and the susceptibility to exhibit the redox associated variation of Hückel aromaticity [2b]. Next, the employment of thiophene/selenophene rings in the development of novel *trans* doubly N-confused porphyrinoids leading to highly aromatic and NIR absorptive *trans*-doubly N-confused dithia/diselena porphyrins **3**/**4** [2c] will be discussed.

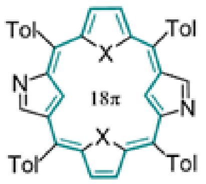
Under the fascinating attributes of N-confused-fused porphyrinoids leading to strong NIR absorption [1], the second part of the talk will be about the first ever ferroceno N-confused β-β fused oxoporphyrinoids **5** with endocyclic extension of macrocyclic π-conjugation via tricyclic [5.5.5] moiety [3]. The three-dimensional structure with built-in fused tricyclic [5.5.5] moiety paved way to three dimensional weak diatropicity with vis-NIR absorptions. The peripheral coordinated Rh(I) complexes **6** also anticipated weak aromaticity with vis-NIR absorptions.

The last part of the talk will be our investigation about how swapping an N-confused N-Methyl pyrrole ring with an N-confused pyrrole ring led to the genesis of the new generation N-confused porphodimethene, N-confused expanded phlorin and corrorin isomer, their electronic properties and the aromaticity/nonaromaticity/antiaromaticity [4].

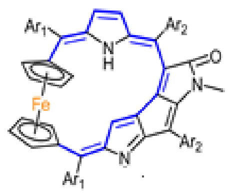


1 a Ar = $C_6H_3F_2$
b Ar = C_6F_5

2 a''-H_2 Ar = $C_6H_3F_2$
b''-H_2 Ar = C_6F_5



3 X = Se
4 X = S



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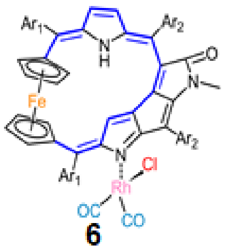

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REFERENCES

1. *Chem. Lett.*, 2019, **48**, 615–622
2. (a) *J. Am. Chem. Soc.*, 2000, **122**, 803-807. (b) *J. Org. Chem.*, **2020, 85**, 2059-2067. (c) *Org. Biomol. Chem.*, **2020,** 18, 6058-6062.
3. *J. Org. Chem.*, **2021, 86**, 8015-8026.
4. *Dalton Trans.*, 2021, **50**, 14421-14431.

Metal-Centre-Driven Supramolecular Chirogenesis using Metalloporphyrin *tweezers*: Structural, Spectroscopic and Theoretical Investigations

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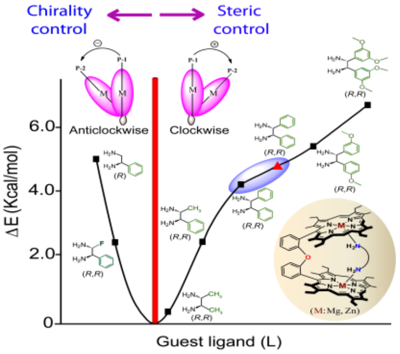
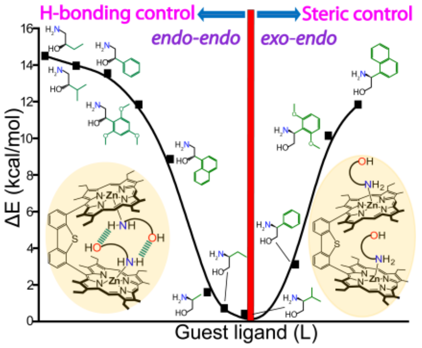
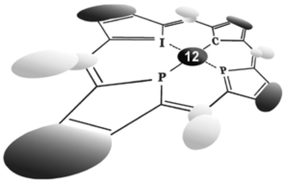


Supramolecular chirogenesis is one of the most important interdisciplinary field to be looked into because of its occurrences in many natural and artificial systems. The fundamental reason of the transfer of chirality depends upon the mechanism of the molecular recognition during the complexation process, and a complete understanding of the origin of chirality transfer information at the electronic and molecular levels would help us to determine absolute configuration of natural products and synthetic compounds. Therefore, understanding of the various influencing factors is extremely important for controlling chirality induction phenomena. A series of supramolecular chiral 1:1 *sandwich* complexes consisting of metallo-bisporphyrin host and chiral diamine guest have been synthesized. Experimental and DFT calculations have demonstrated the possible interconversion between clockwise (steric-controlled) and anticlockwise (chirality-controlled) twisted conformers just upon changing the bulk of the substituent irrespective of the nature of chirality at the stereogenic centre [1-15].



REFERENCES

1. B. Saha, D. Chandel, S. P. Rath *Inorg. Chem.* **2022**, *62*, 0000.
2. A. Dhamija, B. Saha, D. Chandel, H. Malik S. P. Rath *Inorg. Chem.* **2020**, *59*, 801.
3. B. Saha, S. A. Ikbal, S. P. Rath *Inorg. Chem.* **2020**, *59*, 7795.
4. A. Dhamija, P. Mondal, B. Saha, S. P. Rath *Dalton Trans.* **2020**, *49*, 10679.
5. B. Saha, A. G. Petrovic, A. Dhamija, N. Berova, S. P. Rath *Inorg. Chem.* **2019**, *58*, 11420.
6. A. Dhamija, B. Saha, S. P. Rath *Inorg. Chem.* **2017**, *56*, 15203.
7. B. Saha, S. A. Ikbal, A. Petrovic, N. Berova, S. P. Rath *Inorg. Chem.* **2017**, *56*, 3849.
8. S. A. Ikbal, A. Dhamija, S. Brahma, S. P. Rath *J. Org. Chem.* **2016**, *81*, 5440.
9. A. Dhamija, S. A. Ikbal, S. P. Rath *Inorg. Chem.* **2016**, *55*, 13014.
10. S. A. Ikbal, A. Dhamija, S. P. Rath *Chem. Commun.* **2015**, *51*, 14107.
11. S. A. Ikbal, S. Brahma, S. P. Rath *Chem. Commun.* **2015**, *51*, 895.
12. S. A. Ikbal, S. Brahma, S. P. Rath *Chem. Commun.* **2014**, *50*, 14037.
13. S. Brahma, S. A. Ikbal, S. P. Rath *Inorg. Chem.* **2014**, *53*, 2381.
14. S. Brahma, S. A. Ikbal, S. P. Rath *Inorg. Chem.* **2014**, *53*, 49.
15. S. Brahma, S. A. Ikbal, S. P. Rath *Chem. Commun.* **2012**, *48*, 4070.



Small molecule activation at transition metal centers: Structure-function correlations

Kallol Ray

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Small molecule activation constitutes one of the main frontiers of inorganic and organometallic chemistry, with much effort directed towards the development of new processes for the selective and sustainable transformation of abundant small molecules such as dioxygen (O_2), water (H_2O), hydrogen peroxide (H_2O_2) or protons (H^+) into high-value chemical feedstocks and energy resources. Because nature mostly uses metal ions to activate these relatively inert molecules and modulate their reactivity, much inspiration for the field has come from bioinorganic chemistry. This talk will focus on some of the recent highlights from our group on homogenously catalyzed bioinspired activation of small molecules, as well as stoichiometric reactions that further our understanding towards such ends. It will cover many aspects of small molecule activation including: organometallic chemistry, spectroscopy, synthesis, and detailed mechanistic studies involving trapping of reactive intermediates. The demonstrated examples will help to emphasize the continuous effort of our group in uncovering the structure-reactivity relationships of biomimetic model complexes, which may allow vital insights into the prerequisites necessary for the design of efficient catalysts for the selective functionalization of unactivated C–H bonds, O_2/H_2O/H_2O_2 activations, or H^+ reductions by using cheap and readily available first-row transition metals under ambient conditions.

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

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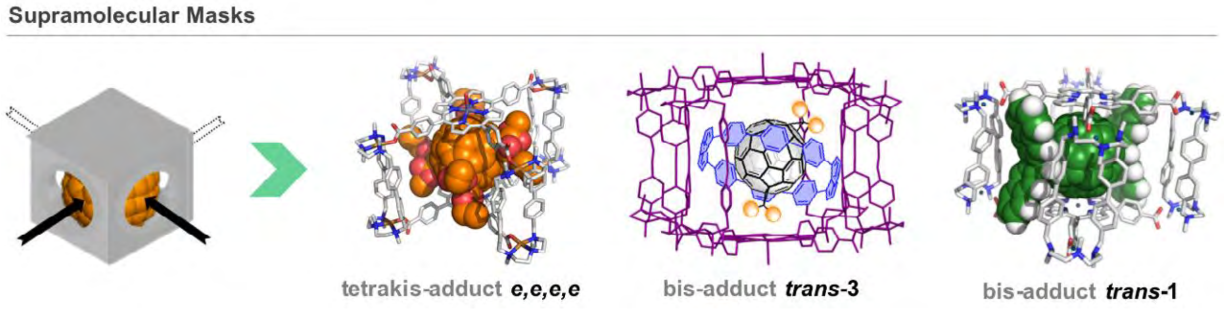
The regioselective functionalization of fullerenes and the control of the number of adducts is highly important to unbar the development of fullerene chemistry. Nowadays, easy-accessible C_{60} and C_{70} fullerene mono-adducts are mainly used in any application[1] due to the hampered accessibility to 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 tetragonal prismatic 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. 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}. 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.



REFERENCES

1. E. Castro, L. Echegoyen et al. *J. Mater. Chem. C*, **2018**, *6*, 2635.
2. C. García-Simón, X. Ribas, et al. *Nat. Commun.* **2014**, *5*:5557.
3. C. Fuertes-Espinosa, X. Ribas, et al, *Chem* **2020**, *6*, 169–186.
4. E. Ubasart, X. Ribas, et al, *Nat. Chem*. **2021**, *13*, 420-427

Shape Matters! How π-Rich Curved Carpyridines Drive Columnar Aggregation

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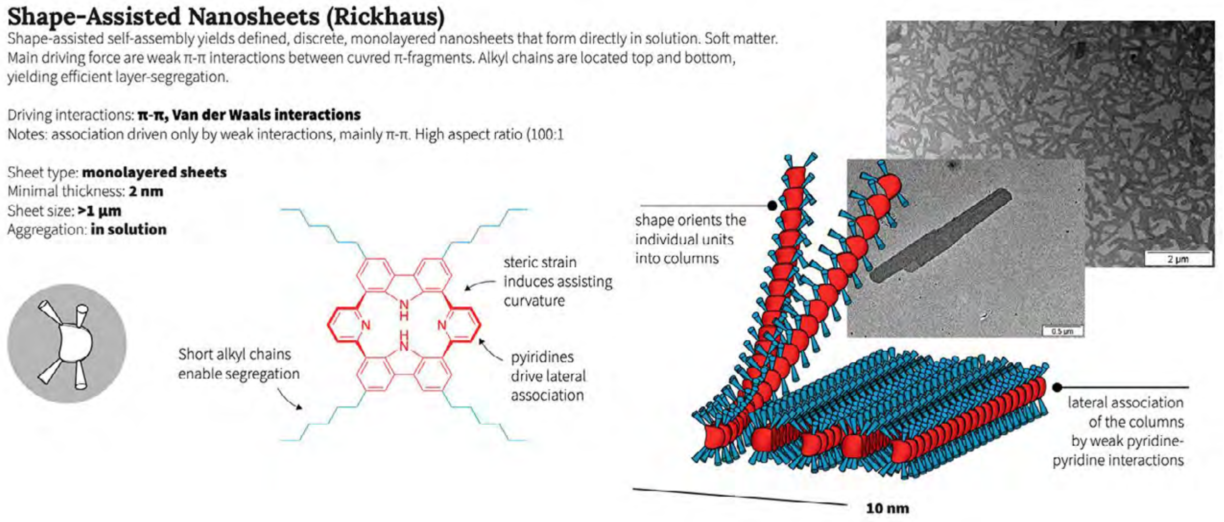
In a typical self-assembly setting, a core is decorated by suitable sidechains that induce supramolecular polymerization. While this approach has led to spectacular assemblies, the core is usually used only as a rigid platform from which to build functionality. We are convinced that the core can play an important role besides holding the chains in a precise spatial arrangement, especially for columnar assemblies. In our lab, we construct molecular core topographies that we think to be beneficial to supramolecular polymerization.



Shape-Assisted Nanosheets (Rickhaus)

Shape-assisted self-assembly yields defined, discrete, monolayered nanosheets that form directly in solution. Soft matter. Main driving force are weak π-π interactions between cuvred π-fragments. Alkyl chains are located top and bottom, yielding efficient layer-segregation.

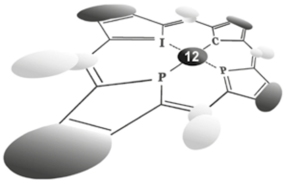
Driving interactions: **π-π, Van der Waals interactions**
Notes: association driven only by weak interactions, mainly π-π. High aspect ratio (100:1

Sheet type: **monolayered sheets**
Minimal thickness: **2 nm**
Sheet size: **>1 µm**
Aggregation: **in solution**

Here we introduce our very new foray into a new class of curved macrocycles we call carpyridines. They are formed from two carbazoles and two pyridines and display a persistent saddle shape.[1] For the first time, we demonstrate as proof of concept that a small, π-rich molecule can show entropy-driven shape-assisted self-assembly (SASA) leading to highly ordered, defined soft-matter sheets in solution. Size ratios of these monolayered sheets exceede 100:1 that can be accessed by a wide range of conventional techniques in the *absence* of classical soft-bonding motifs like coordination, salt- or hydrogen-bridges.[2]

REFERENCES

1. Arnold, L.; Norouzi-Arasi, H.; Wagner, M.; Enkelmann, V.; Müllen, K. *Chem. Commun.* **2010**, *47*, 970–972.
2. Manuscript submitted

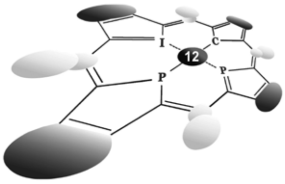


The Enduring Legacy of F. Ann Walker's Career

Mario Rivera[a]

[a]*Department of Chemistry, Louisiana State University*

Francis Ann Walker (May 11, 1940 to January 30, 2022) was a world-renowned chemist and a beloved role model and mentor. Ann, as her family friends and colleagues called her, was the recipient of numerous prestigious awards in recognition of her important contributions to bioinorganic chemistry and metallobiochemistry, including the Eraldo Antonini Lifetime Achievement Award from the Society of Porphyrins and Phthalocyanines. Ann's earlier research concentrated on the study of synthetic porphyrins and their iron complexes, later incorporating recombinant DNA and biochemical strategies to study the roles played by heme and heme proteins in biological processes. Ann's fundamental findings, which exerted significant influence on the direction of her field, also contributed to guide and inspire the research of younger generations of bioinorganic chemists, including the career of the author. Hence, in this presentation, which aims to provide a small tribute to Ann's life and career, the author will describe how Ann's fundamental discoveries in heme electronic structure and NMR of paramagnetic hemes played a pivotal role in investigations leading to the current understanding of the mechanism of heme degradation carried out by the enzyme heme oxygenase.



Molecular photo(electro)chemical reduction of CO_2 to C1 products with 2, 4, 6 and 8 electrons. From mechanistic studies to hybrid systems.

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Reduction of carbon dioxide has as 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 it has been shown that such molecular catalysts may also be tuned for generating highly reduced products such as methanol and methane, leading to new exciting advancements.

Hybridization of these catalysts with conductive or semi-conductive materials may lead to enhance stability and new catalytic properties, as well as inclusion of molecular catalysts in devices for applications. This approach bridges between homogeneous and heterogeneous, and it raises new fundamental questions that may further lead to breakthrough in CO_2 reduction chemistry.

Our recent results in these various areas will be discussed, using earth abundant metal (Fe, Co) porphyrins and phthalocyanines as well as related complexes as catalysts.

REFERENCES

1. B. Ma, M. Blanco, G. Drazic, L. Calvillo, L. Chen, G. Chen, T.-C. Lau, J. Bonin, G. Granozzi, M. Robert *J. Am. Chem. Soc.* **2021**, 143, 22, 8414-8425.
2. E. Boutin, M. Robert, *Trends in Chemistry*, **2021**, 3, 359-372.
3. P. B. Pati, E. Boutin, R. Wang, S. Diring, S. Jobic, N. Barreau, F. Odobel, M. Robert, *Nat. Commun.* **2020**, 11:3499.
4. B. Ma, G. Chen, C. Fave, L. Chen, R. Kuriki, K. Maeda, O. Ishitani, T-C. Lau, J. Bonin, M. Robert, *J. Am. Chem. Soc.* **2020**, *142*, 6188-6195.
5. S. Ren, D. Joulie, D. Salvatore, K. Torbensen, M. Wang, M. Robert, C. Berlinguette, *Science* **2019**, *365*, 367-369.
6. E. Boutin, M. Wang, J. C. Lin, M. Mesnage, D. Mendoza, B. Lassalle-Kaiser, C. Hahn, T. F. Jaramillo, M. Robert, *Angew. Chem. Int. Ed.* **2019**, *58*, 16172-16176.
7. Z. Guo, C. Cometto, G. Chen, L. Chen, B. Ma, H. Fan, T. Groizard, W-L. Man, S-M. Yiu, K-C. Lau, T-C. Lau, M. Robert, *Nat. Catal.* **2019**, 2, 801-808.
8. H. Rao, L. Schmidt, J. Bonin, M. Robert, *Nature* **2017**, 548, 74-77.
9. I. Azcarate, C. Costentin, M. Robert, J-M. Savéant, *J. Am. Chem. Soc.* **2016**, 138, 16639-16644.
10. C. Costentin, S. Drouet, M. Robert, J-M. Savéant, *Science* **2012**, 338, 90-94.

Spectroscopy and Mechanism of O_2-producing Chlorite Dismutases

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The chlorite dismutases (Clds) are heme b-dependent enzymes that efficiently catalyze the decomposition of chlorite (ClO_2^-) to yield Cl^- and O_2 in a rare O–O bond forming reaction. In perchlorate-respiring proteobacteria, pentameric Clds appear to protect the organisms from the toxic effects of ClO_2^-, which is produced during perchlorate reduction. Dimeric Clds tend to occur in non-perchlorate respiring organisms. The function of these Clds remains unclear. As O–O bond forming reactions are rare in nature, we have undertaken a mechanistic study in this reaction. Through a combination of spectroscopic and kinetic investigations, intermediates along the catalytic ClO_2^- decomposition coordinate have been identified. Evidence in support of these intermediates will be presented and discussed in the context of a mechanistic model for catalysis.

Multicomponent nanostructured films based on phthalocyanines as biosensing platforms

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The search of new biosensing platforms is crucial to improve the performance of electrochemical biosensors. Nanostructured films containing combinations of enzymes and materials with different functionalities can be an interesting approach to obtain sensing platforms with improved performance [1-3]. Based on this idea, we have developed catechol and hydroquinone biosensors by depositing tyrosinase (Tyr) or laccase (Lac) on the surface of Layer by Layer (LbL) or Langmuir-Blodgett (LB) films formed by compounds with complementary activity. The nanstructured layers included phthalocyanines (MPc) -acting as the electron mediator-; chitosan (CHI) - a cationic species which acted as enzyme linker-. Other compounds such as ionic liquids (IL) or citrate capped gold nanoparticles (AuNPs) have also been included whose function is to increase the electrical conductivity of the devices while enhancing the electron transfer.

Films with different sequences have been developed and characterized by UV–visible, FTIR spectroscopy and AFM. It is demonstrated that the resulting films provide an efficient immobilization surface for phenol oxidases. At the same time, they improve the electron transfer between the enzymes and the electrode surface. Although all the biosensors obtained exhibited excellent performances, the sequence of the anionic and cationic layers strongly influenced the electron transfer process. The best results were obtained using the LbL fims of [CHI-AuNP-CHI-CuPcS]-Lac which caused a 2-fold increase in the intensity over the response of the biosensor without the LbL platform. The [CHI-AuNP-CHI-CuPcS]2-Tyr bioelectrode showed an LOD of $7.77\cdot10^{-4}$ μM (S/N=3) for hydroquinone and $8.7\cdot10^{-4}$ μM (S/N=3) for catechol. The LbL platform was also efficient for laccase and the [CHI-AuNP-CHI-CuPcS]-Lac biosensor showed a LOD of $1.27\cdot10^{-3}$ μM (S/N=3) for hydroquinone and of $1.84\cdot10^{-2}$ μM (S/N=3) for catechol.

REFERENCES

1. C. Salvo-Comino, C. García-Hernández, C. García-Cabezón, M.L. Rodríguez. Discrimination of Milks with a Multisensor System Based on Layer-by-Layer Films, Sensors, 18 (8). Number 2716 (2018)
2. C. Garcia-Hernandez, C. Garcia-Cabezon, F. Martin-Pedrosa, J.A. de Saja, M.L. Rodriguez-Mendez, Analysis of Musts and Wines with a bio-electronic tongue based on Tyrosinase and Glucose oxidase using a Polypyrrole/gold nanoparticle composite as electron mediator, Food Chemistry, 289, 751-756 (2019)
3. E. G. R. Fernandes, L.C. Brazaca, M.L Rodríguez-Méndez, J.A. de Saja and V. Zucolotto, Immobilization of Lutetium Bisphthalocyanine in Nanostructured Biomimetic Sensors Using the LbL Technique for Phenol Detection, Biosens. Bioelectr. 26 (2011) 4715- 4719

Porphyrin-loaded liposomes and nanoparticles for the photodynamic therapy of cancers

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Photodynamic therapy is a promising approach for anticancer therapy. We are developing nanocarriers for the encapsulation of porphyrins and their targeting to cancer cells. Porphyrins are very effective photosensitizers, but they are poorly soluble in biological fluids and not very specific. They hardly enter cells, or in aggregate form, and lose their activity. We have studied porphyrins modified by sugars to make them more hydrophilic and target specific membrane receptors. We found that although the organization of sugars in the molecule plays an important role in the recognition of molecules by target cells, it does not control the efficiency of molecules [1]. We have encapsulated porphyrins in liposomes [2] or hybrid nanoparticles [3], modified their chemical structure [4, 5] to allow photodynamic therapy combined with photothermal or chemotherapy treatments. Promising results have been obtained for the treatment of various cancers.

REFERENCES

1. Daghildjian K. et al., Mannose distribution in glycoconjugated tetraphenylporphyrins governs their interaction with cells and phototoxicity, *J. Porphyrins Phthalocyanines 23, 175-184, 2019.*
2. Makky A. et al., Assessment of the relevance of supported planar bilayers for modeling specific interactions between glycoconjugated porphyrins and retinoblastoma cells, *Biochim. Biophys. Acta-Biomembranes 1818, 2831-2838, 2012.*
3. N'Diaye M. et al., Hybrid lipid polymer nanoparticles for combined chemo- and photodynamic therapy, *Mol. Pharm., 16, 4045-4058, 2019.*
4. Massiot J. et al., Newly synthesized lipid-porphyrin conjugates: Evaluation of their self-assembling properties, their miscibility with phospholipids and their photodynamic activity in vitro, *Chem. Eur. J. 24, 19179-19194, 2018.*
5. Bronstein LG. et al., Influence of the porphyrin structure and linker length on the interfacial behavior of phospholipid-porphyrin conjugates, *J. Colloid Interface Sci. 611, 441-450, 2022*.

X-ray-induced Reduction of Cytochrome *c* Oxidase

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Cytochrome *c* oxidase (C*c*O) contains four metal redox sites: Cu_A, heme *a*, and Cu_B/heme a_3, the binuclear center (BNC), where dioxygen is reduced to water. Crystal structures of C*c*O in various forms have been reported, based on which ligand binding states of the BNC and the conformations of the two heme groups, as well as the protein matrix surrounding them, have been deduced to elucidate the mechanism by which the oxygen reduction chemistry is coupled to proton translocation. However, metal centers in proteins are known to be susceptible to X-ray induced radiation damage, raising questions about the reliability of the conclusions drawn from these studies. Here, we used microspectroscopy-coupled X-ray crystallography to interrogate how the structural integrity of bovine C*c*O in the fully oxidized state (**O**) is modulated by synchrotron radiation. Spectroscopic data showed that, upon x-ray exposure, **O** is converted to a hybrid **O*** state, where all the metal centers are reduced, but the protein matrix is trapped in the genuine **O** conformation. Annealing the **O*** crystal to above the glass transition temperature brought about the relaxation of the **O*** structure to a new **R*** structure, where the heme *a* and Loop I-II near Cu_A were converted to the fully reduced **R** conformations, while the Helix-X bridging the two heme moieties was only partially transformed to the **R** conformation, and the ligands in the BNC were only partially released. The radiation damage that led to these metastable structures was overcome by determining the structure of the **O** state and the $\mathbf{O_H}$ state, which is formed at the end of the catalytic turnover cycle, with serial femtosecond X-ray crystallography obtained by an X-ray free electron laser. These new structures call for reevaluation of mechanisms based on structures determined by synchrotron light sources.

CuAAC glycosylation of porphyrinoids: preliminary effects of linker length on the photodynamic inactivation of *Mycobacterium*

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Glycoconjugates of porphyrinoids, such as porphyrins and bacteriochlorins have gained attention for their potential as therapeutics for photodynamic therapy (PDT). Here we present a summary of our work developing a reliable and high-yielding copper-catalyzed azide–alkyne 1,3-dipolar cycloaddition (CuAAC) approach to create a series of glycosylated porphyrinoids. This methodology was successfully used to synthesize a library of glycosylated porphyrins [1-3] and, bacteriochlorins [2] in moderate to high yields from readily available azido-carbohydrates. The work highlights the system-dependent reaction conditions required for CuAAC glycosylation to porphyrins and bacteriochlorins and the versatility of this method when applied across porphyrins alkynylated at the *aryl*, *meso*, and *beta* positions [1-2]. To further explore this system, we employed the use of a "linker" to generate a library of porphyrin glycoconjugates that varied in both the nature of the carbohydrate and distance between the porphyrin macrocycle. Trehalose-based glycoporphyrins produced from this work were used to study the effects of linker length in the photodynamic inactivation of *Mycobacterium smegmatis*. Preliminary results demonstrate an increase in photodynamic inactivation with a decrease in linker length [1].

REFERENCES

1. Dixon, C. F.; Nottingham, A. N.; Lozano, A. F.; Sizemore, J. A.; Russell, L. A.; Valiton, C.; Newell, K. L.; Babin, D.; Bridges, W. T.; Parris, M. R.; Shchirov, D. V.; Snyder, N. L.; Ruppel, J. V. "Synthesis and evaluation of porphyrin glycoconjugates varying in linker length: preliminary effects on the photodynamic inactivation of *Mycobacterium smegmatis*" RSC Adv. **2021**, *11*, 7037-7042..
2. Bennion, M.C.; Burch, M. A.; Dennis, D. G.; Lech, M. E.; Neuhaus, K.; Fendler, N. L.; Parris, M. R.; Cuadra, J. E.; Dixon, C. F.; Mukosera, G. T.; Blauch, D. N.; Hartmann, L.; Snyder, N. L.; Ruppel, J. V. "Synthesis of Porphyrin and Bacteriochlorin Glycoconjugates through CuAAC Reaction Tuning" *Eur. J. Org. Chem.* **2019***,* 6496-6503**.**
3. Mukosera, G. T.; Adams, T. P.; Rothbarth, R. F.; Langat, H.; Akanda, S.; Barkley, R. G.; Dolewski, R.; Ruppel, J. V.; Snyder, N. L. "Synthesis of Glycosylated Zinc (II) 5, 15- Diphenylporphyrin and Zinc (II) 5, 10, 15, 20-Tetraphenylporphyrin Analogs Using Cu-Catalyzed Azide-Alkyne 1,3-Dipolar Cycloaddition Reactions" *Tetrahedron Lett.* **2015**, *56*, 73-77.

Oxygenic photochemistry beyond the red limit in chlorophyll f-containing photosystems

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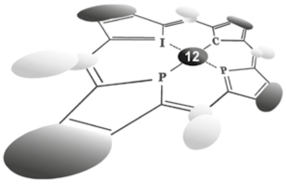
Chlorophyll-a photochemistry using red light (680-700 nm) is near-universal and is considered to define the energy limit for oxygenic photosynthesis [1]. The first isolation and biophysical studies of chlorophyll-f-containing photosystems questioned this view [2]. Far-red/near-IR absorption spectra showed the small number of long-wavelength chlorophylls were resolved from each other and from the majority chlorophyll-a. Charge separation in Photosystem II occurs on a 720 nm pigment. Three even longer-wavelength chlorophylls-f collect light and pass excitation energy up-hill to the 720 nm primary donor. These and other findings provide new insights, e.g., i) the nature of charge separation and excitation transfer in the standard chlorophyll-a-containing photosystems, ii) a new slant on photosystem evolution; and iii) the energy limits on oxygenic photosynthesis.

REFERENCES

1. Rutherford AW, Osyczka A, Rappaport F. (2012) FEBS Lett. 2012;586, 603-616. Back-reactions, short-circuits, leaks and other energy wasteful reactions in biological electron transfer: Redox tuning to survive life in O_2. *FEBS Lett*. 586, 603-616.
2 Nürnberg D.J., Morton J., Santabarbara S., Telfer A., Joliot P., Antonaru L.A., Ruban A.V., Cardona T., Krausz E., Boussac A., Fantuzzi A, Rutherford A.W. (2018) *Science 360*, 1210-1213 Photochemistry beyond the red limit in chlorophyll f–containing photosystems.



Using Pattern Recognition to Correlate DFT Modes

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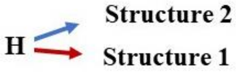
Vibrational spectroscopy is a powerful tool for elucidating the structure of both stable and transient species. DFT calculations are frequently used to interpret these spectral changes. The combination of experimental and DFT calculated spectra provides insight into the electronic structure of the species studies. This insight is usually gained by examining the changes in various vibrational modes. A typical procedure is to use visualization programs such as Gaussview to manually compare modes before and after perturbation in order to identify which modes are similar. For large molecules, this method can be tedious. As a result, usually only a few modes are studied in detail while many other modes may provide important information.

In this work, we will utilize pattern recognition to make these correlations. The aim of this approach will be to develop a model-free, unsupervised method to carry this out. The analysis will be carried out in two steps. The first step will be a sorting of the modes, classifying them into bins based on their vibrational type (stretching, bending, etc). For large molecules, these bins could also be based on where the vibration is located (e.g., for porphyrins, meso-vibrations, ethyl vibrations, phenyl vibrations, etc). This will minimize the number of comparisons that need to be done and to avoid misidentification. After the vibrations have been classified into these bins, the angle between the displacement of each atom during the vibration is calculated, as shown in the figure below. The angle, θ, is the angle between the two displacements of a given atom.



Starting with mode 1 (Structure 1), the angle θ for each atom in each mode in Structure 2 is calculated. The angles for all the atoms are summed for each mode in Structure 2 (all angles will be positive). The more similar the modes are, the smaller will be the sum of the angles. Using angles rather than the size of the displacement will avoid problems that can occur with isotopic substitution. Starting with bin 1 (e.g., stretching), the procedure will compare each mode in Structure 1 with bin 1 of Structure 2. The mode in Structure 2 with the smallest sum of the angles will be assigned to the mode in Structure 1. If there are remaining modes of bin 1 in Structure 2 after this comparison, they will be moved to the next bin, and the matching continues with bin 2.

In order to illustrate this approach in detail, we will begin with a very simple molecule so that the calculations can be illustrated in detail. The types of perturbations that will be examined are isotopic substitution, changes in the functionals used, redox changes and ion pairing. We will then discuss approaches to resolve problems where one mode in Structure 1 is correlated with more than one mode in Structure 2. The aim of this approach is to avoid the "black box" approach typical of pattern recognition. Using this approach, details about the vibration and the changes in the mode upon perturbation will be clear. After completing the detailed analysis of a small molecule, the application of this approach to larger molecules will then be discussed illustrating the power of this approach to correlate modes where isotopic substitution, redox processes and ion pairing occurred.

Cyclic-BODIPYs: A Multifaceted Candidates with Varied Properties

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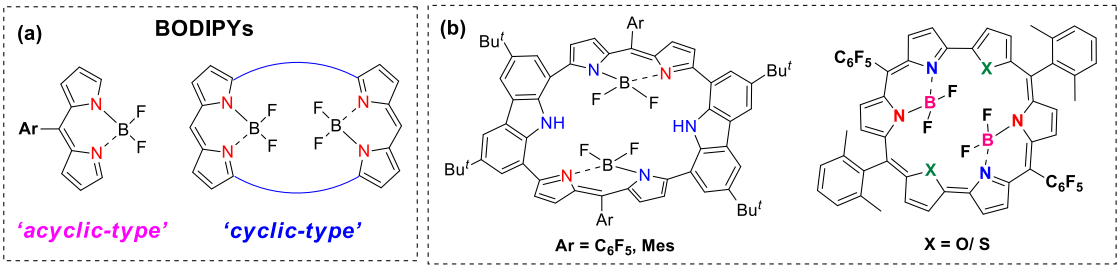
BODIPYs are known for their shape-independent high fluorescence quantum yields, sharp excitation and emission peaks contributing to overall brightness, and high solubility in many organic solvents [1]. Complexation of boron difluoride with expanded porphyrins offers a convincing strategy to access diverse array of cyclic BODIPYs. Owing to their unsurpassed flexibility, robustness as well as ability to tune their photophysical properties via synthetic modification, these cyclic BODIPYs have gained immense interest in recent times and some of them exhibit excitonic coupling due to interaction between transition dipoles [2].



Carbazole has been identified as a key building block in various modified expanded porphyrins exhibiting unique properties [14]. The advantage of incorporating carbazole lies in its close relation to pyrrole, increased electron conductance, structural rigidity, high emission and chemical stability [15]. Recently, various porphyrinoids have been reported using carbazole as the building block due to its intriguing optical and coordination properties [16]. Herein, I will disclose the overview of various cyclic-BODIPYs, their synthesis and ultrafast spectroscopic investigation of carbazole embedded hexaphyrin-like macrocycles and their corresponding *bis*-BODIPY complexes, *bis*-BODIPYs derived from two conformationally distinct [26]rubyrins(1.1.0.1.1) bearing hybrid diheteroles. The present studies are consistent with the dependence of dipole moments orientation leading to excitonically coupled BODIPY chromophores.

REFERENCES

(a) D. Frath, J. Massue, G. Ulrich, R. Ziessel, *Angew. Chem. Int. Ed.*, 2014, **53**, 2290-2310; (b) A. Harriman, G. Izzet, R. Ziessel, *J. Am. Chem. Soc.*, 2006, **128**, 10868-10875; (c) G. Ulrich, R. Ziessel, A. Harriman, *Angew. Chem., Int. Ed.*, 2008, **47**, 1184-1201.

1. (a) T. Sakida, S. Yamaguchi, H. Shinokubo, *Angew. Chem. Int. Ed.* 2011, **50**, 2280-2283; (b) M. H. Chua, T. Kim, Z. L. Lim, T. Y. Gopalakrishna, Y. Ni, J. Xu, D. Kim, J. Wu, *Chem. -Eur. J.*, 2018, **24**, 2232-2241.
2. (a) A. Kalaiselvan, S. Dhamija, C. Aswathi, A. K. De, S. Gokulnath, *Chem. Commun.*, 2021, 57, 11485-11488; (b) A. Kalaiselvan, A. Spergen, I. Sai Vamsi Krishna, V. S. Reddy and S. Gokulnath, *Chem. Commun.* 2021, **57**, 4420-4423.
3. (a) C. Maeda, T. Yoneda, N. Aratani, M. C. Yoon, J. M. Lim, D. Kim, N. Yoshioka, A. Osuka, *Angew. Chem. Int. Ed.*, 2011, **50**, 5691-5694; (b) L. Arnold, M. Baumgarten, K. A. Müllen, *Chem. Commun.*, 2012, **48**, 9640-9642; (c) T. Wu, T. Kim, B. Yin, K. Wang, L. Xu, M. Zhou, D. Kim, J. Song, *Chem. Commun.*, 2019, **55**, 11454-11457.

π-Extended Porphyrinoids: Synthesis, Spectral and Electrochemical Redox Properties and their Application in NLO and Sensing

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β-Functionalization of *meso*-tetraphenylporphyrins is of great interest since the electronic properties of the macrocycle can be tuned by varying the shape, size, number and electronic nature of the *β*-susbtituents. The optical and electrochemical redox properties of porphyrin π-system can be tuned by fusing the exocyclic rings to porphyrin macrocycle which leads to extended π-conjugation or by converting into chlorins or by tuning the conformation of the macrocycle.[1] Herein, we present the facile synthesis of *β*-to-*ortho*-phenyl fused porphyrins and chlorins[1b] having 1,3-indanedione or malononitrile moities by facile oxidative fusion of *trans*-chlorins[1c] using DDQ in good to excellent yields under mild conditions. Monofused porphyrins have been synthesized by oxidative fusion of free base *trans*-chlorins *via* Ni^{II} insertion followed by the skeletal rearrangement of macrocycle.[1d] A new series of *β*-substituted benzoporphyrins and their fused derivatives have been synthesized in good yields.[1e-1h] Further, *β*-tetracyanobutadiene (TCBD) appended porphyrins were synthesised and utilised as optical limiters.[1i] The synthesized fused porphyrinoids exhibited significantly red-shifted electronic spectral features ($\Delta\lambda_{max}$ = 16-85 nm) of Soret band due to the extended π-conjugation and twisted macrocyclic conformation (twist angle ~20-36º). Inner core NHs of fused chlorins exhibited tremendous downfield shift ($\Delta\delta$ = 1.7-2.2 ppm) as compared to their precursors. Fused porphyrins and chlorins exhibit the expected two one-electron oxidations but quite different redox behavior is observed upon reduction, where the free-base indanedione-appended chlorins show four reversible one-electron reductions.[1f] In this presentation, we will describe the facile synthesis, spectral and electrochemical redox properties of fused porphyrinoids and their utilization in anion sensing and nonlinear optics (NLO) in detail.

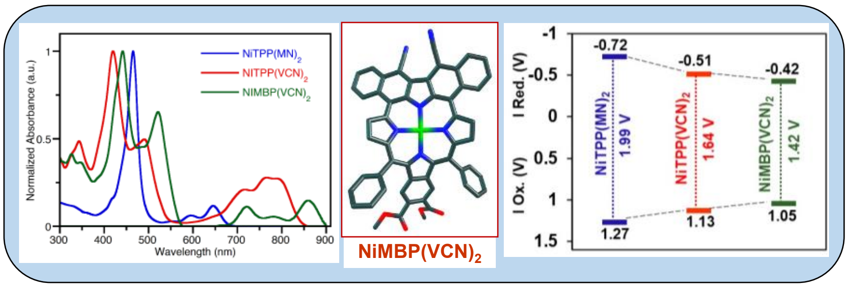

Chart 1. Molecular structure and electronic spectral features of fused porphyrin along with its HOMO-LUMO gap.

REFERENCES

1. (a) R. Kumar and M. Sankar, *Inorg. Chem.* 2014, **53**, 12706-12719; (b) N. Chaudhri, N. Grover and M. Sankar, *Inorg. Chem.* 2018, **57**, 6658-6668; (c) N. Chaudhri, N. Grover and M. Sankar, *Inorg. Chem.* 2017, **56**, 11532-11545; (d) N. Chaudhri, N. Grover and M. Sankar, M. *Inorg. Chem*. 2018, **57**, 11349-11360; (e) N. Grover, N. Chaudhri and M. Sankar, *Inorg. Chem.* 2019, **58**, 2514-2522; (f) N. Chaudhri et al, *Inorg. Chem*. 2020, **59**, 1418-1495; (g) W. R. Osterloh et al., Inorg. Chem. 2020, 59, 16737-16746; (h) S. Kumar et al, Dalton Trans. 2021, 50, 17086-17100; (i) R. K. Rohal, J. N. Acharyya, M. Shanu, G. V. Prakash and M. Sankar, *Inorg. Chem*. 2022, **61**, 1297-1307.

Synthesis of Phthalocyanines as Efficient Hole Transporting Materials in Perovskite Solar Cells

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

In this communication, we will present the synthesis of novel ZnPcs, ZnPc dimers and CuPcs (see as examples Figure 1) as efficient, stable, and low cost HTMs in PSCs. [2] The MPcs are substituted with functional groups that possesses a very good solubility in a wide range of organic solvents, adequate HOMO LUMO levels and thus can be applied from solution processing in a wide range of perovskite solar cell devices.

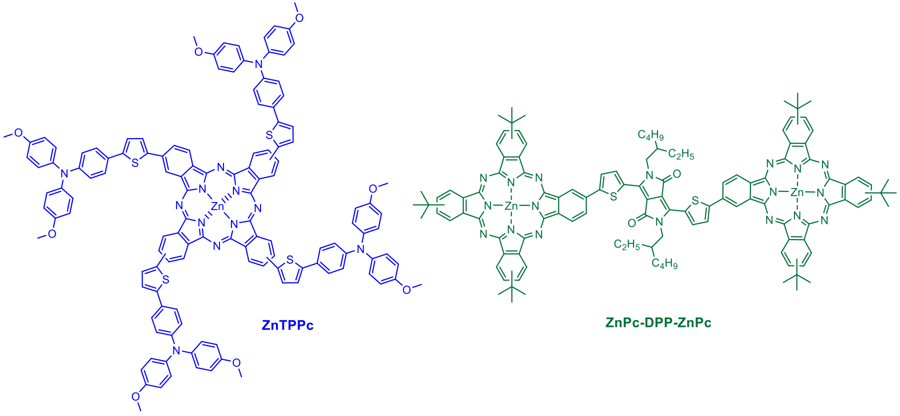

Figure 1 : Different ZnPcs structures as HTMs in PSCs

REFERENCES

1. M. Urbani, M. E. Ragoussi, M. K. Nazeeruddin, T. Torres, Coord. Chem. Rev. 2019, 381, 1-64.
2. a) P. Huang, A. Hernández, S. Kazim, J. Ortíz, Á. Sastre-Santos, S. Ahmad Sustainable Energy &Fuels. 2020, 4, 6188-6195. b) D. Molina, M. A. Ruiz-Preciado, F. Sadegh, M. João Álvaro-Martins, M. Grätzel, A. Hagfeldt, Á. Sastre-Santos, J. Porphyr. Phthalocyanines, 2019, 23, 546–553. c) D. Molina, M. A. Ruiz-Preciado, B. Carlsen, F. T. Eickemeyer, B. Yang, N. Flores-Díaz, M. J. Álvaro-Martins, K. Nonomura, A. Hagfeldt and Á. Sastre-Santos, ChemPhotoChem, 2020, 4, 307–314. d) P. Huang, A. Hernández, J. Follana-Berná, S. Kazim, J. Ortíz, Á. Sastre-Santos, S. Ahmad, ACS Appl. Energy Mater. 2021, 4, 9, 10124–10135. e) D. Molina, P. Huang, L. Ferrer, M. Castillo, S. Kazim, S. Ahmad, Á. Sastre-Santos, submitted.

Porphyrin-substrate systems studied by scanning probe microscopy: Spatial, energetic, and temporal resolution

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Polymeric structures based on porphyrin units exhibit a range of complex properties, such as nanoscale charge transport and quantum interference effects, and have the potential to act as biomimetic materials for light-harvesting and catalysis. These functionalities are based upon the characteristics of the porphyrin monomers but are also emergent properties of the extended polymer system. Incorporation of these properties within solid-state devices requires transfer of the polymers to a supporting substrate and is a motivating factor in the study of porphyrin-surface systems [1].

Investigation of such molecule-substrate systems is often carried out under ultra-high vacuum (UHV) conditions, facilitating contaminant free, highly controllable, fabrication procedures as well as providing access to characterisation on the single-molecule level via scanning probe microscopy techniques [2]. However, the size and thermally labile nature of large, and/or functionalised, porphyrin polymers prohibits the use of standard UHV sublimation protocols. We have demonstrated that porphyrin oligomers, polymers and macrocyclic systems can be deposited via an electrospray deposition technique [3–5], and that porphyrin polymers may be formed by using on-surface synthesis techniques; such as the Glaser coupling of porphyrin monomers [6].

Here I present details of our recent work where the implementation of scanning probe microscopy (SPM) techniques has allowed detailed characterisation of the energetic, and spatial, distribution of the electronic states within cyclic porphyrin polymers [7]. Additionally, we can make use of temperature-dependant SPM measurements to obtain information on the dynamics and energetics of on-surface diffusion of porphyrins, and the use of synchrotron-based photoelectron spectroscopies (e.g. XPS and NEXAFS) provides a route to quantify the chemical changes within on-surface reaction processes.

REFERENCES

1. J. M. Gottfried, Surface Chemistry of Porphyrins and Phthalocyanines, *Surf. Sci. Rep*. **70**, 259 (2015).
2. W. Auwärter, D. Écija, F. Klappenberger, and J. V. Barth, Porphyrins at Interfaces, *Nat. Chem.* **7**, 105 (2015).
3. A. Saywell, *et al.*, Conformation and Packing of Porphyrin Polymer Chains Deposited Using Electrospray on a Gold Surface, *Angew. Chem. Int. Ed.* **49**, 9136 (2010).
4. C. J. Judd, D. V. Kondratuk, H. L. Anderson, and A. Saywell, On-Surface Synthesis within a Porphyrin Nanoring Template, *Sci. Rep.* **9**, 1 (2019).
5. M. C. O'Sullivan, *et al.* Vernier Templating and Synthesis of a 12-Porphyrin Nano-Ring, *Nature* **469**, 72 (2011)
6. A. Saywell, *et al.*, Organisation and Ordering of 1D Porphyrin Polymers Synthesised by On-Surface Glaser Coupling, *Chem. Commun.* **52**, 10342 (2016).
7. C. J. Judd, *et al. Molecular Quantum Rings Formed from a π-Conjugated Macrocycle*, *Phys. Rev. Lett.* **125**, 206803 (2020).

Alkyne-azide cycloaddition reactions of *meso*-alkynyl corroles

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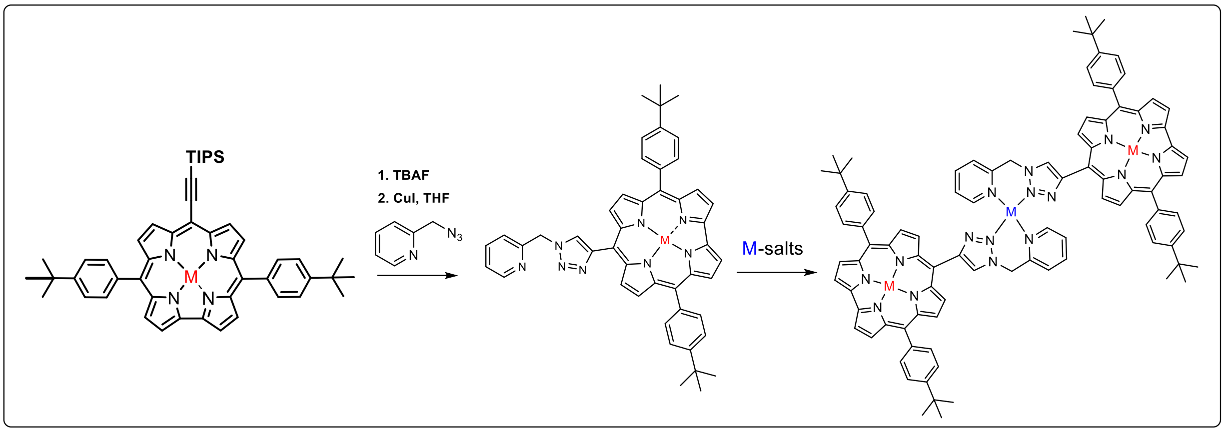
We will present novel synthesis procedures to obtain a series of freebase and metal A_2B- and meso-A_3-ethynylcorroles and demonstrate the successful copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC) "click" reaction of such ethynyl corroles with azidoaryl- and azidomethyl pyridine derivatives.



Scheme 1. Example of a synthesis of metal corrole triazole pyridine ligands and novel bimetallic complexes thereof.

The metalation of the corrole triazole pyridine ligands create novel bimetallic complexes (Scheme 1), linear oligomers, 2D- and 3D-network structures.

REFERENCES

1. M. Haas, S. Gonglach, S. Müllegger, W. Schöfberger, *Monatsh Chem* **2018**, 149, 773-781**.**
2. M. Haas, S. Gonglach, W. Schöfberger, *J. Porph. Phthalocyanines* **2020**, 24, 737-749.
3. M. Haas, D. Krisch, S. Gonglach, M. Bechmann, M. C. Scharber, M. Ertl, U. Monkowius, and W. Schöfberger, *Eur. J. Org. Chem.* **2021**, 10, 1525-1537.

Reengineering the Pigments of Life as Organocatalysts, Sensors, and Functional Materials

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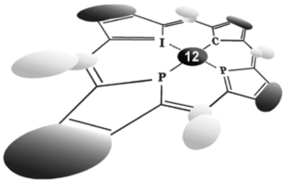
Porphyrins are nature's cofactors par excellence. Next to oxygen transport and storage, their role in electron transport and as photosynthetic pigments, they catalyze a multitude of chemical reactions [1, 2]. All these catalytic functions depend on the presence of a central metal which is intricately involved in the catalytic processes. Thus, all known catalytically active porphyrins are metalloporphyrins. However, we have discovered that, upon appropriate manipulation of the porphyrin macrocycle conformation, the core nitrogen atoms in free base porphyrins can be involved in catalysis as well.

Distorted porphyrins are able to activate small molecules via general base catalysis by participation of the imine groups or through hydrogen bonding catalysis involving the pyrrole units. To make the "active center" more accessible to substrates, the degree of outwards orientation of the pyrrole groups can be fine-tuned depending on the peripheral substitution pattern using *peri*-interactions or core substitution [3]. Various distortion modes exist, and saddle distorted porphyrins have been shown to have an increased basicity which qualifies these tetrapyrroles for catalytic screening [4]. Additionally, it is possible to enhance the basicity via electronic modulation of the β- and meso-substituents through the introduction of electron-withdrawing groups.

An extensive screening of a number of nonplanar porphyrins and substrates, as well as reaction conditions, has been used to develop design criteria for optimizing the catalytic properties of distorted porphyrins. Notably, certain free base porphyrins have been found to function as organocatalysts in Michael addition reactions, indicating a new mode of catalytic action for porphyrins which does NOT require a central metal ion. In addition, similar concepts have been used to develop switchable porphyrin receptors for the detection of analytes and removal of pollutants [5,6]. Further engineering of functional porphyrin materials is possible through logical spatial construction of 1D, 2D, 3D arrays [7]. This involves the use of porphyrins as photoactive components together with rigid hydrocarbon linker groups such as cubane or bicyclo(1.1.1)pentane either in solution, the solid state, or interfaces [8].

REFERENCES

1. M. O. Senge, *Chem. Commun.* **2011**, 1943.
2. M. O. Senge, S. A. MacGowan, J. M. O'Brien, *Chem. Commun.* **2015**, *51*, 17031.
3. M. Kielmann, M. O. Senge, *Angew. Chem. Int. Ed.* **2019**, *58*, 418.
4. M. Roucan, M. Kielmann, S. J. Connon, S. S. R. Bernhard, M. O. Senge, *Chem. Commun.* **2018**, *54*, 26.
5. K. Norvaiša, K. J. Flanagan, D. Gibbons, M. O. Senge, *Angew. Chem. Int. Ed.* **2019**, *58*, 16553.
6. K. Norvaiša, D. J. Gibbons, M. O. Senge, *Chem. Eur. J.* **2021**, *27*, 331.
7. N. Cao, A. Riss, E. Corral-Rascon, A. Meindl, W. Auwärter, M. O. Senge, M. Ebrahimi, J. V. Barth, *Nanoscale* **2022**, in press, https://doi.org/10.1039/D1NR06451G
8. N. Grover, G. M. Locke, K. J. Flanagan, M. H. R. Beh, A. Thompson, M. O. Senge, *Chem. Eur. J.* **2020**, *26*, 2405.



Meso-free Aromatic, Antiaromatic, and Non-topographically Planar Porphyrinoids

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Studies of porphyrin analogues in our group date back to the 1980s, when we published a report on texaphyrins and, in so doing, became the first to introduce the term “expanded porphyrin” into the literature. Since then, considerable activity on the part of dozens of groups have served to make expanded porphyrins and other porphyrin analogues the focus of a wide range of research activities and translational efforts. Our own reesearch, often carried out in collaboration with leaders in the community, has focused on both potential medical applications and advancing out understanding of electronic structure. With the latter goal in mind, we have worked, again often collaboration, to create systems with bona fide antiaromatic character, ones with odd electron counts (e.g., 25 π-electron systems), and those whose structure cannot be mapped onto a 2-dimensional surface. An effort has also been made to apply the tools used to analyze aromaticity to the study of covalency in actinide expanded porphyrin complexes. A summary of this preparative work and analyses of the chemical, structural, photophysical, cation coordination, anion recognition, and ground and excited state electronic properties of these systems will be presented in this lecture.

Thanks are given to the R. A. Welch Foundation for supporting current research efforts underlying this presentation. Prior support from the U.S. DOE, U.S. NSF, the NIH, the Cancer Research and Prevention Institute of Texas, and Shanghai University is also acknowledged. This project has only been possible as the result of collaborations with a number of groups, including those of Profs. Dongho Kim, Jong Sung Kim, Jung Su Park, Shunichi Fukuzumi, T. K. Chandrashekar, Pradeepta Panda, Dirk Guldi, Changhee Lee, Jan Jeppesen, Jun-Long Zhang, Jonathan Arambula, Zahid Siddik, Rick Finch, John Arnold, Andrew Gaunt, and Tomas Torres. Their help and the dedication of lab coworkers who will be thanked during the presentation is deeply appreciated.

REFERENCES

1. Cha, W.-Y.; Kim, T.; Ghosh, A.; Zhang, Z.; Ke, X.-S.; Ali, R.; Lynch, V. M.; Jung, J.; Kim, W.; Lee, S.; Fukuzumi, S.; Park, J. S.; Sessler, J. L.; Chandrashekar, T. K.; Kim, D. “Bicyclic Baird-type Aromaticity,” *Nature Chem.* **2017**, *9*, 1243-1248.
2. Ke, X.-S.; Hong. Y.; Lynch, V. M.; Kim. D.; Sessler, J. L. “A Metal-Stabilized Quinoidal Dibenzo[g,p]chrysene-fused Bis-dicarbacorrole System,” *J. Am. Chem. Soc.* **2018**, *140*, 7579–7586.
3. Anguera, G.; Cha, W.-Y.; Moore, M. D.; Brewster, J. T. II, Zhao, M. J.; Lynch, V. M.; Kim, D.; Sessler, J. L. “An expanded porphycene with high NIR absorptivity that stabilizes two different kinds of metal complexes,” *Angew. Chem. Int. Ed.* **2018**, *57*, 2575-2579
4. Ke, X.-S.; Kim, T.; He, Q.; Lynch, V. M. Kim, D.; Sessler, J. L. “A 3-Dimensional Fully Conjugated Carbaporphyrin Cage,” *J. Am. Chem. Soc.* **2018**, *140*, 16455–16459.
5. Brewster, J. T. II, Mangel, D. N.; Gaunty, A. J.; Saunder, D. P.; Zafa, H.; Lynch, V. M.; Boreen, M. A.; Garner, M. E.; Goodwin, C. A. P.; Settineri, N. S.; Arnold, J.; Sessler, J. L. “In-Plane Thorium (IV), Uranium (IV), and Neptunium(IV) Expanded Porphyrin Complexes,” *J. Am. Chem. Soc*. **2019**, *141*, 17867-17874.

Coupling mechanism between O_2 reduction and proton-pumping reaction driven by cytochrome *c* oxidase.

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Mammalian cytochrome *c* oxidase (CcO), a heme-copper protein locating at the respiratory chain terminus, pumps protons across the mitochondrial inner membrane coupled with a molecular oxygen (O_2) reduction reaction. CcO has 4 metal sites (heme *a*, Cu_A, heme a_3, and Cu_B), and O_2 bound to O_2 reduction site comprised of heme a_3 and Cu_B receives 4 electrons from cytochrome *c* via Cu_A and heme *a*. Four protons used for O_2 reduction to water are transferred from mitochondrial matrix through D and K-pathways. It has been proposed that each proton to be pumped is transferred via H-pathway, driven by electrostatic repulsion between the proton to be pumped and a net positive charge created in heme *a* upon the sequential electron transfer from heme *a* to the O_2 reduction site. Intriguingly, despite of the fact that the electrostatic repulsion itself doesn't govern the direction of the proton migration after the repulsion, the repulsed protons strictly transferred unidirectionally toward inter membrane region, giving the very high proton pumping efficiency ($H^+/e^- = 1$). Spectroscopic analyses have revealed that CcO passes through distinct 6 intermediates (Figure) during each catalytic cycle.

For the sake of unveiling the reaction mechanism of CcO, we determined the crystal structures of all these catalytic intermediate forms [1, 2]. The structure of A-form showed that the O_2 reduction site is an oxymyoglobin type structure, in which O_2 is bound closer to heme a_3 than to Cu_B, suggesting the stability of the A-form. A novel water molecule hydrogen-bonded to Tyr244-OH was identified in the intermediate forms from P to E in Figure. This water molecule, accessible to any ligand at the O_2 reduction site, provides a facile proton transfer system between Tyr244 and the bound ligand at heme a_3. Furthermore, the OH^--Cu_B distance in the O-form is unusually longer than those of ordinary Cu^{2+}-OH^- compounds, suggesting that the electron affinity of Cu_B in O-form is enhanced by the distantly located negative charge of OH^-. This high electron affinity contributes the efficient electron transfer from O to E-form preventing from electron backflow, giving the high proton pumping efficiency. The present X-ray structural analyses showed that a water channel, located in the bottom half of the H-pathway, was closed in all the forms except for the R-form for preventing back-leak of the protons to be pumped. Thus, before O_2-binding, the four protons to be pumped are likely to be incorporated and stored in a large water cluster attached to the H-pathway, which has been identified crystallographically before [3].

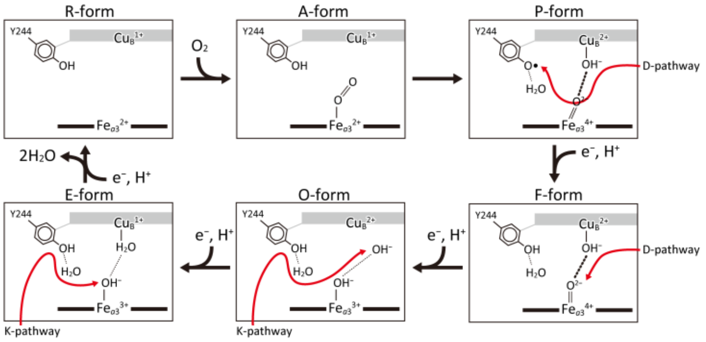

Figure. The shcematic structure of O_2 reduction site in bovine heart cytochrome *c* oxidase
The thick gray line shows a side view of the Cu_B coordination plane consisting of three histidine nitrogen atoms.

REFERENCES

1. Atsuhiro Shimada, et al. (2020) *J. Biol. Chem.,* 295, 5818-5833. 2. Atsuhiro Shimada, et al. (2021) *J. Biol. Chem.,* 297, 100967 3. Naomine Yano, et al. (2016) *J. Biol. Chem,* 291, 23882-23894

Bioinspired Catalytic Reactions with and Beyond the Vitamin B_{12} Enzyme Function

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Bioinspired catalyst system was developed in the interdisciplinary fields of bioorganic chemistry and bioinorganic chemistry. In nature, enzymes catalyze various molecular transformations under mild conditions at room temperature and physiological pH with a high efficiency and selectivity. Therefore, we can learn about many excellent systems from nature. As for the catalyst design, a metal complex inspired from the active site of a metal enzyme has been developed. Since metal enzymes catalyze a variety of molecular transformations by the action of the metal ion, they have been considered as one of the desirable catalyst in organic synthesis. Among the metal enzymes, tetrapyrrole pigments, such as porphyrin, chlorophyll, and corrin, that have emerged in nature concerned with various metabolisms have attracted a lot of attention. The characteristic feature of the tetrapyrrole metal complex is its abundant redox property both at the metal center and macrocyclic ligand [1]. Various intermediates for the reaction could be formed in the redox active metal complex. Therefore, the combination of the metal complex with a redox system should form an excellent catalytic system. Based on this concept, we can utilize various redox systems such as electrochemistry and photo-excited chemistry, for construction of a catalyst system [2-4]. This is one of the characteristic features and advantages of the bioinspired catalyst system. Among the metal complexes inspired from natural metal enzymes, the cobalt ion containing the B_{12} (cobalamin) derivative is the focus of this lecture. The development of a hybrid catalyst with the B_{12}-dependent enzyme-inspired photochemical and electrochemical reactions are introduced.

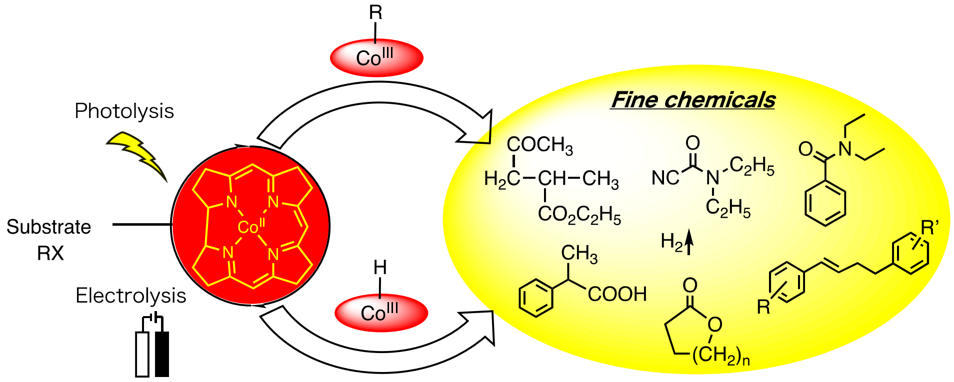

Fig. 1 Bioinspired reactions catalyzed by vitamin B_{12} derivatives.

REFERENCES

1. H. Shimakoshi, Y. Hisaeda, *Chem. Rec.* **2021**, *21*, 2080.
2. K. Shichijo, M. Fujitsuka, Y. Hisaeda, H. Shimakoshi, *J. Organomet. Chem.* **2020**, *907*, 121058.
3. Z. Luo, K. Imamura, Y. Shiota, Y. Yoshizawa, Y. Hisaeda, H. Shimakoshi, *J. Org. Chem.* **2021**, *86*, 5983.
4. M. Moniruzzaman, Y. Yano, T. Ono, K. Imamura, Y. Shiota, Y. Yoshizawa, Y. Hisaeda, H. Shimakoshi, *J. Org. Chem.* **2021**, *86*, 16134.

ORALS

Synthesis of aza-BODIPY Analogues by a Schiff Base Forming Reactions and Their NIR Optical Properties

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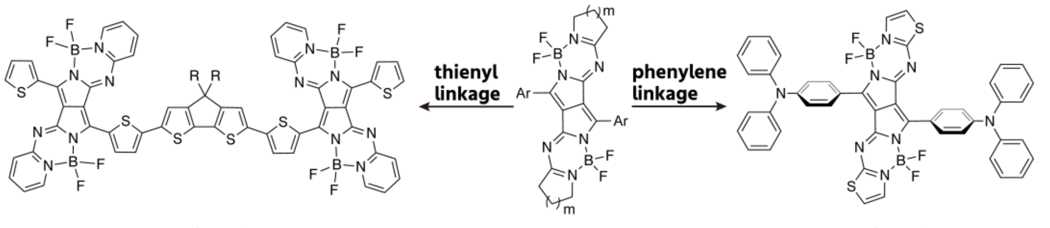
In recent years, functional chromophore molecules, whose optical properties in the visible (vis) and near infrared (NIR) regions can be controlled in a simple manner, have become increasingly important because of their potential application in various research fields. Recently, we have succeeded in the synthesis of novel aza-BODIPY analogues from a Schiff base forming reaction of lactams and heteroaromatic amines [1]. Among a series of aza-BODIPY analogues developed based on this strategy, dimeric aza-BODIPY analogues called pyrrolopyrrole aza-BODIPYs (PPABs) exhibit intense absorption and fluorescence in the far-red region, and their absorption and fluorescence spectra can be shifted to the NIR region by changing the heteroaromatic ring units [2,3]. The optical properties are also significantly perturbed by the substituents on the pyrrolopyrrole core, and the perturbation is controlled by the dihedral angles of the linker units. This effect of the linker can be seen for the PPAB dimers; the bithienyl-linked dimer exhibits panchromatic absorption in the vis/NIR regions, whereas a monomer-like intense absorption is observed for the biphenyl-linked one [4]. Considering the linker effect, two donor-acceptor (D-A) systems were developed for organic photovoltaics (OPV) and organic light emitting diode (OLED) applications. In the OPV studies, A-D-A triads and D-A polymers bearing thienyl linkers exhibited the highest power conversion efficiency of 3.88% and 2.27%, respectively, despite their panchromatic absorption extending to 1000 nm [5,6]. In the OPV studies, D-A-D molecules bearing phenylene linkers were developed. Owing to the high fluorescence brightness, the OLED of this D-A-D triad exhibited high external quantum efficiency (EQE) of 3.7% at an electroluminescence maximum of ca. 760 nm [7].

In this presentation, the NIR optical properties of PPABs and their OPV and OLED applications will be discussed.



A−D−A Triad for OPV **PPAB** **D−A−D Triad for OLED**

REFERENCES

1. Shimizu S. *Chem. Commun.* 2019; **55**: 8722–8743.
2. Shimizu S, Iino T, Araki Y, Kobayashi N. *Chem. Commun.* 2013; **49**: 1621–1623.
3. Shimizu S, Iino T, Saeki A, Seki S, Kobayashi N. *Chem. Eur. J.* 2015; **21**: 2893–2904.
4. Kage Y, Mori S, Ide M, Saeki A, Furuta H, Shimizu S. *Mater. Chem. Front.* 2018; **2**: 112–120.
5. (a) Feng R, Sato N, Yasuda T, Furuta H, Shimizu S. *Chem. Commun.* 2020; **56**: 2975–2978.
6. Feng R, Sato N, Nomura M, Saeki A, Nakanotani H, Adachi C, Yasuda T, Furuta H, Shimizu S. *J. Mater. Chem. C* 2020; **8**: 8770–8776.
7. Kage Y, Kang S, Mori S, Mamada M, Adachi C, Kim D, Furuta H, Shimizu S. *Chem. Eur. J.* 2021; **27**: 5259–5267.

Close Stacking of Norcorrole Metal Complexes

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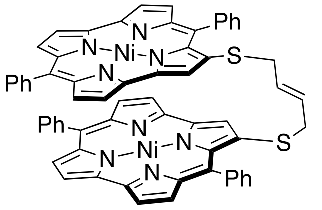
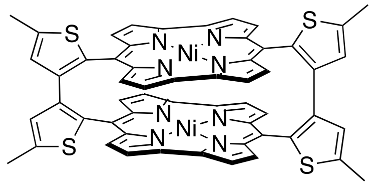
Stacked-ring aromaticity arising from the close stacking of two antiaromatic π-conjugated macrocycles has received considerable attention.[1] Recently, we have reported that tethered norcorrole dimer **1** and cyclophane **2** exhibit closely stacked orientation.[2,3] The remarkable proximity of the two norcorrole units has been rationalized by the emergence of the stacked-ring aromaticity owing to the three-dimensional delocalization of π-electrons between two antiaromatic systems.

Next, we have prepared a cyclophane **3** consisting of two antiaromatic Ni(II) norcorrole units tethered with two flexible alkyl chains.[4] Norcorrole cyclophane **3** exhibited crystal polymorphism leading to three different solid-state structures, in which the orientation of the two norcorrole units is substantially different. The stacked-ring aromaticity of **3** is dependent on the twist angle between two stacking norcorrole units.



1



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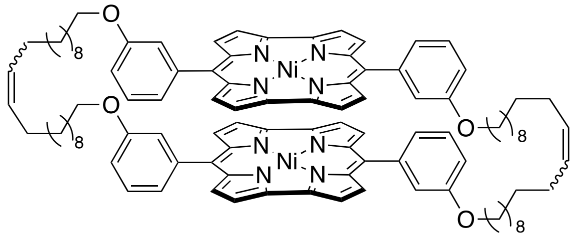

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REFERENCES

1. (a) C. Corminboeuf, P. v. R. Schleyer, P. Warner, Org. Lett. 2007, 9, 3263. (b) D. E. Bean, P. W. Fowler, Org. Lett. 2008, 10, 5573.
2. R. Nozawa, H. Tanaka, W.-Y. Cha, Y. Hong, I. Hisaki, S. Shimizu, J.-Y. Shin, T. Kowalczyk, S. Irle, D. Kim, H. Shinokubo, Nat. Commun. 2016, 7, 13620.
3. R. Nozawa, J. Kim, J. Oh, A. Lamping, Y. Wang, S. Shimizu, I. Hisaki, T. Kowalczyk, H. Fliegl, D. Kim, H. Shinokubo, Nat. Commun. 2019, 10, 3576.
4. H. Kawashima, S. Ukai, R. Nozawa, N. Fukui, G. Fitzsimmons, T. Kowalczyk, H. Fliegl, H. Shinokubo, J. Am. Chem. Soc. 2021, 143, 10676.

Designed Radical-Chromophore Exchange Controls Magnitude of Photoinduced Electron Spin Polarization in Electronic Ground States

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[c]*Brock University, St. Catharines, Ontario, Canada*

Modulation of ground-state electron spin polarization (ESP) in an organic radical (nitronylnitroxide, NN) covalently attached to donor-acceptor chromophores, (**bpy)Pt(CAT-Bridge-NN**), where bpy = 5,5'-di-*tert*-butyl-2,2'-bipyridine, CAT = 3-*tert*-butylcatecholate, Bridge = organic fragments, has reported.[1,2] These molecules represent a class of chromophores that can be photoexcited with visible light to produce an initial exchange-coupled, 3-spin (bpy•-, CAT+• (= semiquinone, SQ) and NN•), charge-separated doublet $^2S_1$ (S = chromophore excited spin singlet configuration) excited state that rapidly decays by magnetic exchange enhanced internal conversion to a $^2T_1$ (T = chromophore excited spin triplet configuration) state. The absorptive- or emissive ESP observed results from transitions between the chromophoric $^2T_1$ and $^4T_1$ states or between chromophoric $^2T_1$ and NN-based excited states, the magnitude of which results from either steric alteration of these excited state energy gaps. Here we show a correlation between the magnitude of ground state ESP and an excited state exchange parameter

REFERENCES

1. "Metal Ion Control of Photoinduced Electron Spin Polarization in Electronic Ground States," Kirk, M. L.; Shultz, D. A.; Chen, J.; Hewitt, P.; Daley, D.; Paudel, S.; van der Est, A. *J. Am. Chem. Soc.* **2021**, *143*, 10519-10523.
2. "Chromophore-Radical Excited State Antiferromagnetic Exchange Controls the Sign of Photoinduced Ground State Spin Polarization," Kirk, M. L.; Shultz, D. A.; Hewitt, P.; Stasiw, D. E.; Chen, J.; van der Est, A. *Chem. Sci.* **2021**, *12*, 13704-13710.

Photosensitizers-peptides and Photosensitizers-polysaccharides complexes for antimicrobial photodynamic therapy applications

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Wound infection is a prominent topic in hospitals. Infections may delay wound healing, increase the cost of treatment and in some cases lead to the patient's death. The emergence of antibiotic-resistant bacteria or superbugs makes infected wounds more difficult to cure. The bacteria responsible of infected wounds come from surroundings or from normal flora of the skin. Additionally, bacteria proliferate and form a biofilm which increases their resistance to antimicrobial treatment. Therefore, new approaches had to be developed in order to overcome this problem. Antimicrobial photodynamic therapy (aPDT) is a promising alternative to inhibit microbes, and has already inspired the creation of innovative materials. Interesting results were achieved against Gram-positive bacteria, but it also appeared that Gram-negative strains, especially Pseudomonas aeruginosa, were less sensitive to aPDT. In previous studies, an enhanced efficacy of aPDT against Gram-negative bacteria was obtained by binding photosensitizers to peptides.

In this work, we have developped cationic or neutral photosensitizers covalently bind to polymyxin B nonapeptide [1, 2] or poly and oligosaccharides [3] for photo-antimicrobial applications against different bacteria strains.

REFERENCES

1. Florent Le Guern, Vincent Sol, Catherine Ouk, Philippe Arnoux, Céline Frochot, Tan-Sothea Ouk. Enhanced photobactericidal and targeting properties of a cationic porphyrin following attachment of Polymyxin B. *Bioconjugate Chemistry* **2017,** 9, 2493-2506.
2. Florent Le Guern, Tan-Sothea Ouk, Catherine Ouk, Regis Vanderesse, Yves Champavier, Emilie Pinault, Vincent Sol Lysine analogue of Polymyxin B as a significant opportunity for photodynamic antimicrobial chemotherapy. *ACS Medicinal Chemistry letters* **2018**, 9, 12-17.
3. Abdechakour Elkihel, Camille Christie, Charlotte Vernisse, Tan-Sothea Ouk, Romain Lucas, Vincent Chaleix; Vincent Sol Vincent. A Xylan-based Cross-linked Hydrogel for Photodynamic Antimicrobial Chemotherapy *ACS Applied Bio Materials* **2021**, 4, 7204-7212. doi.org/10.1021/acsabm.1c00760

Phthalocyanine Complexes: Expanding Toolbox for Carbene Transfer Reactions

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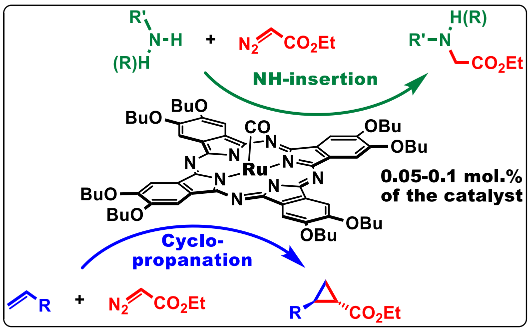
Carbene transfer reactions to X-H bonds (X = N, C, O…) and olefins have emerged as a powerful strategy for the construction of the elaborated molecules. These reactions are believed to involve carbene metal complexes and metalloporphyrins as well as engineered hemoproteins which have been extensively studied [1]. Although metal phthalocyanine complexes (MPc) are efficient catalysts for many reactions [2] they have been rarely explored as catalysts for the carbene transfer reactions. Phthalocyanines have been often regarded as porphyrin analogues but their catalytic properties do differ from those of the porphyrin counterparts. Increasing number of examples shows that phthalocyanine complexes are superior over porphyrin ones in many reactions [2c]. Mononuclear and binuclear iron phthalocyanine complexes exhibit remarkable catalytic properties in the oxidation [2b]. Given the similarity of oxidizing oxo species with isoelectronic carbene and nitrene putative intermediates which might perform carbene and nitrene transfer reactions, the high catalytic efficiency of phthalocyanine complexes in oxidation suggests that they deserve a more careful evaluation in the carbene transfer reactions.



Indeed, Fe and Ru mono- and binuclear phthalocyanine complexes show a particular efficiency in cyclopro-panation of olefins and carbene transfer to N-H bonds of amines [3]. For instance, RuPc complexes show a large substrate scope in the carbene N-H insertion with 80-100 % yields under practical reaction conditions (0.05 mol% catalyst loading, high amine concentration, 1.1 eq. of EDA). The substrate scope, reactivity of FePc and mechanistic features as well as the relationship between the FePc structure and catalytic activity in carbene transfer reactions will be discussed.

Acknowledgment This study was supported by RFBR and CNRS, IEA project n° 21-53-15004.

REFERENCES

1. a) C. Damiano, P. Sonzini, E. Gallo, *Chem. Soc. Rev.* **2020**, *49*, 4867-4905; (b) Y. Yang, F. H. Arnold, *Acc. Chem. Res.* **2021**, *54*, 1209-1225.
2. a) A. B. Sorokin, *Chem. Rev.* **2013,** *113*, 8152-8191; b) P. Afanasiev, A. B. Sorokin, *Acc. Chem. Res*. **2016**, *49*, 583-593; c) selected example: S. M. Paradine, M. C. White, *J. Am. Chem. Soc.* **2012**, *134*, 2036-2039.
3. a) L. P. Cailler, A. P. Kroitor, A. G. Martynov, Yu. G. Gorbunova, A. B. Sorokin, *Dalton Trans.* **2021**, *50*, 2033-2031; b) L. P. Cailler, A. G. Martynov, Yu. G. Gorbunova, A. Yu. Tsivadze, A. B. Sorokin, *J. Porphyrins Phthalocyanines* **2019**, *23*, 497-506 ; c) L. P. Cailler, A. G. Martynov, Yu. G. Gorbunova, A. Yu. Tsivadze, A. B. Sorokin, *Dalton Trans.* **2017**, *46*, 15651-15655.

Highly Effective Photosensitizers for Photodynamic Therapy (PDT)

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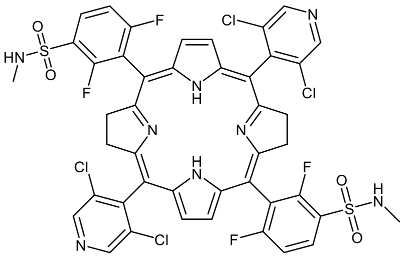
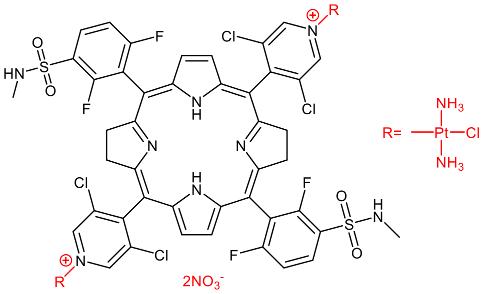
In the recent years, we have synthesized various photosensitizers, which were obtained after reaction with *trans*-bis(ammine)platinum-monochloride (see Figure below) [1-6]. In five out of five studied cases [1,2,4-6], the platinated photosensitizers were found to have an improved phototoxic index (ratio of dark toxicity to light toxicity) compared with the non-platinated photosensitizers.

Name	l (irradiation) [nm]	Phototoxic index PS-(py)n against HeLa cells	Phototoxic index PS-(py-[Pt(NH_3)$_2$Cl]$^+$)n against HeLa cells	Improvement of p.i.	ref.
4-Tetrapyridyl-porphyrin	420	>17.3	1210	<70	1
3-Tetrapyridyl-porphyrin	450	>263	4500	<17	6
Tetrapyridino-phthalocyanine	>600	0.8	7.5	9.4	2
Pyridyldistyryl-BODIPY	680	>33	>543	~16	4
Dipyridyl-Bacteriochlorin (see Fig.)	**750**	590	**4000**	6.8	5





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REFERENCES

1. A. Naik, R. Rubbiani, G. Gasser, B. Spingler, *Angew. Chem. Int. Ed.*, **2014**, *53*, 6938-6941.
2. L. Schneider, M. Larocca, W. Wu, V. Babu, R. Padrutt, E. Slyshkina, C. König, S. Ferrari, B. Spingler, *Photochem. Photobiol. Sci.*, **2019**, *18*, 2792-2803.
3. R. Rubbiani, W. Wu, A. Naik, M. Larocca, L. Schneider, R. Padrutt, V. Babu, C. König, D. Hinger, C. Maake, G. Gasser, S. Ferrari, B. Spingler, *Chem. Commun.*, **2020**, *56*, 14373-14376.
4. R. Padrutt, V. Babu, S. Klingler, M. Kalt, F. Schumer, M. I. Anania, L. Schneider, B. Spingler, *ChemMedChem*, **2021**, *16*, 694-701.
5. N. A. Le, V. Babu, M. Kalt, L. Schneider, F. Schumer, B. Spingler, *J. Med. Chem.*, **2021**, *64*, 6792–6801.
6. L. Schneider, M. Kalt, M. Larocca, V. Babu, B. Spingler. *Inorg. Chem.*, **2021**, *60*, 9416–9426.

ORALS

Porphyrinoids with Higher Analogues of Arene and Pyridine Units in the core

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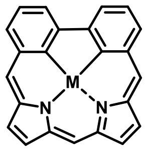
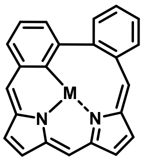
[b]*Department of Chemistry, Jagiellonian University, 30-387 Kraków, Poland*
[c]*Department of chemistry, Imperial College, London, London W12 7TA, United Kingdom.*

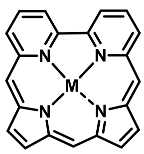
By decreasing or increasing an atom in the inner core of porphyrin leads to contracted or expanded porphyrinoids. The contracted derivatives are utilized for stabilizing high oxidation state metal ions, whereas the expanded analogues are exploited for aromatic – antiaromatic switching, conformational flexibility and stabilizing multi-metal ions in the core. By introducing an arene or a pyridine unit in the framework alters the electronic structure, thus leading to unusual optical, photophysical and coordination properties. The chemistry of arene ring incorporated carbaporphyrinoids and pyridine unit embedded pyriporphyrinoids and their contracted and expanded analogues are well-known in the literature. [1-3] However, recent developments of porphyrin analogues by introducing higher analogues of arenes and pyridine units are not adequately inspected. In this talk, we will mainly focus on biphenyl (**1**-**2**), bipyridine (**3**), terphenyl (**4**) and mixed arene pyridine (**5**) embedded porphyrin analogues and their coordination chemistry (**1**-**5**) [4].



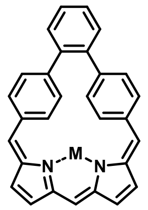
1. M: Cu(III)



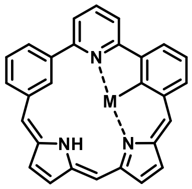
2. M: B(III)-Ph



3. M: Zn(II)-Cl



4. M: Rh(CO)$_2$



5. M: Pt-Cl

REFERENCES

1. T. D. Lash, Chem. Rev. 2017, 117 (4), 2313-2446.
2. B. Szyszko and L. Latos-Grażyński, Angew. Chem., Int. Ed. 2020, 59 (39), 16874-16901
3. K. Laxman, A. Kumar and M. Ravikanth, Asian J. Org. Chem. 2020, 9, 162-180.
4. Mainak Das, B. Adinarayana and A. Srinivasan, ACS Omega, 2021, 10.1021/acsomega.1c05444.

Tuning tetrapyrroles for enhanced function: Combining advanced optical methods and electronic structure studies

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Ever since tetrapyrroles were recognised as dyes in ancient times their properties as dyes has been developed and utilized. Beyond dyes based on the electronic structure, the major natural applications of tetrapyrroles mix ligand binding, redox chemistry and photochemistry – a remarkably wide palette of function. Technology has kept pace with the discovery of synthetic analogs for a myriad of applications. In this paper I describe our work to understand the electronic effects of structural modifications to porphyrins, chlorins and phthalocyanines allowing prediction of enhanced function using optical spectroscopy, and particularly magnetic circular dichroism spectroscopy, coupled with analysis of the geometric distribution of the molecular orbitals and the changes in predicted absorption spectra from TDDFT calculations.

Non-metal complexes of electron-deficient porphyrazinoids

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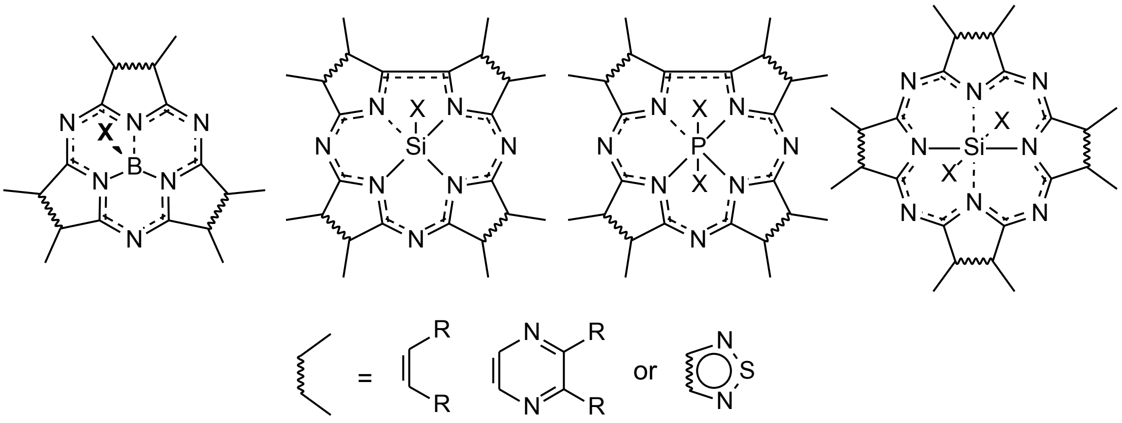
Complexes of porphyrazines with fused electron-deficient heterocycles (pyridine, pyrazine, 1,2,5-thia(selena)diazole) are known and due to their enhanced electron affinity widely studied as perspective functional materials for application in organic electronics as n-type semiconductors, in bioimaging as pH-sensitive fluorophores and in other fields. In our resent works we have prepared novel porphyrazines, their derivatives with fused heterocycles and ring contracted analogues - corrolazines and subporphyrazines containing non-metal (boron(III), silicon(IV) or phosphorus(V)) as a central coordinating atom and studied their spectral-luminescence, photophysical, electrochemical and other properties.



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Every photon counts:
Tip-enhanced electroluminescence of single molecules

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Exploration of fundamental photophysical phenomena at the level of individual quantum objects requires highly specialized optical spectroscopy with subnanometer, single-photon capabilities. Thanks to recent progress in light microscopy with scanning probes, excited states of molecules and their interaction can now be investigated at the nanoscale with unprecedented detail. Precise injection of charges [1] into molecules leads to formation of transient charged states and excited states (excitons). The photons produced by decay of these states carry a rich information about energies, charges, transient dipoles, vibronics and temporal evolution of the studied systems. Using an optical path to collect photons from the nanocavity between the tip and sample in a cryogenic scanning probe microscope, it is possible to tackle some photophysical phenomena occurring in organic dyes.

In this contribution, I will present our investigation that focused on the local Coulombic effects of the ionic substrate on single Copper-phthalocyanines (CuPc) [2], electrofluorochromism of Zinc-phthalocyanine (ZnPc), and describe a new phase fluorometry scheme, that combines radio-frequency-modulation of the picocavity with time-resolved single photon detection [3,4]. With this method, the molecular transient states could be resolved and the evolution of the system could be tracked down to the picosecond range. I will also discuss the spectral fingerprints of various phthalocyanine librations on the surface, coupled to electronic transitions and explain them using the Franck-Condon picture.

REFERENCES

1. Charge carrier injection electroluminescence with CO functionalized tips on single molecular emitters. J Doležal, P Merino, J Redondo, L Ondič, A Cahlík and M Švec, Nano letters 19 (12), 8605-861, 2019
2. Mechano-Optical Switching of a Single Molecule with Doublet Emission. J Doležal, P Mutombo, D Nachtigallová, P Jelínek, P Merino and M Švec ACS Nano 14 (7), 8931-8938, 2020
3. Constant amplitude driving of a radio frequency excited plasmonic tunnel junction. J Doležal, P Merino and M Švec, Applied Physics Letters 118 (19), 193301, 2021
4. Exciton-Trion Conversion Dynamics in a Single Molecule. J Doležal, S Canola, P Merino and M Švec, ACS Nano 15, 7694–7699, 2021

Mesoporous Silica Nano-vehicles for the Delivery of Chemotherapeutics and Photosensitisers

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In the last years, our group has been working on the preparation of drug delivery systems (DDSs) for the release of multiple drugs intended for combination therapies of cancer [1]. Our DDSs are based on mesoporous silica nanoparticles, which present outstanding properties for drug delivery applications owing to their good biocompatibility, high encapsulation capacity and easy chemical modification [2,3]. This chemical versatility opens the door to the design of stimuli-responsive DDSs, which allow the selective release of the payload by means of smart gates installed at the external surface of the nanoparticle. In this presentation, we would like to report on our recent results in the development of novel MSNs nano-vehicles for the delivery of chemotherapeutics and photosensitizers [4].

REFERENCES

1. Llinàs, M. C.; Martínez-Edo, G.; Cascante, A.; Porcar, I.; Borros, S.; Sánchez-García, D. *Drug Deliv,* 2018, 25, 1137–1146.
2. Wong, R. C. H.; Ng, D. K. P.; Fong, W.-P.; Lo, P.-C. *Chem. Eur. J.* 2017, 23, 16505–16515.
3. Martínez-Carmona, M.; Lozano, D.; Baeza, A.; Colilla M.; Vallet-Regí, M. *Nanoscale* 2017, 9, 15967–15973.
4. Martínez-Edo, G.; Xue, E.Y.; Ha, S.S.Y.; Pontón, I.; González-Delgado, J.A.; Borrós, S.; Torres, T.; Ng, D.K.P.; Sánchez-García, D. *Chem. Eur. J.* 2021, 27, 14610–14618.

Direct removal of a peripheral vinyl group in nickel chlorophyll derivatives

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Nickel(II) and oxovanadium(IV) deoxophylloerythroetioporphyrins (Ni/VO-DPEPs, see the right drawing of Fig. 1) were found from the geological samples including sediments, petroleum, and oil shale [1]. Ni/VO-DPEPs were proposed to be produced from (bacterio)chlorophylls in ancient photosynthetic organisms. Typically, chlorophyll(Chl)-*a* (Fig. 1, center) in oxygenic phototrophs is transformed into 3-ethylated, 3-methylated, 3-unsubstituted Ni/VO-DPEPs via the 13^1-deoxygenation, the removal of esterifying groups at the 13^2,17^2-positions, the 17,18-dehydrogenation, and substitution of the central magnesium to a nickel atom or an oxovanadium moiety as well as the transformation of the 3-vinyl to 3-ethyl group, 3-methyl group, and 3-hydrogen atom, respectively.
The 3-functional group in Chl-*a* derivatives has been reported to be removed under the following conditions. Pyrolysis of iron(III) methyl pyropheophorbide-*a* (R^3 = CH=CH$_2$ and M = FeCl in the right drawing of Fig. 1) and metal-free methyl 3-carboxy-pyropheophorbide-*a* (R^3 = COOH and M = H$_2$) gave methyl 3-devinyl-pyropheophorbide-*a* (R^3 = H and M = H$_2$) thorough the 3-devinylation and 3-decarboxylation, respectively [2,3]. In addition, photolysis of zinc(II) methyl pyropheophorbide-*d* (R^3 = CHO and M = Zn) afforded the corresponding zinc 3-unsubstituted chlorin via the 3-deformylation [4]. Recently, we observed the 3-devinylation in nickel(II) methyl pyropheophorbide-*a* (R^3 = CH=CH$_2$ and M = Ni) after heating in benzene and toluene (1:2) with *p*-toluenesulfonic acid at 80 °C overnight [5]. Here we report the acidic removal of a peripheral vinyl group in nickel complexes of various Chl derivatives under mild conditions.

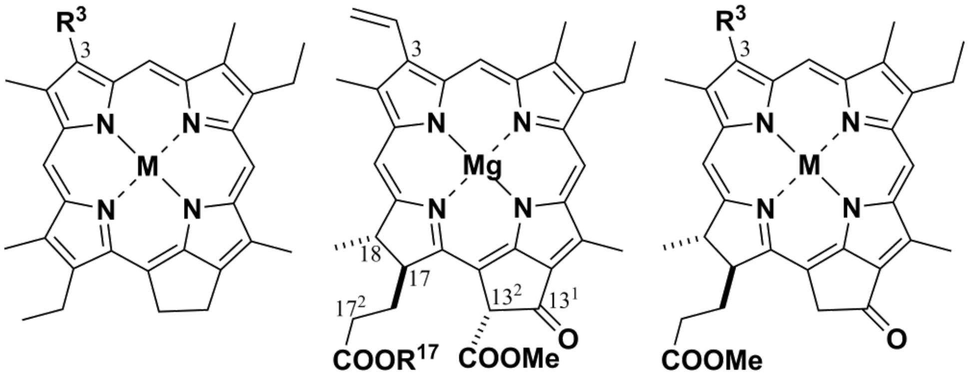

Figure. Molecular structures of sedimanetal Ni/VO-DPEPs (M = Ni/VO and R^3 = Et/Me/H), natural Chl-*a* (R^{17} = phytyl), and semi-synthetic Chl derivatives.

REFERENCES

1. M. Tahoun, C. T. Gee, V. E. McCoy, P. M. Sander, C. E. Müller, *RSC Adv.* **2021**, *11*, 7552–7563.
2. H. Fisher, A. Wunderer, *Justus Liebigs Ann. Chem.* **1938**, *533*, 230–254.
3. H. Tamiaki, S. Machida, K. Mizutani, *J. Org. Chem.* **2012**, *77*, 4751–4758.
4. H. Tamiaki, M. Xu, S. Machida, *Chem. Lett.* **2012**, *41*, 820–821.
5. M. Doi, H. Tamiaki, *Chem. Lett.* **2020**, *49*, 287–289.

Molecular Memories, Molecular Receptors and Catalysts Based on Supramolecular Conjugates of Porphyrinoids

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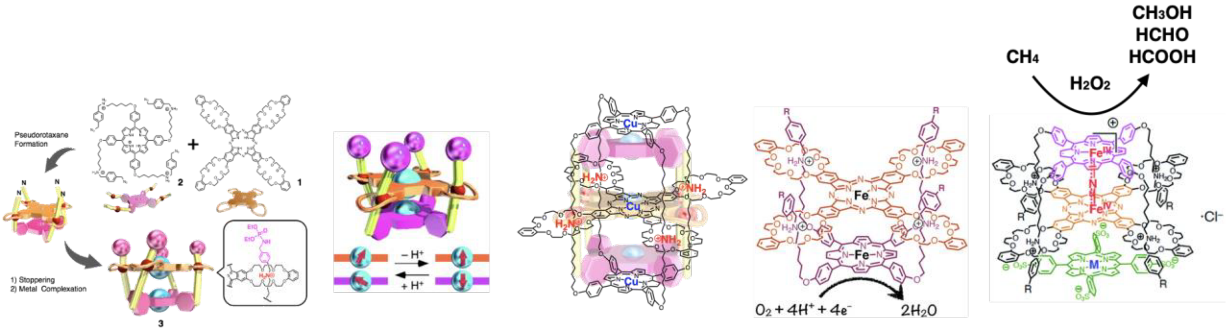
We have reported supramoleculary stacked arrays of porphyrins and phthalocyanines connected by four-fold rotaxanes **3**.[1-13] The four-fold rotaxane was prepared from tetradactyl porphyrin with four alkyl ammonium chains, **2**, and phthalocyanine with four peripheral crown ethers, **1**.[1,3] The mechanically interlocked supramolecule has potential to be functional molecular conjugates reflecting combination of their spatial restraint and structural flexibility. We have demonstrated a switchable spin-spin interaction between central metal ions [1], molecular accommodation with elevator motion of a multiply interlocked catenane [10], catalytic properties for oxygen reduction or methane oxidation reactions [9,12,13], and so on. Herein, we will report redox bistability of the four-fold rotaxane. The porphyrin in the conjugate showed two different redox equilibrium states at a given redox potential according to the direction of the potential scan.



REFERENCES

1. Y. Yamada, M. Okamoto, K. Furukawa, T. Kato, and K. Tanaka, *Angew. Chem. Int. Ed.,* **51**, 709 (2012).
2. Y. Yamada, N. Mihara, and K. Tanaka, *Dalton Trans.*, **42**, 15873 (2013).
3. Y. Yamada, N. Mihara, S. Shibano, K. Sugimoto, and K. Tanaka, *J. Am. Chem. Soc.*, **135**, 11505 (2013).
4. Y. Yamada, M. Okada, and K. Tanaka, *Chem. Commun.*, **49**, 11053 (2013).
5. Y. Yamada, T. Kubota, M. Nishio, and K. Tanaka, *J. Am. Chem. Soc.*, **136**, 6505 (2014).
6. Y. Yamada, S. Akine, K. Sugimoto, and K. Tanaka, *Chem. Euro. J.*, 22, 12371 (2016).
7. N. Mihara, Y. Yamada, S. Akine, K. Sugimoto, and K. Tanaka, *Chem. Commun.*, **53**, 2230 (2017).
8. N. Mihara, Y. Yamada, and K. Tanaka, *Bull. Chem. Soc. Jpn.*, **90**, 427 (2017).
9. N. Mihara, Y. Yamada, H. Takaya, Y. Kitagawa, S. Aoyama, K. Igawa, K. Tomooka, and K. Tanaka, *Chem. Euro. J.*, **23**, 7508 (2017).
10. Y. Yamada, R. Itoh, S. Ogino, T. Kato, and K. Tanaka, *Angew. Chem. Int. Ed.,* **56**, 14124 (2017).
11. N. Mihara, Y. Yamada, K. Furukawa, T. Kato, and K. Tanaka, *Dalton Trans.*, **47**, 7044 (2018).
12. N. Mihara, Y. Yamada, H. Takaya, Y. Kitagawa, K. Igawa, K. Tomooka, H. Fujii and K. Tanaka, *Chem. Eur. J.*, **25**, 3369 (2019).
13. Y. Yamada, K. Morita, N. Mihara, K. Igawa, K. Tomooka and K. Tanaka, *New J. Chem.*, **43**, 11477 (2019).

Porphyrin and phthalocyanine electron donors in molecular and organic-semiconductor charge transfer systems

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Porphyrin and phthalocyanine derivatives are popular electron donors in molecular donor-acceptor (DA) architectures and sensitizers in dye sensitized solar cells (DSSC) where they act also as electron donors. The photoinduced electron transfer (PET) reaction in molecular DA systems is under active investigation for a few decades already and these DA systems are one of the key benchmarks for understanding PET in molecular assemblies [1]. The electron transfer across the organic-semiconductor interface in DSSCs is another important PET reaction which is under intensive investigation for a few past decades as well [2]. However, these two PET take place in systems composed of very different classes of the electron donors and acceptors, and assembled in a very different types of the DA systems, and therefore typically, these two systems are considered separately despite both are focused on optimizing the efficiency of PET. The presentation will compare approaches used to optimize PET in molecular and hybrid systems, namely the charge separation in porphyrin/phthalocyanine-based molecular DA dyads [3, 4] and the cross-interface ET in organic-semiconductor structures similar to DSSC devices [5, 6]. A relatively new class of DA systems is semiconductor quantum dot – organic hybrids, in which the quantum dot takes an intermediate position between bulk semiconductors and organic molecules [7]. Along with the molecular engineering, the photophysics of PET will be compared from both experimental and theoretical points of view. The results of comparison will be used to discuss optimization of the solar applications of porphyrin and phthalocyanine derivatives.

REFERENCES

1. M. E. El-Khouly, E. El-Mohsnawy, S. Fukuzumi, *J. Photochem. Photobiol. C*, **2017**, *31*, 36-83.
2. C. Martín, M. Ziółek, A. Douhal, *J. Photochem. Photobiol. C*, **2016**, *26*, 1-30
3. R. Caballero, J. Calbo, J. Aragó, P. de la Cruz, E. Ortí, N. V. Tkachenko, F. Landa, *J. Mater. Chem. C*, **2021**, *9*, 10889-10898.
4. A. A. Strelnikov, A. S Konev, O. V. Levin, A. F. Khlebnikov, A. Iwasaki, K. Yamanouchi, N. V. Tkachenko, *J. Phys. Chem. B*, **2020**, *124*, 10899-10912.
5. K. Virkki, E. Tervola, M. Ince, T. Torres, N. V. Tkachenko, *R. Soc. Open Sci.*, **2018**, *5*, 180323.
6. K. Virkki, H. Hakola, M. Urbani, L. Tejerina, M. Ince, M. V. Martínez-Díaz, T. Torres, V. Golovanova, V. Golovanov, N. Tkachenko, *J. Phys. Chem. C*, **2017**, *121*, 9594–9605.
7. S. Mandal, L. George, N. Tkachenko, *Nanoscale*, **2019**, *11*, 862-869.

(SE)RR view of the active site architecture in DyPs governing their electrocatalysis

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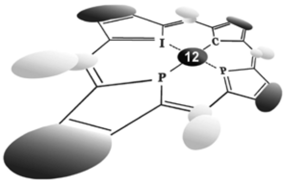
DyP-type peroxidases (DyPs) are heme b-containing enzymes that possess a number of unique properties in comparison with classical heme peroxidases: i) distinct amino acid sequence, catalytic residues and tertiary structure; ii) a broad substrate specificity, which includes anthraquinone-based and azo dyes, complex phenolic and non-phenolic molecules like kraft lignin, as well as carotenoids, phenols, aromatic sulphides and metal ions; iii) an unusually low optimal pH for the catalytic activity; and iv) still largely unexplored physiological role [1-3]. Resonance Raman spectroscopy (RR) demonstrates that multiple heme spin populations typically co-exist in DyPs in solution. Unlike in the case of classical peroxidases, a surprisingly high abundance of catalytically incompetent low spin heme population is observed in a number of DyPs, and tentatively related to an alternative physiological function [1].

We couple the insights on molecular details of DyP heme active site, elucidated by RR, with those obtained for the immobilized DyPs by surface-enhanced resonance Raman (SERR) spectro-electrochemistry, as a guide for biotechnological exploitation of DyPs, and in particular for development of H_2O_2 biosensors. In SERR spectro-electrochemistry the modified plasmonic metal that serves as a surface amplifier of spectroscopic signal simultaneously acts as a working electrode, revealing whether the native, solution properties have been preserved upon immobilization of the enzyme. We probe structure, redox potential and electro-catalytic activity towards H_2O_2 of a number of DyPs from different bacteria upon immobilization on biocompatible silver electrodes. While some immobilized DyPs outperform all currently existing peroxidase-based biosensors, including those that employ advanced materials (e.g. carbon nanotubes and nano-dots, ceramic and gold nanostructures), others fail to fulfil the essential requirements for the use in the immobilized state [2, 3]. Among the former is DyP from *P. putida* (PpDyP); the PpDyP based 3rd generation H_2O_2 biosensor shows superior sensitivity and shorter response times than other reported H_2O_2 biosensors [3]. In the light of our findings, we discuss in this talk the prerequisites that an immobilized DyP has to fulfill in order to be considered as a promising candidate for biotechnological applications, which can be assesses by SERR spectroelectrochemistry in a straightforward manner.

REFERENCES

1. Silveira, C. M., Moe, E., Fraaije, M., Martins, L. O., & Todorovic, S. (2020). Resonance Raman view of the active site architecture in bacterial DyP-type peroxidases. *RSC Advances*, *10* (19), 11095.
2. Zuccarello, L.; Barbosa, C.; Galdino, E.; Lončar, N.; Silveira, C.M.; Fraaije, M.W.; Todorovic, S. (2021) SERR Spectroelectrochemistry as a Guide for Rational Design of DyP-Based Bioelectronics Devices. *Int. J. Mol. Sci*. 22, 7998.
3. Barbosa, C., Silveira, C. M., Silva, D., Brissos, V., Hildebrandt, P., Martins, L. O., & Todorovic, S. (2020). Immobilized dye-decolorizing peroxidase (DyP) and directed evolution variants for hydrogen peroxide biosensing. *Biosensors and Bioelectronics*, 153, 112055.



Biopyrrin Pigments as Electron Reservoirs and Redox-Switchable Fluorophores

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Naturally occurring bipyrrin pigments are heme metabolites featuring three or two pyrrole rings and the characteristic pyrrolin-2-one termini of tetrapyrrolic bile pigments, such as biliverdin and bilirubin. Whereas linear tetrapyrroles enforce a helical geometry in metal complexes, the biopyrrin fragments coordinate as planar chelates and allow access to the metal center for additional ligands. Critically, these scaffolds maintain the ligand-based redox chemistry of many macrocyclic oligopyrroles (e.g., porphyrins, corroles) while avoiding irreversible degradation problems that characterize other linear oligopyrroles. [1] We discovered that the tripyrrin-1,14-dione scaffold coordinates multiple transition metals (e.g., Pd(II), Cu(II), Zn(II)) as a planar dianionic radical. [2-4] The resulting complexes, which are stable at room temperature and exposed to air, undergo reversible one-electron processes to access different redox states of the ligand system. The more compact propentdyopent pigments, which feature a dipyrrin-1,9-dione scaffold, [5] are also suitable to host unpaired electrons both in homoleptic and heteroleptic complexes. [6,7] Spectroelectrochemical and electron paramagnetic resonance (EPR) experiments indicate that the ligands act as electron reservoirs. Supported by computational analyses, our spectroscopic investigations document the stabilization of a diradical on a binuclear palladium dipyrrindione [8] as well as a redox-switchable boron difluoride complex. [9] Overall, the portfolio of properties revealed by our studies takes the tripyrrindione and dipyrrindione motifs of heme metabolites to the field of redox-active ligands, where they are positioned to offer new opportunities in catalysis, supramolecular systems, and molecular materials.

REFERENCES

1. Tomat, E.; Curtis, C. J. *Acc. Chem. Res.* **2021**, *54*, 4584–4594
2. Gautam, R.; Loughrey, J. J.; Astashkin, A. V.; Shearer, J.; Tomat, E. *Angew. Chem. Int. Ed.* **2015**, *54,* 14894
3. Gautam, R.; Astashkin, A. V.; Chang, T. M.; Shearer, J.; Tomat, E. *Inorg. Chem.* **2017**, *56*, 6755-6762
4. Gautam, R.; Petritis, S. J.; Astashkin, A. V.; Tomat, E. *Inorg. Chem.* **2018***, 57,* 15240-15246.
5. Tomat, E. *J. Porphyrins Phthalocyanines* **2019**, *23*, 1265-1272.
6. Gautam, R.; Chang, T. M.; Astashkin, A. V.; Lincoln, K. M.; Tomat, E. *Chem. Commun.* **2016**, *52,* 6585-6588
7. Curtis, C. J.; Tomat, E. *J. Porphyrins Phthalocyanines* **2020**, *24*, 112-120.
8. Curtis, C. J.; Astashkin, A. V.; Conradie, J.; Ghosh, A.; Tomat, E. *Inorg. Chem.* **2021**, *60*, 12457-12466
9. Gautam, R.; Petritis, S. J.; Tomat, E. *Eur. J. Inorg. Chem.* **2019***,* 68-72

Bioconjugates for enhanced cancer photodynamic therapy

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In the last two decades we have been committed to the development of novel third generation PSs for improved cancer photodynamic therapy (PDT), which include glycoderivatives, photoimmunoconjugates and photoactive (nano)formulations [1-3]. The main idea with these combinations is to offer novel photosensitisers (PSs) with high selectivity for cancer cells and consequently high PDT efficacy [4]. Actually, improving the efficacy of the photoactive drugs is one of the key innovation aspects that is indeed needed for the broad use of PDT [5]. PS bioconjugates and nanoformulations have been developed for drug target and for light-controlled $^1O_2$ and/or drug release [3-5]. Most of the examples that will be presented in this seminar comprise of the development of new targeted PSs: porphyrinoids (Por, Chls and Pcs) functionalized with monomeric and dendrimeric units of galactose (Gal) [1], monoclonal antibodies [2] and silica nanoparticles-PS formulations [3], in this case used on biomedical applications (figure 1). In light of the above, I will show our recent contributions on bioconjugated PSs, highlighting their synthetic preparation.

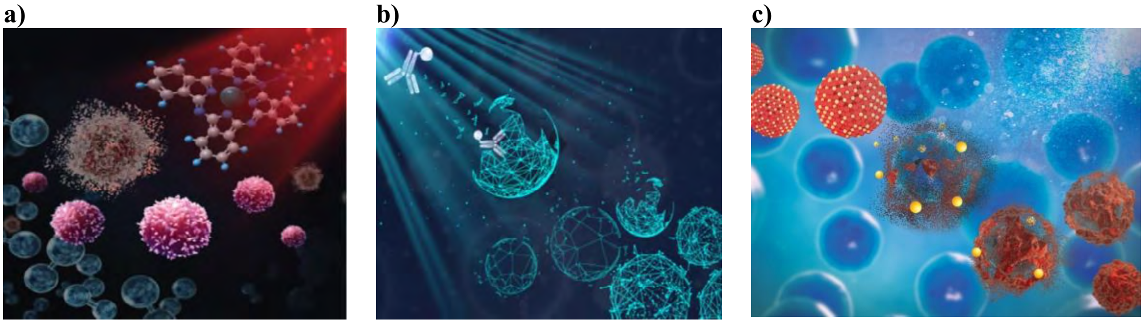

Figure 1. Example of: a) PS glycoderivatives; b) photoimmunoconjugates; c) silica nanoparticles-PS nanoformulations.

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REFERENCES

1. a) F. Figueira, *et al. JPP*, **2020**, 24, 330; b) J. T. Ferreira, *et al. Chem. Eur. J.,* **2020**, 26, 1789; c) P. M. R. Pereira, *et al. Mol. Pharm.,* **2020**, 17, 2145; d) M. Bispo, *et al. ChemPlusChem*, **2018**, 83, 855.
2. a) S. R. G. Fernandes, *et al. OBC*, **2019**, 17, 2579; b) B. Korsak, *et al. Int. J. Cancer*, **2017**, 141, 1478.
3. a) W. Borzecka, *et al. J. Mater. Chem. B.*, **2022**, 10, *in press*; b) W. Borzecka, *et al. Mater. Adv.,* **2021**, 2, 1613.
4. a) W. Fan, *et al. Chem. Rev.*, **2017**, 117, 13566; b) S. Singh, *et al. Chem. Rev.*, **2015**, 115, 10261.
5. a) J. Li, *et al. View*, **2021**, 20200121; b) V. Almeida-Marrero, *et al. Chem. Soc. Rev.,* **2018**, 47, 7369.

Towards PDT-MRI molecular theranostics: TEMPO-substituted phthalocyanines

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Theranostics combine an imaging agent and a therapeutic agent within the same scaffold, both agents being thus delivered at the same time and with the same biodistribution, which is useful to follow the therapeutic agent as well as the treatment outcome. Combination of MRI and PDT is expected to provide real-time monitoring of therapy. Organic radicals such as TEMPO-based MRI agents are expected to overcome Gd complexes' drawbacks which have detrimental nephrotoxicity [1]. Only a few MRI-PDT theranostics are reported [2], and even less with phthalocyanine [3] as the photosensitiser despite its well-known advantages [4].

Phthalocyanines with various numbers of TEMPO units have therefore been designed and synthesized. Preliminary assessment of their MRI and PDT potential will also be presented.

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REFERENCES

1. a) Rajca A, Wang Y, Boska, M, Paletta JT, Olankitwanit A, Swanson MA, Mitchell DG, Eaton SS, Eaton GR and Rajca S. *J. Am. Chem. Soc.*, 2012; **134:** 15724-15727. b) Rajca A, Wang Y, Boska, M, Paletta JT, Olankitwanit A, Swanson MA, Mitchell DG, Eaton SS, Eaton GR, and Rajca S. *J. Am. Chem. Soc.* 2014; **136:** 3318-3318.
2. Tekdas DA, Atilla D and Ahsen V. *In Imaging in Photodynamic Therapy*, 2017, 233-270, CRC Press.
3. Tekdaş DA, Garifullin R, Şentürk B, Zorlu Y, Gundogdu U, Atalar E, Tekinay AB, Chernonosov AA, Yerli Y, Dumoulin F, Guler MO, Ahsen V and Gürek, A G. *Photochem. Photobiol.*, 2014; **90:** 1376-1386.
4. Lo PC, Rodríguez-Morgade, MS, Pandey RK, Ng DK, Torres, T and Dumoulin, F. *Chem. Soc. Rev.*, 2020; **49:** 1041-1056.

ORALS

Elucidation of Mechanisms for Catalytic Reaction of Nitric Oxide Reductases by Time-resolved Techniques

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Nitric oxide (NO) plays diverse and pivotal roles in various biological processes although NO shows high cytotoxicity. In microbial denitrification process, a form of anaerobic respiration, in which nitrate or nitrite is reduced to dinitrogen in a step-wise manner, NO is produced as an intermediate product. To eliminate the cytotoxic effect of NO, microorganisms utilize NO reductase (NOR), which decomposes two NO molecules to nitrous oxide (N_2O) using two protons and electrons ($2NO + 2H^+ + 2e^- \rightarrow N_2O + H_2O$). There are two types of NORs in microbial denitrification; one is soluble NOR (P450nor) observed in fungi and the other is bacterial membrane-integrated NOR (cNOR). Although the extensive efforts for understanding the mechanisms for NO reduction by NORs, the reaction mechanisms are still in debate mainly due to the limited information on the short-lived reaction intermediates. In this study, we utilized caged NO (BNN5) [1], which releases NO within micro-second time domain upon UV illumination, as a trigger for the NOR reaction, and applied it for time-resolved spectroscopic and structural analyses for the reaction intermediates. The time-resolved techniques combined with caged NO provided invaluable information on the reaction mechanisms both in P450nor and cNOR.

1) P450nor. P450nor catalyzes NO reduction at a thiolate-coordinated heme active center. The resting ferric enzyme reacts with one NO molecule to form ferric NO-bound species, followed by a hydride transfer from NADH to produce a short-lived reaction intermediate called intermediate *I* [2]. Then, intermediate *I* reacts with second NO molecule to produce N_2O. Because the structural characterization of intermediate *I* is a key to understand the reaction mechanism in P450nor, we aimed to determine the atomic and electronic structures of intermediate *I*. The time-resolved X-ray crystallography using X-ray free electron laser (XFEL) and caged NO gave the molecular structure of intermediate *I* [3-4]. In addition, the time-resolved IR analysis showed that the N-O stretching frequency (νNO) of intermediate *I* was detected at 1290 cm^{-1} [4]. Using these structural information, we can conclude that intermediate *I* is a Fe^{3+}-$NHO^{\bullet-}$ species. Thus, NO reduction by P450nor proceeds via radical coupling reaction.

2) cNOR. The active site of cNOR consists of heme and non-heme iron (Fe_B). Since the NO reduction reaction by cNOR is finished within milli-second time domain, the reaction intermediates were poorly understood. The time-resolved visible absorption measurement using caged NO showed that the fully reduced cNOR produced N_2O via three steps [5]. In the 1st step, one NO molecule binds to reduced cNOR to form a NO-bound species in ~5 μs. The NO-bound species is converted to an other chemical species without protonation and second NO binding at ~100 μs (2nd step). Finally, the second NO biding and the protonation to the reaction intermediate yield N_2O in the milli-second 3rd step. These findings allow us to propose a revised mechanism for the NO reduction reaction by cNOR [5].

REFERENCES

1. Namiki et al. *J. Am. Chem. Soc.* **119**, 3840-3841 (1997).
2. Shiro et al. *J. Biol. Chem.* **270**, 1617-1623 (1995).
3. Tosha et al. *Nat. Commun.* **8**, 1584 (2017).
4. Nomura et al. *Proc. Natl. Acad. Sci. USA*, **118**, e2101481118 (2021).
5. Takeda et al. *Bull. Chem. Soc. Jpn.* **93**, 825-833 (2010).

Preparation and Property of Free-Base Corroles with No Substituents at *meso* Positions[1]

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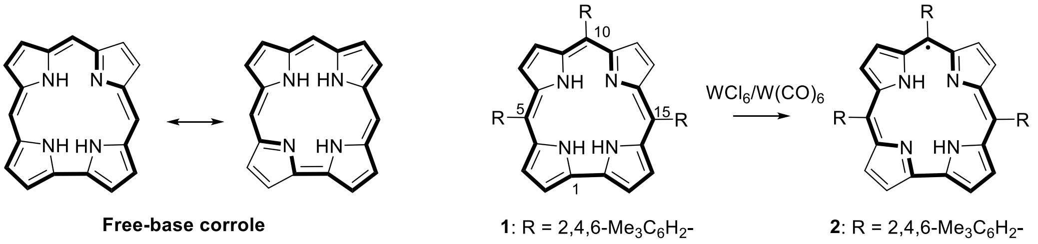
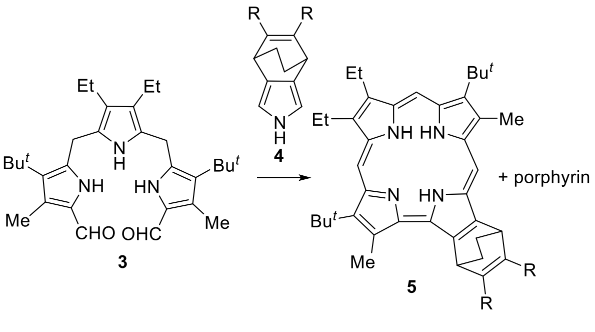
The tetrapyrrolic corrole skeleton is found in the life of pigments as corrin (vitamin B_{12}), in which only 13 core atoms are sp2-hybridized and others are sp3-hybridized. Preparation of corroles with all sp2-hybridized atoms have been extensively investigated by many groups due to their importance not only for dyes but also for the use of non-innocent ligands. Preparation of such free-base corroles, however, is not so easy due to the steric repulsion of inner three proton atoms and/or easily oxidizable nature of 18π-electron system incorporated with three electron-rich pyrrole units. Stable neutral radical **2** was reported to be formed on the oxidation of trimesitylcorrole **1** with WCl_6/$W(CO)_6$.[2] Corroles with bulky and/or electron-deficient aryl substituents at three *meso* positions are commonly employed for many investigations. We encountered the formation of corroles with no substituents at the meso positions in the [3+1]-porphyrin and [3+2]-sapphyrin syntheses. In this session, we will discuss about the details in the reactions and properties of the corrole products.



Free-base corrole   **1**: R = 2,4,6-$Me_3C_6H_2$-   **2**: R = 2,4,6-$Me_3C_6H_2$-

Figure 1. Free base corroles with 18π- or 17π-electron circuits

The [3+1]-porphyrin synsthesis with tripyrrane-dicarbaldehyde **3** and BCOD-fused pyrrole **4a** (R = H) was carried out (CH_2Cl_2/EtOH) in the presence of TFA to give porphyrin and corrole **5a** in the yields of 7-25% and 9-15%, respectively. Similar results were obtained in the case of fluoranthoBCOD-fused pyrrole **4b**. The BCOD unit of corroles **5** was converted by the retro-Diels-Alder reaction and π-system enlarged corroles were successfully obtained.



REFERENCES

1. Financial support by NSFC-JSPS Joint program (JPJSBP 120197420)
2. Schweyen, K. Brandhorst, R. Wicht, B. Wolfram, and M. Brçring, Angew. Chem. Int. Ed. 2015, 127, 8331-8334.

Inducing magnetism in one-dimensional porphyrinoid polymers synthesized via oxidative coupling of isopropyl substituents on a metal surface

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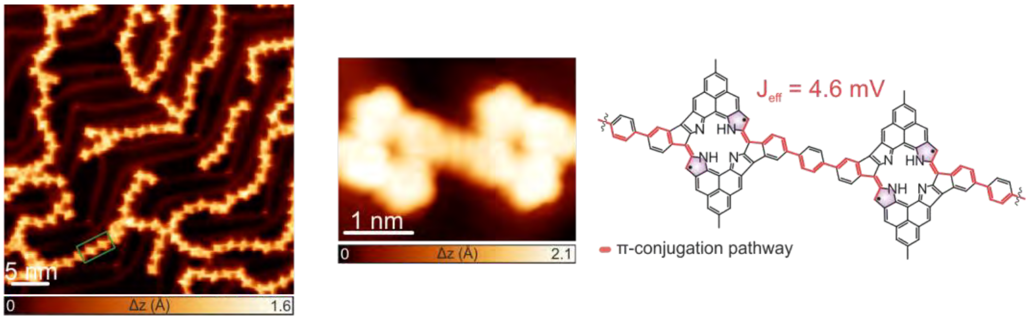
The synthesis of novel polymeric materials attracts widespread interest from several scientific fields in view of their extraordinary variety of functional properties. The vast majority of such polymers present a closed-shell ground state and only recently, as the result of improved synthetic strategies and spectroscopic techniques, the engineering of open-shell porphyrinoid polymers has been achieved [1,2]. Here, we present a combined strategy toward the fabrication of one-dimensional porphyrinoid-based polymers homocoupled via surface-catalyzed [3 + 3]cycloaromatization of isopropyl substituents on Au(111). Scanning tunneling microscopy and noncontact atomic force microscopy describe the thermal-activated intra- and intermolecular oxidative ring closure reactions as well as the controlled tip-induced hydrogen dissociation from the porphyrinoid units. In addition, scanning tunneling spectroscopy measurements, complemented by computational investigations, reveal the open-shell character, i.e. antiferromagnetic singlet ground state of the formed polymers, characterized by singlet-triplet inelastic excitations. Our approach sheds light on the crucial relevance of the π-conjugation in the correlations between spins expanding the on-surface synthesis toolbox and opening new avenues toward the synthesis of innovative functional nanomaterials with prospects in carbon-based spintronics [3].



REFERENCES

1. Sun, Q. et al. Bottom-up Fabrication and Atomic-Scale Characterization of Triply Linked, Laterally π-Extended Porphyrin Nanotapes. ACIE 2021, 60, 16208–16214.
2. Wang, S. et al. Realization of Quantum Nanomagnets in Metal-Free Por-phyrins; preprint; In Review, 2021.
3. Song, S. et al. On-surface synthesis of graphene nanostructures with π-magnetism. Chemical Society Reviews 2021.

The intriguing story of bis-porphyrins in chemical sensors

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The preparation of porphyrin dimers and oligomers covalently linked by rigid spacer groups is currently a prolific area of research. The exploration of their properties in fields such as molecular electronics, chemical sensors, energy storage, etc., has demonstrated that constrained coplanarity is preferable. Red-shifted absorption bands in these compounds in comparison with monomers and other tetrapyrrolic cycles manifest a contraction of the HOMO-LUMO band gap towards the region assigned to semiconductors. Therefore, these porphyrins dimers have been regarded as potential electron-donating components in artificial systems for gas sensing devices.

The preferential technique of immobilization of bis-porphyrins employed in our research group is the Langmuir-Blodgett methods together with the Langmuir-Schäfer modification. Ease of deposition and good control over multilayer thickness coupled with the chance of tailoring organic molecules to obtain desired physical properties mark these films out as serious alternatives of the future in devices applications of today.

We have investigated LB films of porphyrin dimers which have the two macrocycles (metallated or free bases) connected by different bridges and found that the central metals and the bridges play an important influence on the behaviour of the multilayers as the active part in gas-sensors. The different performances of the bisporphyrins will be discussed with the proposal of appropriate rationales.

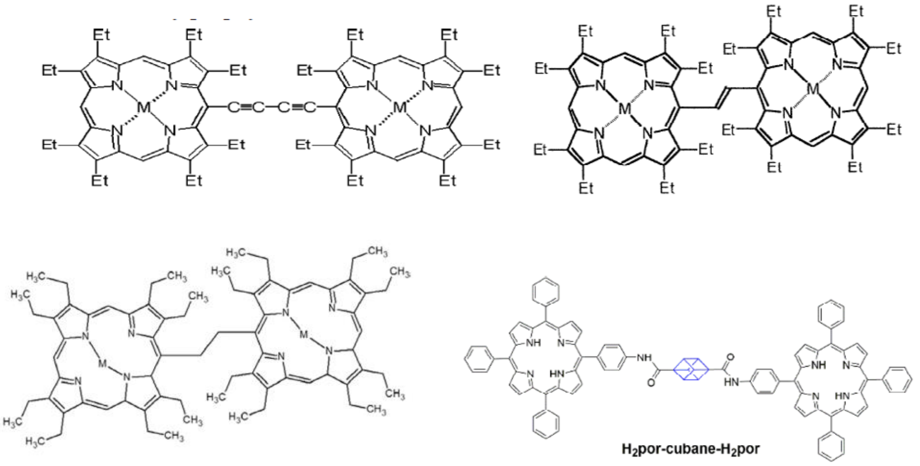

Figure 1. General structures of some investigated bis-porphyrins

Transient EPR Studies of Main Group Element in Porphyrin-Based Donor Acceptor Complexes

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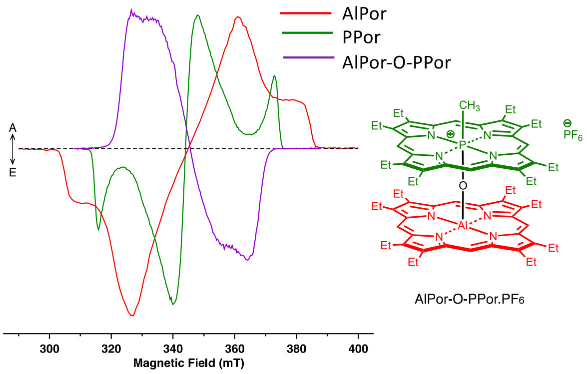
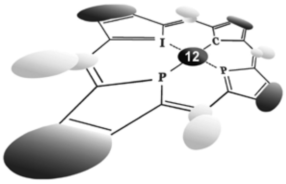
The main group element porphyrins exhibit properties that make them ideal candidates for the photosensitizers donor acceptor complexes.[1,2] In particular, the Al(III) and P(V) are of interest because of their ability to form axial covalent and coordination bonds and because their redox potentials can be tuned over a wide range. We have been investigating various dyads and triads based on these compounds using time resolved EPR methods and density functional theory calculations. The electron spin polarization patterns obtained from a variety of triads show that electron transfer between axially bound donors and acceptors occurs and in favourable cases allows details of the electron transfer pathway and spin selectivity to be determined. The ability of these porphyrin to form axial bonds also makes it possible to construct co-facial dimers, which serve as models for the primary donors in photosynthetic reaction centres. The transient EPR data of a heterodimer comprised of P(V)-porphyrin and Al(III)-porphyrin in which the two porphryins are in close contact shows evidence of charge transfer character in the lowest excited triplet state[3,4]. The triplet state is found to be populated by intersystem crossing and the ISC rates to the zero-field sublevels are altered in the dimer as a result of the interaction between the porphyrins. The solvent dependence of the charge transfer character leads to a decrease in the value of the zero-field splitting parameter *D* as the polarity of the solvent increases.



REFERENCES

1. P.K. Poddutoori, G.N. Lim, A.S. Sandanayaka, P.A. Karr, O. Ito, F. D'Souza, M. Pilkington, and A. van der Est (2015) *Axially Assembled Photosynthetic Reaction Center Mimics Composed of Tetrathiafulvalene, Aluminum (III) Porphyrin and Fullerene Entities*, Nanoscale 7, 12151-12165
2. P.K. Poddutoori, Yu.E. Kandrashkin, C.O. Obondi, F. D'Souza, and A. van der Est (2018) *Triplet Electron Transfer and Spin Polarization in a Palladium Porphyrin–Fullerene Conjugate* Phys. Chem. Chem. Phys. 20, 28223–28231.
3. B.J. Bayard, N. Zarrabi, S. Seetharaman, P. Karr, A. van der Est, F. D'Souza, P. K. Poddutoori (2021) Photoinduced energy and electron transfer in a cofacial aluminum(III) porphyrin – Phosphorus(V) porphyrin heterodimer J. Photochem. Photobiol. 8 100069.
4. N. Zarrabi, B.J. Bayard, S. Seetharaman, N. Holzer, P. Karr, S. Ciuti, A. Barbon, M. Di Valentin, A. van der Est, F. D'Souza, P.K. Poddutoori (2021) *A charge transfer state induced by strong exciton coupling in a cofacial μ-oxo-bridged porphyrin heterodimer*. Phys. Chem. Chem. Phys. **23**, 960-970



New insights into B-class dye-decolorizing peroxidases: tracing radical sites with electron paramagnetic resonance

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The catalytic activity of dye-decolorizing peroxidases (DyPs) towards bulky substrates is in strong contrast to their sterically restrictive active site. In two of the three known subfamilies (A- and C/D-type DyPs) catalytic protein radicals at surface exposed sites, which are connected to the heme cofactor by electron transfer path(s), have been identified. In contrast, no radicals apart from the Compound I porphyrin radical were reported in B-type DyPs upon reaction with H_2O_2. Surprisingly, we observed two persistent organic radicals in the resting state B-type *Klebsiella pneumoniae* dye-decolorizing peroxidase (*Kp*DyP) using multi-frequency electron paramagnetic resonance (EPR) spectroscopy [1, 2]. Based on a comprehensive mutational and EPR study of computationally-predicted tyrosine and tryptophan variants in *Kp*DyP, we demonstrate the formation of tyrosyl radicals (Y247 and Y92) and a radical stabilizing Y-W dyad between Y247 and W18 in *Kp*DyP, which are unique to enterobacterial B-type DyPs [2]. Y247 is connected to Y92 by a hydrogen bonding network, is solvent accessible in simulations and is involved in 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) oxidation. This suggests the existence of long-range electron path(s) in B-type DyPs. The mechanistic and physiological relevance for the reaction mechanism of B-type DyPs will be discussed in detail.

REFERENCES

1. V. Pfanzagl, K. Nys, M. Bellei, H. Michlits, G. Mlynek, G. Battistuzzi, K. Djinovic-Carugo, S. Van Doorslaer, P. G. Furtmüller, S. Hofbauer, C. Obinger, *J. Biol. Chem*., **2018**, *293*, 14823-14838.
2. K. Nys, P. G. Furtmüller, C. Obinger, S. Van Doorslaer, V. Pfanzagl, *Biochemistry*, **2021**, *60*, 1226-1241

Diketopyrrolopyrrole-porphyrin arrays as NIR emitters and NIR-activated photosensitizers

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Porphyrins are attractive photoactive molecules widely used in energy conversion structures, linear and non-linear materials for optoelectronics and biomedical research.

Extending the porphyrin π-system by conjugation with proper units is an advantageous tool to control and finely tune the HOMO-LUMO gap of porphyrin-based arrays and to modulate their absorption and emission features. This approach is particularly interesting to develop systems with absorption and/or luminescence in the near-infrared (NIR) spectral region, promising for biomedical (imaging, sensing), optoelectronic and energy conversion applications [1]. The extended conjugation, moreover, favours non-linear optical properties such as two-photon (TP) absorption [2], useful for TP-activated photodynamic therapy with increased 3D spatial resolution and reduced tissue damaging.

In this contest, in collaboration with the group of Prof. V. Heitz (University of Strasbourg), we recently investigated several diketopyrrolopyrrole-porphyrin conjugates, where the arrays are composed by monomeric or dimeric porphyrin systems conjugated to diketopyrrolopyrrole units. These systems have been proven to be promising photosensitizers for one- and two-photon photodynamic therapy and efficient NIR emitters [3-5], with potential as active materials in luminescent solar concentrators. Further combination of the conjugates with selected functional units allowed to achieve MRI contrast [6, 7] or tumour targeting [8], leading to promising systems for theranostics and tumour-targeted photodynamic therapy. Detailed investigation of the photophysical properties of the arrays allowed to characterize singlet and triplet excited states features and to understand structural-property relationships, important to optimize the design of efficient NIR-responsive materials.

REFERENCES

1. A. Barbieri, E. Bandini, F. Monti, V. K. Praveen, N. Armaroli, *Top. Curr. Chem.*, **2016**, *374,* 47; T. Tanaka, A. Osuka, *Chem. Soc. Rev.,* **2015**, *44*, 943.
2. F. Bolze, S. Jenni, A. Sour, V. Heitz, *Chem. Commun.*, **2017**, *53*, 12857; M. Pawlicki, H. A. Collins, R. G. Denning, H. L. Anderson, *Angew. Chem. Int. Ed.*, **2009**, *48*, 3244.
3. J. Schmitt, V. Heitz, A. Sour, F. Bolze, H. Ftouni, J.-F. Nicoud, L. Flamigni, B. Ventura, *Angew. Chem. Int. Ed.*, **2015**, *54*, 169.
4. Md. M. Alam, F. Bolze, C. Daniel, L. Flamigni, C. Gourlaouen, V. Heitz, S. Jenni, J. Schmitt, A. Sour, B. Ventura, *Phys.Chem.Chem.Phys.*, **2016**, *18*, 21954.
5. J. Schmitt, V. Heitz, S. Jenni, A. Sour, F. Bolze, B. Ventura, *Supramol. Chem.*, **2017**, *29(11)*, 769.
6. J. Schmitt, V. Heitz, A. Sour, F. Bolze, P. Kessler, L. Flamigni, B. Ventura, C. S. Bonnet, É. Tóth, *Chem. Eur. J.*, **2016**, *22*, 2775.
7. S. Jenni, F. Bolze, C. S. B., A. Pallier, A. Sour, É. Tóth, B. Ventura, V. Heitz, *Inorg. Chem.* **2020**, *59*, 14389−14398.
8. S. Jenni, A. Sour, F. Bolze, B. Ventura, V. Heitz, *Org. Biomol. Chem.*, **2019**, *17*, 6585.

Nanoparticle Encapsulated Porphyrinic Photosensitizers – Insights Gained from NMR Spectroscopy

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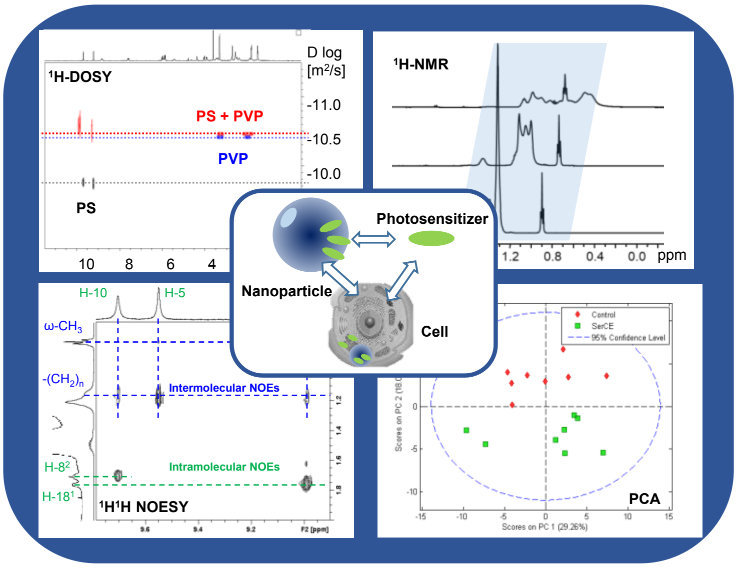
The association of porphyrinic photosensitizers (PSs) with nano-sized particles for drug delivery has become an essential part in their application in photodynamic therapy (PDT). In these systems the nanoparticles fulfil several functions like enhancing the solubility, bioavailability and stability of the encapsulated PS as well as maintaining the photophysical properties, improve targeting via functionalization of the particles and enhancing overall PDT efficiency. The design and prediction of suitable efficient carrier systems requires a thorough understanding of how the PSs interact with their carrier and what their fate is in physiological environments and inside the cell.
While optical methods are essential and often the first method of choice for characterizing PSs, a substantial amount of complementary aspects can be learnt from NMR spectroscopy. The different NMR techniques can provide insights into PS-nanoparticle interactions with atomic resolution. In addition, dynamic properties that determine the pharmacokinetic properties of PS-carrier systems can be well studied by NMR diffusometry and relaxometry [1, 2]. Moreover, induced changes onto the immediate molecular environment as well as metabolic responses in living cells provide further aspects that can be addressed by NMR.
In this presentation, an overview of the various applications to porphyrin-nanoparticle systems will be given along with specific examples for porphyrins physically entrapped into polymeric carriers and their interactions with cells.



REFERENCES

1. Gjuroski I., Furrer J., Vermathen M. *Molecules* 26 (2021) 1942. doi.org/10.3390/molecules26071942
2. Franconi F., Lemaire L., Gimel J.-C., Bonnet S., Saulnier P. *J. Controlled Release* 337 (2021) 155-167. doi.org/10.1016/j.jconrel.2021.07.025

Non-Linear Spectroscopy of π-Extended Porphyrins

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Aromatically π-extended porphyrins possess exceptionally intense one-photon (1P) and sometimes two-photon (2P) absorption bands, presenting interest for construction of optical imaging probes and photodynamic agents. Over the past two decades we developed synthetic approaches to various types of π-extended porphyrins and explored Pd(II) and Pt(II) complexes as functional elements for phosphorescent probes for a broad range of oxygen imaging applications: from fiber-optic oximetry to different forms of *in vivo* imaging, including the newly developed optical tomographic method termed Cherenkov-Excited Luminescence Scanned Imaging (CELSI) [1]. At the same time, Pd(II) and Pt(II) complexes of porphyrins extended by way of fusion with aromatic fragments containing electron-withdrawing groups [2], such as in fully D_{4h}-symmetric tetraarylphthalimidoporphyrins (TAPIP) [3] and D_{2v}-symmetric diarylphthalimidoporphyrins [4], proved to be extremely potent two-photon-absorbers, and hence rapidly became popular as probes for two-photon phosphorescence lifetime micrscopy (2PLM) of oxygen [5] - a technique with broad applications in neurosceince, stem cell biology, immunology and other areas of biological research. In this presentation we will discuss the interplay between symmetric and asymmetric π-extension of the porphyrin macrocycle and its non-linear optical properties on the fundamental level, focusing on two-photon and the most recently studied three-photon absoprtion [5]. In practical sense, exploring higher order non-linearity should enable deeper imaging with higher resolution in intact biological tissues, such imaging of metabolic activity in live brain.

REFERENCES

1. Cao, X.; Allu, S. R.; Jiang, S. D.; Jia, M. Y.; Gunn, J. R.; Yao, C. P.; LaRochelle, E. P.; Shell, J. R.; Bruza, P.; Gladstone, D. J.; Jarvis, L. A.; Tian, J.; Vinogradov, S. A.*; Pogue, B. W.* *Nature Commun.* **2020**, *11*, 9.
2. Esipova, T. V.; Rivera-Jacquez, H. J.; Weber, B.; Masunov, A. E.; Vinogradov, S. A. *J. Am. Chem. Soc.* **2016**, *138*, 15648.
3. Esipova, T. V.; Rivera-Jacquez, H. J.; Weber, B.; Masunov, A. E.; Vinogradov, S. A. *J. Phys. Chem. A.* **2017**, *121*, 6243.
4. Allu, S. R.; Ravotto, L.; Troxler, T.; Vinogradov, S. A. *J. Phys. Chem. A.* **2021**, *125*, 2977.
5. Esipova, T. V.; Barrett, M. J. P.; Erlebach, E.; Masunov, A. E.; Weber, B.; Vinogradov, S. A. *Cell Metabolism* **2019**, *29*, 736.
5. Ravotto, L.; Meloni, S. L.; Esipova, T. V.; Masunov, A. E.; Anna, J. M.; Vinogradov, S. A. *J. Phys. Chem. A* **2020**, *124*, 11038.

Spectroscopy, Photophysics, and Tautomerism in Porphycenes

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Electronic absorption and magnetic circular dichroism (MCD) spectra of porphyrins and porphycenes react differently to peripheral substitution. The intensity pattern remains similar for porphycenes, but it can change dramatically for porphyrins. This is a consequence of different relative energy gaps in the two pairs of frontier π orbitals. Porphyrins can be classified as “soft” (ΔHOMO ≈ ΔLUMO), whereas porphycenes are “hard” chromophores (ΔHOMO << ΔLUMO).[1]

Absorption spectra of porphycene derivatives vary in an approximately linear fashion with the number of substituents.[2, 3] In contrast, the additivity may break down completely with respect to photophysics.[3, 4] For instance, isomeric porphycenes doubly substituted at the *meso* positions can fluorescence with completely different yields, depending on whether the substituents are located next to each other (9,10-substitution pattern) or on the opposite sides of the molecule (9,19- and 9, 20- substitutions).

We have demonstrated that huge variations in fluorescence intensity can be correlated with the dimensions of the inner macrocycle cavity, which, in turn, determine the strength of the intramolecular hydrogen bonds.[4] Delocalization of the inner protons has been proposed as the crucial factor responsible for the photophysical behaviour. This model is supported by growing evidence, obtained from studies in ensemble [5-6] and single molecule [7-8] regimes, which indicates the dominant role of tunnelling in tautomerization of porphycenes in different environments.

REFERENCES

1. Waluk J, Müller M, Swiderek P, Köcher M, Vogel E, Hohlneicher G, Michl, J. *J. Am. Chem. Soc.* 1991, *113*, 5511.
2. Kijak M, Nawara K, Listkowski A, Masiera N, Buczyńska J, Urbańska N, Orzanowska G, Pietraszkiewicz M, Waluk J. *J. Phys. Chem. A* 2020, *124*, 4594.
3. Listkowski A, Kharchenko A, Ciąćka P, Kijak M, Masiera N, Rybakiewicz R, Luboradzki R, Fita P, Waluk J. *ChemPlusChem* 2020, *85*, 2197.
4. Listkowski A, Masiera N, Kijak M, Luboradzki R, Leśniewska B, Waluk J. *Chem. Eur. J.* 2021, *27*, 6324.
5. Kasprzycki P, Kopycki P, Listkowski A, Gorski A, Radzewicz C, Birch D J S, Waluk J, Fita. P. *Phys. Chem.Chem.Phys.* 2020, 22, 17117.
6. Ciąćka P, Fita P, Listkowski A, Radzewicz C, Waluk J. *J. Phys. Chem. Lett.* 2016, *7*, 283.
7. Koch M, Pagan M, Persson M, Gawinkowski S, Waluk J, Kumagai T. *J. Am. Chem. Soc.* 2017, *139,* 12681.
8. Piatkowski L, Schanbacher C, Wackenhut F, Jamrozik A, Meixner A J, Waluk J. *J . Phys. Chem. Lett.* 2018, *9*, 1211.

Pi-Extended Porphyrins Fused with Five-,Six, and 8-Membered Rings: Synthesis, Characterization and Property Studies

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Largely π-extended structures represent one most fascinating yet very challenging frontiers in chemistry and materials science. Incorporating both porphyrins and polycyclic aromatic hydrocarbons to obtain largely π-extended multichromophoric systems is especially attractive as the resulted largely π-extended systems are reminiscent of "nanographenes" doped with heteroatoms.[1, 2] Several new synthetic methods to fuse different type of aromatic rings to the porphyrin periphery at the β, β-positions have been developed in our laboratory in the past two years. Using these methods, a number of novel π-extended porphyrin systems with fused 5- and 6-membered rings including pentacene-, pentaquinone-, acenaphtho[1,2-*b*] pentacene- and 12*H*-benzo[*f*]benzo[4,5]imidazo[2,1-*a*]isoindole-fused porphyrins have been designed and prepared.[3-6] Nickel porphyrin-fused pentacenes demonstrated unusual stability. Investigation of the abnormal stability using femtosecond transient absorption technique suggested nickel porphyrin centered photo-events leading to a short-lived intermediate charge transfer state, consequently blocking the photodegradation pathways of pentacene.[3] Unsymmetrical pentacene-fused molecular systems exhibited broad and intense near-IR absorptions in the 1800-2200 nm range for both radical cation and radical anions, illustrating the exceptional ability of these pentacene-fused systems to accommodate both positive and negative charges.[5] These largely π-extended molecular systems displayed unusual UV-Vis absorption patterns and rich redox chemistry with up to 8 observable redox states.

REFERENCES

1. M. Stepien, E. Gonka, M. Zyla and N. Sprutta, *Chem Rev*, 2017, **117**, 3479-3716.
2. A. Narita, X. Y. Wang, X. Feng and K. Mullen, *Chem Soc Rev*, 2015, **44**, 6616-6643.
3. Y. Hu, M. B. Thomas, W. A. Webre, A. Moss, R. G. W. Jinadasa, V. N. Nesterov, F. DQSouza and H. Wang, *Angew. Chem. Int. Ed.*, 2020, **59**, 20075-20082.
4. L. Jiang, J. T. Engle, R. A. Zaenglein, A. Matus, C. J. Ziegler, H. Wang and M. J. Stillman, *Chem. Eur. J.*, 2014, **20**, 13865-13870.
5. A. Moss, D. Nevonen, V. Nemykin and H. Wang, *unpublished result*.
6. A. Moss, Y. W. Jang, F. D'Souza and H. Wang, *unpublished result*.

The metalation of the corrin ring

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The careful and precise insertion of cobalt into the corrin ring moiety of cobalamin is a key and often limiting step in its biogenesis (1). For the aerobic synthesis of the corrin macrocycle cobalt is added at a relatively late stage in the biosynthetic pathway, with the metal being added to an intermediate called hydrogenobyrinic acid *a,c*-diamide. The enzyme that mediates this cobalt-insertion step is composed of three subunits termed CobN, S and T, and is related to the magnesium chelatase system associated with chlorophyll biosynthesis. The enzyme complex requires ATP for activity and under physiological conditions it also requires the cobalt to be delivered by a chaperone called CobW (2). We have now characterised several cobaltochelatase complexes, which not only highlight some degree of variance with respect to substrate preference but also reflect differences in control. Our work on the cobaltochelatases required the construction of bacterial strains that produced high levels of metal-free corrin-based substrates, which have also served another purpose as acting as material that can be used for the chemical insertion of different metal ions to generate a suite of different corrin-metal analogues that have been converted into a range of metal-substituted cobalamins or metbalamins (3-6).

REFERENCES

1. Warren, M. J., Raux, E., Schubert, H. L. and Escalante-Semerena, J. (2002) The biosynthesis of adenosylcobalamin (vitamin B$_{12}$). *Natural Product Reports* 19 (4), 390-412.
2. Young TR, Martini MA, Foster AW, Glasfeld A, Osman D, Morton RJ, Deery E, Warren MJ, Robinson NJ (2021) Calculating metalation in cells reveals CobW acquires CoII for vitamin B12 biosynthesis while related proteins prefer ZnII. *Nat Commun.* 12(1):1195. doi: 10.1038/s41467-021-21479-8.
3. Widner FJ, Lawrence AD, Deery E, Heldt D, Frank S, Gruber K, Wurst K, Warren MJ, Kräutler B (2016) Total Synthesis, Structure and Biological Activity of Adenosylrhodibalamin - the Nonnatural Rhodium Homologue of Coenzyme B$_{12}$. *Angew. Chem. Int. Ed.* 55(37):11281-6.
4. Kieninger C, Deery E, Lawrence A, Podewitz M, Wurst K, Nemoto-Smith E, Widner FJ, Baker JA, Jockusch S, Kreutz CR, Liedl KR, Gruber K, Warren MJ, Kräutler B (2019) The Hydrogenobyric Acid Structure Reveals the Corrin Ligand as an Entatic State Module Empowering B$_{12}$-Cofactors for Catalysis. *Angew Chem Int Ed Engl*. 58(31):10756-10760.
5. Kieninger C, Baker JA, Podewitz M, Wurst K, Jockusch S, Kreutz CR, Lawrence A, Deery E, Gruber K, Liedl KR, Warren MJ, Kräutler B (2019) Zinc Substitution of Cobalt in Vitamin B12 - Zincobyric acid and Zincobalamin as Luminescent Structural B12-Mimics. *Angew Chem Int Ed Engl.* 58(41):14568-14572.
6. Kieninger C, Wurst K, Podewitz M, Stanley M, Deery E, Lawrence AD, Liedl KR, Warren MJ, Kräutler B (2020) Replacement of the Cobalt Center of Vitamin B12 by Nickel: Nibalamin and Nibyric Acid Prepared from Metal-Free B12 Ligands Hydrogenobalamin and Hydrogenobyric Acid. *Angew Chem Int Ed Engl.* 59(45):20129-20136.

Understanding energy conversion in molecular (photo)electrocatalysis through operando vibrational spectroelectrochemistry

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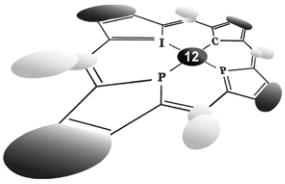
Molecularly defined (photo)electrocatalysts have great potential to perform important energy conversion reactions with high efficiency and selectivity. A particular advantage is their modular design, which allows their reactivity to be tailored to a specific reaction. However, to advance their rational development, a deep mechanistic understanding of the catalytic reactions is required. In situ vibrational spectrochemistry, in particular confocal Raman and infrared absorption spectroscopy, is an extremely powerful method to gain deep insights into the structure and reactivity of electrode-immobilized molecular catalytic systems under operando conditions [1]. In my talk, selected research examples will be used to present the different aspects and features of (photo)electrocatalysis that can be visualized using vibrational spectrochemistry. The target systems presented include porphyrin- and phthalocyanine-based systems for electrocatalytic oxygen and CO_2 reduction [2, 3] as well as conjugated acetylene polymers for photoelectrocatalytic hydrogen and oxygen evolution [4]. Spectra evaluation under operando conditions allowed us to monitor photoinduced charge separation, redox changes and ligand binding within these catalysts. We furthermore identified reaction intermediates and could demonstrate synergistic effects of dual active sites in catalysis.

REFERENCES

1. H. K. Ly, I. M. Weidinger, Chem. Commun. 2021, 57, 2328-2342
2. T. R. Ramuglia, V. Budhija, K. H. Ly, M. Marquardt, M. Schwalbe, I. M. Weidinger, *Chem Cat Chem*, 2021, 13, 3934.
3. H. Zhong, M. Ghorbani-Asl, K. H. Ly, J. Zhang, J. Ge, M. Wang, Z. Liao, D. Makarov, E. Zschech, E. Brunner, I.M. Weidinger, J. Zhang, A. V. Krasheninnikov, S. Kaskel, R. Dong, X. Feng, *Nat. Comm.* 2020, 11, 1409.
4. M. Borelli, C. J. Querebillo, D. L. Pastoetter, T. Wang, A. Milani, C. Casari, H. K. Ly, F. He, Y. Hou, C. Neumann, A. Turchanin, H. Sun, I. M. Weidinger, X. Feng, *Angew. Chemie Int. Ed*. 2021, 60 (34), 18876-18881.



Probing O_2 Affinity, Reactivity, and Signaling in Globin Coupled Sensors

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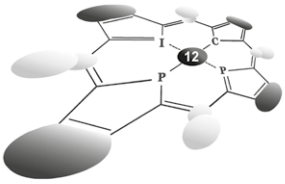
Globin coupled sensors (GCSs) are bacterial heme proteins that consist of a globin domain linked by a central domain to an output domain, such as diguanylate cyclase domains that synthesize c-di-GMP, a major regulator of biofilm formation. While O_2-binding typically activates enzymatic activity of GCS proteins, we have recently characterized a GCS from *Paenibacillus dendritiformis* (DcpG) that exhibits differential modulation of two enzymatic domains by O_2 and NO [1]. DcpG also exhibits markedly weaker O_2 affinity than typical sensor globins, as well as unmeasurable autooxidation. Comparison of DcpG with the GCS protein from *Pectobacterium carotovorum* (*Pcc*GCS) has identified heme pocket residues involved in modulating O_2 affinity and redox potential of GCS proteins. Using FTIR, O_2 binding measurements, enzyme kinetic assays, structural techniques, and resonance Raman spectroscopy, we have identified key interactions at the heme edge that modulate O_2 affinity, midpoint potential, and ligand-dependent signal transduction [2]. Results from these studies highlight novel ways to modulate O_2 affinity and reactivity of heme proteins, as well as the role of heme edge residues in signal transduction.

REFERENCES

1. Patterson, D.C.; Yoon, H.; Perez Ruiz, M.; Walker, J.A.; Armache, J.-P..; Yennawar, N.H.; Weinert, E.E. Differential ligand-selective control of opposing enzymatic activities within a bifunctional c-di-GMP metabolic protein. *Proc. Natl. Acad. Sci.* **2021**. DOI: 10.1073/pnas.2100657118
2. Patterson, D.C.; Liu, Y.; Das, D.; Yennawar, N.H.; Armache, J.-P.; Kincaid, J.R.; Weinert, E.E. Heme Edge Residues Modulate Signal Transduction Within a Bifunctional Homo-Dimeric Sensor Protein. *Biochemistry*. In press.



Learning how Nature Handles Indoles: Mapping the Mechanistic Intermediates of Heme Enzyme mediated Dioxygenation, Monooxygenation, and Nitration of Indole Motifs using Synthetic Model Systems

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Heme enzymes are powerhouses for the interconversion of indole moieties within biological systems, wherein synthetically challenging transformations are mediated with remarkable precision on a broad scope of indole motifs under environmentally benign reaction conditions. Comprehending these pathways in great detail pose significant implications in human pathogenesis and prognosis, thereby offering useful insight into the rational design of superior therapeutic agents with enhanced effectivity and specificity. Moreover, a clear, unequivocal understanding of these biological pathways hold significant promise in the development of environmentally benign catalytic protocols both in acquiring challenging synthetic architectures as well as in alternative energy applications. Synthetic heme model systems are appealing probes in this endeavour, which can be generated in high yield using relatively straightforward pathways and are typically capable of withstanding a much broader range of experimental conditions in comparison to their biological counterparts. These model compounds therefore enable detailed interrogations into structure function relationships and mechanisms of bio-inspired reaction pathways mediated by heme systems that are virtually impossible to execute on enzymatic systems. We, in our recent studies have rigorously described first examples of indole dioxygenating, monooxygenating, and nitrating heme model systems drawing close parallels to analogous heme enzymes that are emerging drug targets against a vast variety of diseases, especially cancer. We have discovered subtle bio-relevant mechanistic details that are likely monumental in the design of novel, selective, mechanism-based drug candidates that could revolutionize future human therapeutics.

Advanced Photoresponsive Materials from Porphyrins and Phthalocyanines: The Metal–Organic Framework Approach

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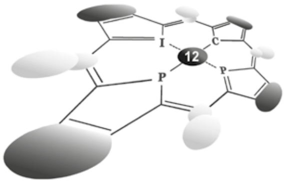
For the fabrication of macroscopic devices exploiting the properties of organic chromophores, the availability of well-defined thin films of high optical quality is an important prerequisite. Optical absorption properties are often strongly affected by inter-chromophore interactions, and therefore periodic assemblies with low defect densities offer substantial advantages over amorphous compounds. In addition, crystalline chromophoric arrangements offer the chance to exploit band-structure effects, e.g. the occurrence of indirect band gaps [1]. The latter would reduce the chance for radiative recombination and thus improve the performance of solar cells.

In this context, crystalline reticular networks have recently attracted considerable interest. By appropriate functionalization, most organic chromophores can be converted to function as di- or higher-topic linkers, which can coordinate to metal or metal-oxo centers, so as to yield stable, metal-organic frameworks, or MOFs. Of particular interest in this context are light-switchable MOFs. However, the conventional powder form of MOFs obtained using solvothermal approaches, exhibits substantial drawbacks with regard to optical applications, e.g. limited efficiency resulting from absorption and light scattering caused by the (micrometer-sized) powder particles. Providing MOFs in the form of thin films avoids these problems. We have developed a layer-by-layer (lbl) deposition method to produce well-defined, highly oriented and monolithic MOF thin films on a number of different substrates. The resulting films are referred to as SURMOFs [2]. The fabrication of hetero-multilayers containing well-defined hetero-interfaces is rather straightforward with this lbl method. A particularly attractive option is to exploit the porous nature of the MOFs in connection with the lbl method to integrate C60 into SURMOF-based devices, e.g. in the context of photoconductivity [3]. In the context on nonlinear optical properties, using sophisticated assembly strategies were recently used to fabricate non-centrosymmetric SURMOFs with high SHG activity [4]. Phthalocyanine-based SURMOFs are also well suited for the fabrication of optical cavities, an exciting new field with regard to the tuning of materials properties [5].

REFERENCES

1. J. Liu, W. Zhou, J. Liu, I. Howard, G. Kilibarda, S. Schlabach, D. Coupry, M. Addicoat, S. Yoneda, Y. Tsutsui, T. Sakurai, S. Seki, Zh. Wang, P. Lindemann, E. Redel, Th. Heine, Ch. Wöll, Angew. *Chemie Intl. Ed*., **54**, 7441-7445 (2015)
2. R. Haldar, L. Heinke, Ch. Wöll, *Adv. Mater.,* 1905227, **32** (20), 1905227 (2019)
3. X. Liu, M. Kozlowska, T. Okkali, D. Wagner, T. Higashino, G. Brenner-Weiß, S. M. Marschner, Z. Fu, Q. Zhang, H. Imahori, S. Bräse, W. Wenzel, C. Wöll, L. Heinke, Angew. *Chem. Int. Ed.* 2019, **58**, 9590
4. A. Nefedov, R. Haldar, Z. Xu, H. Kühner, D. Hofmann, D. Goll, B. Sapotta, S. Hecht, M. Krstić, C. Rockstuhl, W. Wenzel, S. Bräse, P. Tegeder, E. Zojer, Ch. Wöll, *Adv. Mat.* 2103287 (2021)
5. R. Haldar, Z. Fu, R. Joseph, D. Herrero, L.Martín-Gomis, B. S. Richards, I.A. Howard, Á. Sastre-Santos, Ch. Wöll, *Chem. Sci.,* 11, 7972, **11**, 7972-7978 (2020)



Very efficient catalytic and photocatalytic oxidations with phthalocyanines

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Catalysis by a binuclear Co(II)Pc: It is well known that Co(II)Pcs are worldwide used in the Merox Process as catalyst for the desulfuration of petroleum fractions to convert thiols with oxygen to disulfides. Therefore it is important how it is possible to enhance the catalytic activity by CoPc derivatives. In the scientific literature the catalytic activity of Co(II)Pcs is usually tested in the oxidation of 2-mercaptoethanol (RSH; R= HOCH2CH2-) to the corresponding disulfide (RS-SR) in weakly-alkaline media.

In our work we compared the catalytic activities for the oxidation of 2-ME of the mononuclear CoPc 1 with the annulated binuclear CoPc-CoPc 2 both substituted by 2,6,-methylphenoxy groups for better solubility [1]. The measurements were carried under O2 in 50 mL weakly alkaline THF solution containing 2-ME and CoPcs in a molar ratio of ~142.000:1. The oxygen consumption over time was measured. The catalytic activity can be described by the turnover frequency (TOF, number of moles of thiol converted per mole of CoPc per minute).

The commercially used mononuclear 1 provides a TOF of 250 min-1. However, the catalytic activity for the binuclear 2 exhibits an extremely high TOF of ~9000 min-1. The catalyst 2 is very stable, and turnover numbers exceeding 2 000 000 were achieved, and the unprecedented catalytic activity of 2 remains practically unchanged. A mechanisms is proposed based on the electronic contact between two Co centres through the extended π-electron system in 2 which facilitates the electron transfer from thiolate to oxygen.

Photocatalysis by a npAu-Zn(II)Pc hybrid system: Nanoporous gold (npAu) supports with a high surface were prepared as disks, foils and powders by corrosion of an AgAu alloy with concentrated HNO3. Then functionalization of the npAu with a ZnPc derivative 3 to obtain the npAu-ZnPc hybrid system 4 was carried out. The ZnPc 3 is homogenously distributed through the whole outer and interior surface of the nanoporous structure. Both components of the hybrid material, npAu (~520 nm) and ZnPc (~680 nm), are absorbing in the visible region of light. The powdered hybrid system 4 suspended in a solvent was investigated as heterogeneous photocatalyst under oxygen atmosphere and irradiation with visible light in photooxidations of [4 + 2] cycloaddition reactions of eight different substrates [2]. 100 mL of a solvent contains 5 μmol of a substrate and 28 mg the suspended powdered hybrid 4 loaded with only 0.5 nmol active ZnPc (molar ratio substrate:ZnPc = 10.000:1). Irradiation with visible light was conducted under oxygen. Exemplarily, after 10 min 100% conversion of 1,3-diphenylisobenzofuran to 1,2-dibenzoylbenzene was measured with the hybrid photocatalyst. But only 25% of the same substrate was converted with the same amount of dissolved ZnPc in solution. Another example is α-terpinene: 85% conversiojn after 120 min with the hybrid photocatalyst and 45% with ZnPc in solution. In contrast, npAu showed no photocatalytic activity under irradiation.

The reactive species for the photooxidation is singlet oxygen formed by irradiation of ZnPc from triplet oxygen. The much higher activity of the hybrid photocatalyst 4 is explained by energy transfer from localized plasmon resonance (LSPR) to the immobilized ZnPc 3 under irradiation with visible light.

REFERENCES

1. Makarov SG, Ketkov SYu, Wöhrle D. Chem. Commun. 2020; 56: 5653—5656.
2. Steinebrunner D, Schnurpfeil G, Wöhrle D, Wittstock A. Photochem. Photobiol. Sci. 2021; 20: 547-558.

Synthesis of 10,20-substituted-tetrabenzo-5,15-diazaporphyrins and evaluation of their application to organic semiconductors

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Tetrabenzoporphyrin (TBP) and phthalocyanine (Pc) are widely studied molecules as the functional dyes and the p-type organic semiconductors due to their high stability, large absorption coefficient at visible region, and good hole transporting property. 5,15-Tetrabenzodiazaporphyrin (TBDAP) is a structural hybrid molecule of TBP and Pc and has several potential advantages as an organic semiconductor [1]. The replacement of two *meso*-carbons of TBP to nitrogen atoms stabilizes the energy levels of the frontier orbitals because of the higher electronegativity of nitrogen compared with the carbon. Lowering the HOMO levels of the p-type organic semiconductors is effective to achieve large open-circuit-voltage in organic photovoltaic application. Moreover, since the substituents at the meso positions are important for tuning not only optoelectronic properties but also solubility and solid-state molecular arrangement, the structural versatility of TBDAP is a great advantage compared to Pc. Herein, we report the synthesis of meso-substituted BCOD-fused DAP-copper complexes by the metal-templated cyclization using NaN_3/CuI/ligand system with moderate yield [2]. We also report the thermal conversion of the precursors to TBDAPs on the substrate and their optoelectronic properties.

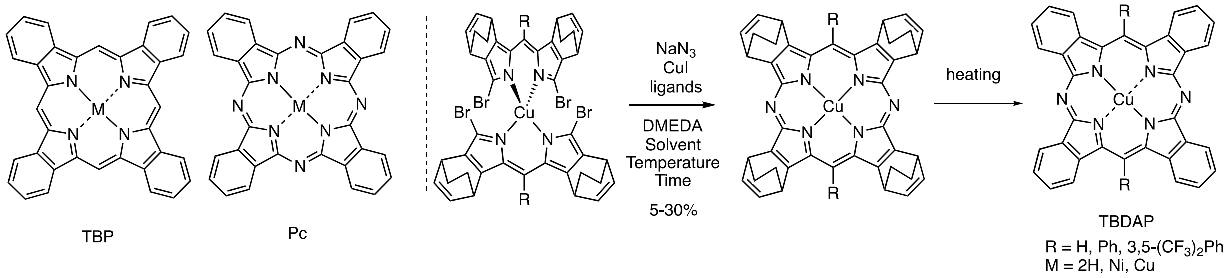

Figure 1. Chemical structures of TBP, Pc, and TBDAP and the synthetic route of TBDAP.

REFERENCES

1. Y. Matano, *Chem. Rev.* **2017**, 117, 3138–3191.
2. Y. Sugano, K. Matsuo, H. Hayashi, N. Aratani, and H. Yamada, *J. Porphyrins Phthalocyanines* **2021**, *25*, 1186-1192.

Redox-Switchable Structurally Well-Defined *meso*-Aminoporphyrin Oligomers Analogous to Polyanilines

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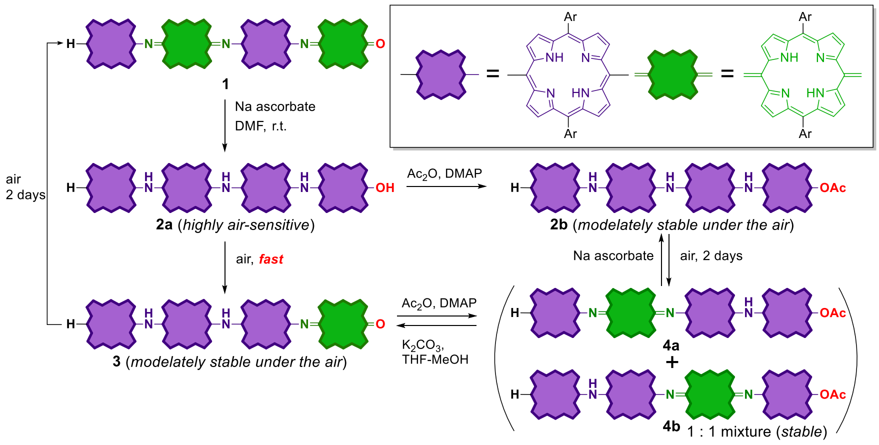
Polyaniline (PANI) is one of the most famous conducting polymers whose structure and redox behavior have been well-studied. PANIs have three stable redox states; fully reduced state (leucoemeraldine), fully oxidized state (pernigraniline), and partially oxidized state (emeraldine). In addition, those protonated states, in which proton was added on the bridged nitrogen atoms, are present for all oxidation states. Those electrochemical and spectroscopic properties are quite different. Herein, we present the synthesis and the reversible redox switching of novel linear π-conjugated *meso*-aminoporphyrin oligomers analogous to polyanilines.

A *meso*-aminoporphyrin[1] undergoes oxidative oligomerization reactions in the presence of dioxygen and an acid catalyst to afford the oligomers with a similar structure to fully-oxidized polyaniline. The obtained oligomers exhibit narrow HOMO–LUMO gaps and broad NIR electronic absorptions assignable for the intramolecular charge transfer (ICT) transitions from porphyrinoid moieties to quinoid moieties (Fig. 1). The quinoid moieties in the fully oxidized oligomers are reversibly reduced by sodium ascorbate to afford all-porphyrinoid oligomers, which do not have an ICT band. Three types of the partially reduced tetramers having one quinoid moiety (**3**, **4a**, and **4b**) were also obtained, and **4a** and **4b** were interconverted to each other in solution. Moreover, this interconversion was significantly accelerated in the presence of a protic solvent. This result is consistent with high electron transport on the partially-oxidized polyanilines upon protonation.



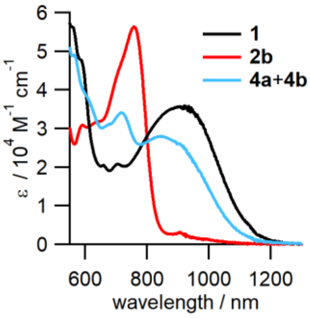


Fig. 1 Vis/NIR absorption spectra of **1**, **2b**, and the mixture of **4a** and **4b** in toluene.

REFERENCES

1. K. Yamashita, K. Kataoka, S. Takeuchi, K. Sugiura, *J. Org. Chem.* **2016**, *81*, 11176–11184.

Triplet biradical states of multiple-decker phthalocyaninato-terbium(III) single-molecule magnets

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Construction of the extended π-system is one of the main topics in synthetic chemistry. There are two kinds of π-extension, one of which is in-plane extension, and the other being longitudinal extension, so called π-π stacks. Phthalocyaninato multiple-decker complexes composed by lanthanoid and cadmium ions are one rare examples of stacked π-oligomers [1-2]. In addition, oligomers containing terbium ions as the lanthanoid ions are known to show single-molecule magnetic behavior. In this presentation, we will report unusual biradical states and decrease in the magnetic anisotropy of oxidized oligomers proofed by means of ^{1}H NMR analyses and DFT calculations. Because of the strong magnetic anisotropy of Tb(III), the ^{1}H signals show large paramagnetic shift down to -100 ppm. Ligand oxidations result in the decrease in amounts of the paramagnetic shifts, indicating the decrease in the magnetic anisotropy. In addition, there is a large discrepancy between calculated and estimated ^{1}H signals in +2e charged tetramer and pentamer, indicating the triplet biradical states which act as the additional spin source to induce unusual paramagnetic shift [3-4].

REFERENCES

1. T. Fukuda, T. Biyajima and N. Kobayashi, J. Am. *Chem. Soc.* **2010,** 132, 6278-6279.
2. H. Wang, N. Kobayashi and J. Jiang, *Chem. Eur. J.* **2012**, 18, 1047-1049.
3. Y. Horii, M. Damjanovic, M. R. Ajayakumar, K. Katoh, Y. Kitagawa, L. Chibotaru, L. Ungur, M. MasTorrent, W. Wernsdorfer, B. K. Breedlove, M. Enders, J. Veciana and M. Yamashita, *Chem. Eur. J.*, **2020**, 26, 8621-8630.
4. Y. Horii, M. Damjanovic, K. Katoh, and M. Yamashita, Dalton Trans., 50, 9719-9724(2021)

Conformational Plasticity in Human Heme-Based Dioxygenases

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Human indoleamine 2,3-dioxygenase 1 (hIDO1) and human tryptophan dioxygenase (hTDO) are two important heme proteins that degrade the essential amino acid, L-tryptophan (Trp), along the kynurenine pathway. The two enzymes share a similar active site structure and an analogous catalytic mechanism, but they exhibit a variety of distinct functional properties. Here we used carbon monoxide (CO) as a structural probe to interrogate how the functionalities of the two enzymes are encoded in their structures. With X-ray crystallography, we detected an unexpected photochemical intermediate trapped in a crystal of the hIDO1-CO-Trp complex (denoted as hIDO-CO-Trp*), where CO is photolyzed from the heme iron by X-rays at cryogenic temperatures (100 K) (Figure 1). The CO photolysis triggers a large-scale migration of the substrate Trp, as well as the photolyzed CO, from the active site to a temporary binding site, Sa*. It is accompanied by a large conformational change to an active site loop, JK-Loop^{C}, despite the severely restricted protein motion under the frozen conditions, which highlights the remarkable conformational plasticity of the hIDO1 protein. Comparative studies of a crystal of the hTDO-CO-Trp complex show that CO and Trp remain bound in the active site under comparable X-ray illumination, indicating a much more rigid protein architecture. The data offer important new insights into the structure and function relationships of the heme-based dioxygenases and provide new guidelines for structure-based design of inhibitors targeting them [1].

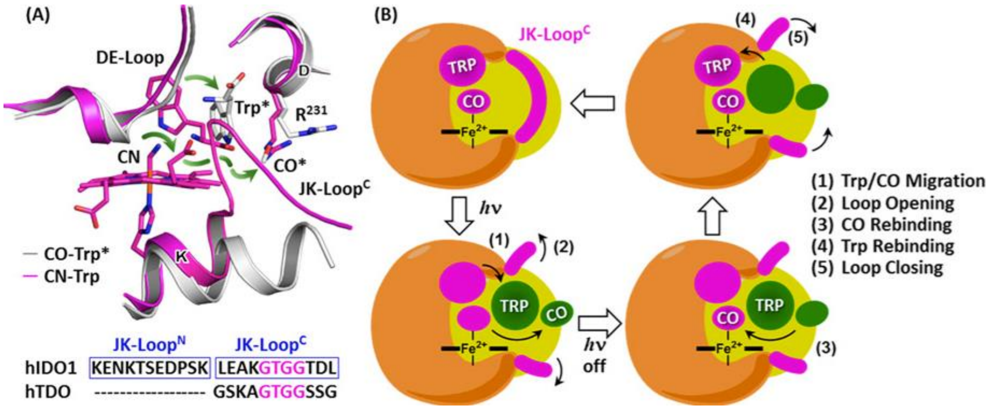

Figure 1. Photoinduced ligand and substrate migration in hIDO1. (A) Active site structure of hIDO1-CO-Trp* (gray) superimposed with that of the hIDO1-CN-Trp complex (PDB: 5WMU) (magenta), used as a model for the intact hIDO1-CO-Trp complex, to illustrate the CO photolysis induced relocation of Trp and CO, as indicated by the green arrows. The bottom panel shows sequence alignment of the JK-Loops of hIDO1 and hTDO. The conserved "GTGG" motif is highlighted in magenta. (B) Schematic illustration of the ligand and substrate migration and the accompanied opening of the JK-Loop^{C} induced by X-rays or visible light (steps 1 and 2) and their subsequent rebinding and the closure of the JK-Loop^{C} upon the termination of the photolysis light (steps 3–5).

REFERENCES

1. Pham KN, Lewis-Ballester A, Yeh SR. *J Am Chem Soc,* **143**, 1836-1845, 2021. doi.org/10.1021/jacs.0c09970.

Corrinoids as Cofactor F430 Models and Antibiotic Agents

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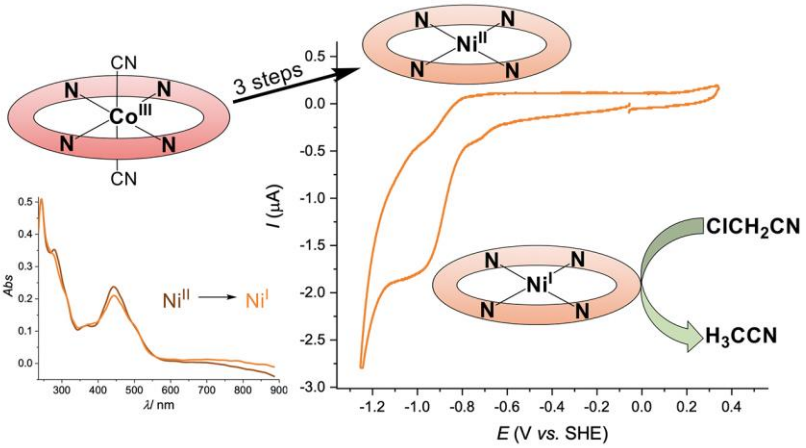
Cobalt-containing vitamin B_{12} catalyses difficult biological methyl transfer and [1, 2] rearrangement reactions. Inspired by its versatile chemistry, my group synthesizes modified corrins with new properties and functions. In this lecture, I will highlight the preparation and study of a catalytically active Ni(I) corrin derivative reminiscent of cofactor F430 [1, 2]. Apart from fundamental studies, the antibiotic properties of modified Cbls are discussed.



Financial support by the University of Zurich, the Schweizerischer Nationalfonds (SNFS-73537-02-01), the “Forschungskredit” of the University of Zurich is gratefully acknowledged. We acknowledge generous gifts of B_{12} from DSM Nutritional Products AG (Basel/Switzerland) as well as from Prof. em. Bernhard Jaun (ETH Zurich).

REFERENCES

1. C. Brenig, L. Prieto, R. Oetterli, F. Zelder, *Angew. Chem. Int. Ed*. 57 (2018) 16308-16312.
2. C. Brening, L. Mosberger, O. Blacque, R. Kissner, F. Zelder, *Chem. Commun*. 57 (2021) 7260-7263.

Porphyrin Supramolecular Assemblies for Ultrasound Applications

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Porphyrins are a class of organic molecules abundant in nature with unique photophysical properties rooted in their aromatic macrocyclic structure, and their integration into supramolecular assemblies has advanced their biomedical utility. By mimicking these light harvesting systems in photosynthetic bacteria, we have created a family of supramolecular assemblies of highly ordered porphyrin aggregates possessing unique photonic properties [1, 2] making them high suited for multimodal imaging and therapeutic applications.

These assemblies, much like other nanoscale agents, rely on the leaky vasculature and poor lymphatic drainage of tumours to extravasate or leak out. While this passive delivery is widely applied and established in pre-clinical mouse models, it remains controversial in a clinical context, prompting an exploration of active strategies. One such strategy involves ultrasound stimulation of exogenous microbubbles – particles 1-8 um in diameter with a lipid monolayer encapsulating a gaseous core. Currently clinically approved for imaging, and in clinical trials for various therapeutic applications, microbubbles expand and contract under ultrasound causing a range of vascular events while emitting acoustic signatures for feedback control in real time.

We recently created novel multimodal porphyrin-encapsulated microbubbles, and demonstrated their ultrasound-triggered conversion [3] to a new submicron ultrasound agent – nanobubbles – with actively increased accumulation in targeted tumour tissue [4,5]. While traditionally the large diameter of microbubbles has confined them to the vasculature, the presence of gas in the daughter nanobubbles in combination with the photoactive porphyrin opens the possibility of stimulating further optical- and ultrasound-mediated imaging as well as photo-/and sono-dynamic therapeutic applications beyond the vasculature. In this talk we will discuss porphyrin supramolecular assemblies, and highlight their novel applications with ultrasound.

REFERENCES

1. Lovell et al. *Nature Materials,* 10, 2011.
2. Harmatys et al. *Acc Chem Res,* 52, 2019.
3. Huynh et al. *Nature Nanotechnology,* 10(4), 2015.
4. Pellow et al. *Nano Letters,* 20(6), 2020.
5. Pellow et al. *Theranostics,* 10(25), 2020.

Isoindoline-Based Open Macrocycles

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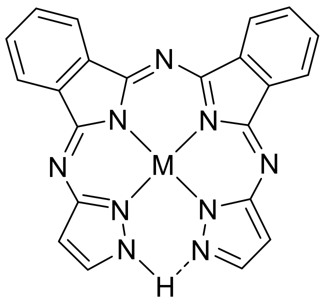
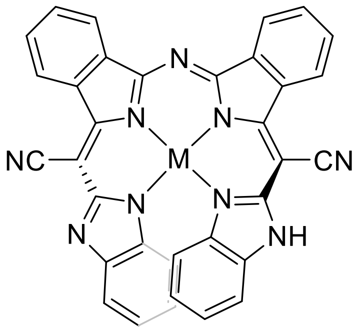
Diiminoisoindoline continues to be a useful reagent for the synthesis of phthalocyanine inspired macrocycles and chelate systems. When combined with pyrazole, indazole, and benzimidazole-based heterocycles, this compound forms a chelate that can condense at metal sites to form phthalocyanine analogue compounds. These analogues are ring open macrocycles, where the ring either closes via a non-covalent interaction (biliazine and subbiliazine) or forms a helical structure, the new heliphyrin chelates. This talk will present recent developments in these open macrocycle compounds and will also introduce new isoindoline and pthalazine-based bidentate chelates.





On the Structural Factors Influencing Photodynamic Activity in Phthalocyanines

Petr Zimcik, Miloslav Machacek, Veronika Novakova, Miroslav Miletin, Jan Kollar and Lucia Kociscakova

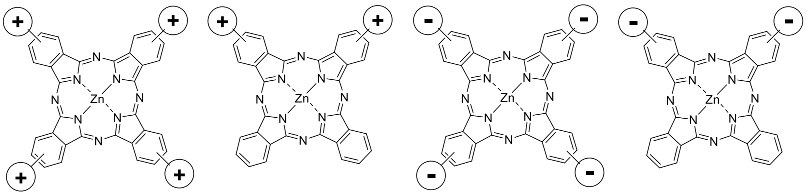
Faculty of Pharmacy in Hradec Kralove, Charles University, Ak. Heyrovskeho 1203, Hradec Kralove, 50005, Czech Republic, zimcik@faf.cuni.cz

Phthalocyanines (Pcs) belong to widely investigated structural type of synthetic dyes. Thanks to wide absorption in (far) red region and good ability to produce singlet oxygen, they have also found their place in photodynamic therapy (PDT) of cancerous conditions. Number of Pcs have been synthesized and tested for anticancer PDT on cells. The structural factors influencing the final photodynamic effect, however, are not still very clear. In our research, we focused first on the direct comparison of Pcs bearing anionic and cationic peripheral substituents (Figure A) since the analysis of the published data indicated substantial difference between these two groups. On the series of Pcs bearing the same number of charged and bulky substituents, we demonstrated that the main reasons laying behind this difference are found in presence on non-ionized form at lower pH and strong binding of anionic Pcs to serum albumin that leads to inactivation of excited states and decreased escape of singlet oxygen from the protein environment [1].

Besides this project, we also focused on the supramolecular approach for decreasing aggregation of Pcs in water. Pcs bearing adamantyl moieties as peripheral substituents were therefore designed and synthesized (Figure B). It has been proven that substantial monomerization in water can be achieved upon interaction with cucurbituril (CB[7]). Despite such monomerization, the photodynamic activity of Pcs was found lower due to lower cellular uptake upon interaction with such bulky hydrophilic host.

Bearing in mind that in vitro photodynamic properties on cells are often evaluated under different irradiation conditions, we decided to compare various Pcs under the same conditions. Large series of published Pcs (anionic, cationic, nonionic, hydrophilic, amphiphilic, axially substituted, etc.) from various top research groups in area of Pcs have been collected and tested. The first analysis of the obtained data will be presented during lecture.

A)



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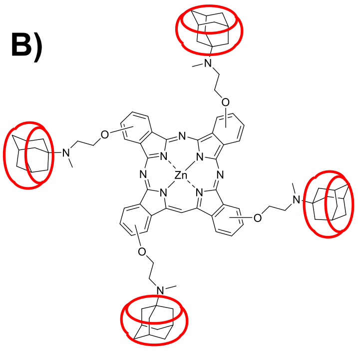

The work was supported by Czech Science Foundation (20-09212S).

REFERENCES

1. Kollar J, Machacek M, Halaskova M, Lenco J, Kucera R, Demuth J, Rohlickova M, Hasonova K, Miletin M, Novakova V, Zimcik P, Cationic Versus Anionic Phthalocyanines for Photodynamic Therapy: What a Difference the Charge Makes, *J. Med. Chem.*, 2020, 63, 7616-7632.

Antibiotic and Anticancer Rhenium Carbonyl Complexes and Cobalamin Functionalized Microalgae for their Delivery

Fabio Zobi[a], **Sara Nasiri Sovari[a]**, **Natasa Radakovic[b]**, **Joachim Delasoie[a]**, **Aleksandar Pavic[b]**, and **Jasmina Nikodinovic-Runic[b]**

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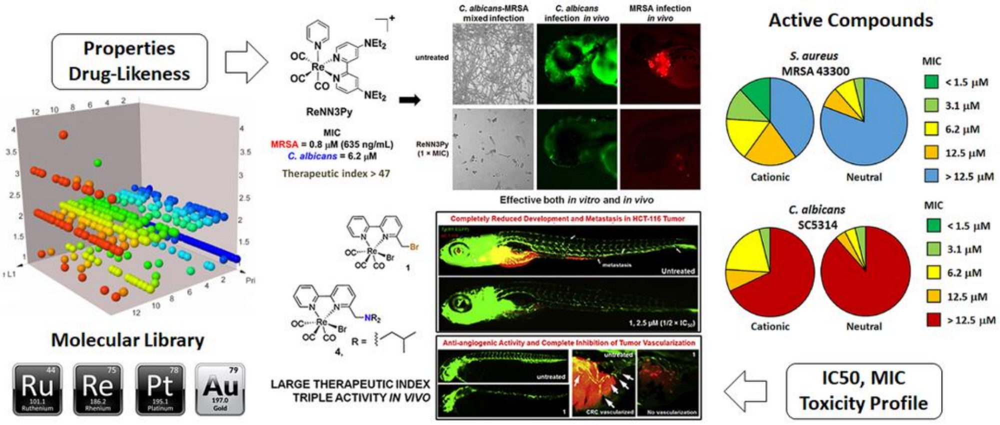
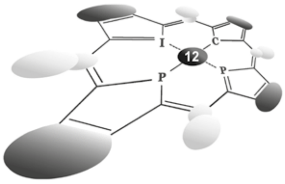
We present in this contribution our molecular approach to the discovery of active and non-toxic antibiotic [1-2] and anticancer [3] metal complexes and the preparation of surface-functionalized diatom microalgae for the targeted delivery and enhanced cytotoxicity of the anticancer compounds against colorectal cancer (CRC) [4-5]. The complexes we identified are active *in vivo* (zebrafish-lethal *C. albicans* or MRSA infection and -human HCT-116 xenograft models respectively) in low μM to nM concentrations and show no sign of cardio-, hepato-, hematotoxiciy or teratogenicity. A bio-inspired hybrid multifunctional drug delivery system based on diatom microalgae for the targeted delivery of the complexes was designed by chemically modifying the microalgae's surface with hybrid vitamin B12-photoactivatable molecules and the materials further loaded with active compounds. The constructs showed enhanced adherence to CRC cells and slow release of the chemotherapeutic drugs. The overall toxicity of the hybrid multifunctional drug delivery system was further enhanced by photoactivation of the microalgae surface.



REFERENCES

1. Sovari, S.N.; Vojnovic, S.; Bogojevic, S.S.; Crochet, A.; Pavic, A.; Nikodinovic-Runic, J.; Zobi, F. *Eur. J. Med. Chem.* **2020**, *205*, 112533.
2. Sovari, S.N.; Radakovic, N.; Roch, P.; Crochet, A.; Pavic, A.; Zobi, F. *Eur. J. Med. Chem.* **2021**, *226*, 113858.
3. Delasoie, J.; Pavic, A.; Voutier, N.; Vojnovic, S.; Crochet, A.; Nikodinovic-Runic, J.; Zobi, F. *Eur. J. Med. Chem.* **2020**, *204*, 112583.
4. Delasoie, J.; Schiel, P.; Vojnovic, S.; Nikodinovic-Runic, J.; Zobi, F. *Pharmaceutics* **2020**, *12*, 480.
5. Delasoie, J.; Rossier, J.; Haeni, L.; Rothen-Rutishauser, B.; Zobi, F. *Dalton Trans.* **2018**, *47*, 17221



Impact of different physicochemical parameters in the antimicrobial Photodynamic Therapy success

Maria Bartolomeu[a], Carlos J. P. Monteiro[b], Milton Fontes[c], Cátia Vieira[a], M. Graça P. M. S. Neves[b], M. Amparo F. Faustino[b] and Adelaide Almeida[a]

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Wastewater (WW) containing identified and emergent pathogenic microorganisms (MO), is subject of great concern, due to the impact of these effluents on the quality of natural receiving waters [1,2]. A secondary biological treatment in a well-operated treatment plant can be very efficient for the removal of carbon (85-95%), nutrients (nitrates and phosphates) and suspended solids content in raw WW. However, this process is inefficient on the inactivation of MO, including pathogens that can survive through the treatment and an additional oxidation process is often required for effluent disinfection [1]. The traditional tertiary treatments, based on disinfection methods to reduce pathogens concentration in WW (e.g., chlorination, ozonation, UV) are expensive, sometimes ineffective, and unsafe, highlighting the need for new technologies [3]. The promising *in vitro* results of antimicrobial Photodynamic Therapy (aPDT) to eradicate MO suggest its effective application as a disinfection process to improve WW quality before its release into the environment [4].

One of the aims of our work was to assess if the principles of aPDT can be successfully extended to real contexts, namely for the microbial inactivation on WW. We have been performed experiments with different water matrices compositions to inquire about the influence of some of their physicochemical parameters in the effectiveness of microbial photodynamic inactivation of the bacterium *Escherichia coli* (used as bacterial model of faecal contamination) [2]. The results of bacterial photoinactivation in water samples from aquaculture and wastewater treatment plants (receiving domestic or industrial WW, or a mixture of domestic and industrial WW) facilities, seawater (from different locations) will be presented and discussed.

Acknowledgements: Thanks are due to the University of Aveiro and FCT/MCT for the financial support for the LAQV-REQUIMTE (UIDB/50006/2020) and CESAM (UIDB/50017/2020 + UIDP/50017/2020), and to the FCT projects PREVINE - FCT-PTDC/ASP-PES/29576/2017 through national founds (OE) where applicable co-financed by the FEDER-Operational Thematic Program for Competitiveness and Internationalization-COMPETE 2020, within the PT2020 Partnership Agreement. M.B. and C.V. are thankful to the Fundação para a Ciência e a Tecnologia (FCT) for their PhD Grants (SFRH/BD/121645/2016 and SFRH/BD/150358/2019, respectively).

REFERENCES

1. United Nations Quality and Wastewater | UN-Water Available online: https://www.unwater.org/water-facts/quality-and-wastewater/ (accessed on Oct 21, 2021).
2. Bartolomeu, M.; Reis, S.; Fontes, M.; Neves, M.G.P.M.S.; Faustino, M.A.F.; Almeida, A. Photodynamic Action against Wastewater Microorganisms and Chemical Pollutants: An Effective Approach with Low Environmental Impact. *Water* **2017**, *9*, 630.
3. Tchobanoglous, G.; Burton, F.L.; Stencel, H.D. *Wastewater Engineering: Treatment and Reuse*; McGraw-Hill, B., Ed.; 4th ed.; Metcalf & Eddy, Inc., 2003; ISBN 0071122508.
4. Almeida, A.; Faustino, M.A.F.; Tomé, J.P.C. Photodynamic inactivation of bacteria: finding the effective targets. *Future Med. Chem.* **2015**, *7*, 1221–1224.

Chlorin conjugates for antimicrobial and antitumor photodynamic therapy: From synthesis and disaggregation to biodistribution and photocytotoxicity assays

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Photodynamic therapy (PDT) is a well-known low-invasive technique used as an important part of the combined treatment including surgery, chemo- or antibiotic therapy, to eliminate both tumors and superficially located drug-resistant microbial infections and induced a significant immune responce in organism of the patient [1-5]. The photodynamic treatment is realized in combination of visible light, oxygen and photosensitizer (PS), which is very often a macrocyclic dye such as chlorin e_6 [2, 5]. Chlorin PS molecules are usually functionalized by covalently bound fragments of bioactive molecules like amino acids, sugars, glycols or some nitrogen containing compounds. These groups are implemented into the structure of PSs to reduce their aggregation and thereby to improve both solubility in aqueous solutions and reactive oxygen species (ROS) generation, to increase the tropism of PSs to the membranes of tumor and/or microbial cells and to enhance the induction of their apoptosis [1, 2]. Here we present our results on the synthesis, photophysical characteristics, aggregation and interaction with carriers in aqueous media, distribution of chlorin PSs between blood proteins and modeling of their membrane transport as well as photoinactivation of malignant and/or microbial cells *in vitro* using PDT.

This work was supported by the Russian Science Foundation (project N 21-13-00398).

REFERENCES

1. O.I. Koifman, T.A. Ageeva, I.P. Beletskaya, et al., *Macroheterocycles*, **2020**, *13(4)*, 311-467.
2. A.V. Kustov, D.B. Berezin, A.I. Strelnikov, N.P. Lapochkina. Antitumor and antimicrobial photodynamic therapy: mechanisms, targets, clinical laboratory research. A practical guide. A.K. Gagua ed., Moscow, Largo, 2020, 108 p. (*in Russian*).
3. A.V. Kustov, T.V. Kustova, D.V. Belykh, I.S. Khudyaeva, D.B. Berezin, *Dyes Pigm.*, **2020**, 173, 107948.
4. C. Giancola, M. Caterino, F. D'Aria, A.V. Kustov, D.V. Belykh, I.S. Khudyaeva, O.M. Starseva, D.B. Berezin, Y.I. Pylina, T. Usacheva and J. Amato, *Intern. J. Biol. Macromol.*, **2020**, *145*, 244-251.
5. A.V. Kustov, N.L. Smirnova, Ph.K. Morshnev, O.A. Privalov, T.M. Moryganova, A.I. Strelnikov, O.I. Koifman, A.V. Lubimtsev, T.V. Kustova, D.B. Berezin, *J. Clin. Med.*, **2022**, *11(1)*, 233.

A tool to explore macrocyclic aromaticity, intermetallic interactions, and organometallic chemistry under confinement – cobalt azuliporphyrin

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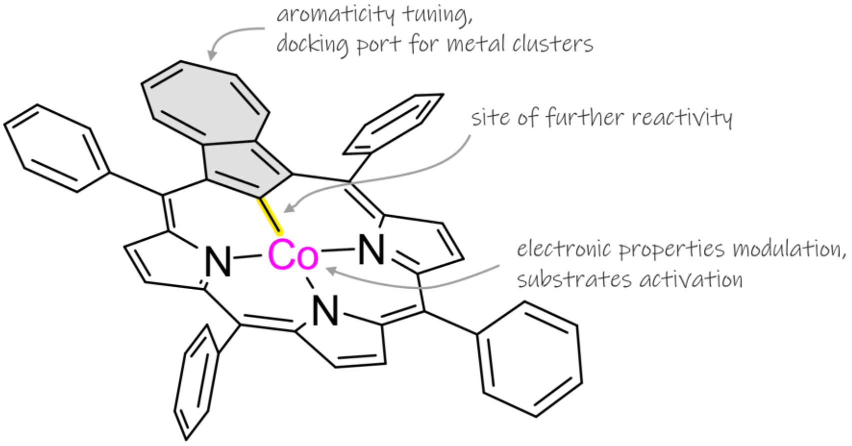
Modified porphyrins and, in particular, carbaporphyrins may differ significantly in properties and reactivity from their regular counterparts [1,2]. By introducing new motifs, we investigate the influence of the modification of the scaffold on the resulting molecules' behaviour. I would like to show the rich chemistry of cobalt meso-substituted azuliporphyrin we reported recently [3].

A cobalt ion may transiently interact with the azulene fragment, altering the overall borderline aromaticity. However, it also readily activates the inner C–H bond, forming a reactive organometallic species. The most fun comes from the richness of that reactivity. We can either focus on the azulene fragment attaching a metal cluster to force it into interacting with the cobalt(II) center. We reach a diamagnetic and aromatic cationic complex by oxidizing the center itself.

Eventually, the greatest chance for post-coordination modifications comes from the lability of the Co(II)–C bond. The insertion of an oxygen atom results in the electronic structure changes within the cobalt ion. Though, further reactivity starts emerging as it is possible that the center activates particular small molecules and transfers them onto the inner carbon atom. The confinement of a new molecular fragment brings a promise of further expansion of the research scope for carbaporphyrins, which I currently pursue.



REFERENCES

1. T. Lash, *Chem. Rev.* **2017**, 117, 4, 2313
2. T. Chatterjee, V.S. Shetti, R. Sharma, M. Ravikanth, *Chem. Rev.* **2017**, 117, 4, 3254
3. M.J. Białek, P.J. Chmielewski, L. Latos-Grażyński, *Chem. Eur. J.* **2019**, 25, 14536

The Enhancement of Photodynamic Breast Cancer Treatment with Phthalocyanine-Polymeric Nanomicelles Delivery Systems

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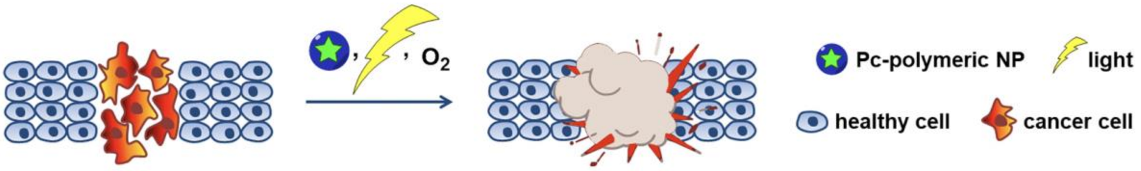
Cancer was responsible for about 10 million deaths in 2020, making it one of the biggest civilizational health problems [1]. Among all cancers, breast cancer was the most common in terms of new cases of cancer last year and in general is the most prevalent cancer among women, alone accounting for 30% of female cancers [2]. Although significant progress has been made to improve cancer treatment over the past decade, patients are still waiting for new cancer breakthrough treatments.



In such a breakthrough, photodynamic therapy (PDT) which is a minimally invasive treatment that combines photosensitising drugs (PSs), oxygen, and light to kill cancer cells, could play an important role. PDT is a selective approach with minimal side effects on normal tissues, offering a promising alternative to standard chemotherapy, radiotherapy, and surgery. Phthalocyanines (Pcs) are one of the most promising second-generation PSs and meet many requirements for being ideal PSs [3]. Unfortunately, very often Pcs are hydrophobic species and undergo self-aggregation in aqueous solutions, which drastically reduces their photosensitizing efficiency. In this research, the limitations of Pcs were overcome by encapsulating them into polymeric nanomicelles delivery systems which greatly improved their photophysical properties. *In vitro* studies reviled that the novel micelles were effectively taken up by breast cancer cell lines. Moreover, the PDT results showed that these photoactive nanomicelles delivery systems were much more efficient than the non-encapsulated Pcs, enhancing their future application in the clinical PDT.

REFERENCES

1. Available online: https://www.who.int/en/news-room/fact-sheets/detail/cancer (accessed on 3 Feb 2022).
2. Siegel, R.L. *et al.*; *CA Cancer J. Clin*. 2020, **70**, 7–30.
3. a) Borzęcka, W. *et al.*; Nanomaterials 2021, 11, 2426; b) P.-C. Lo *et al.*; *Chem. Soc. Rev*. 2020, **49**, 1041
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Applications of Phthalocyanine Modified Electrospun Fibers

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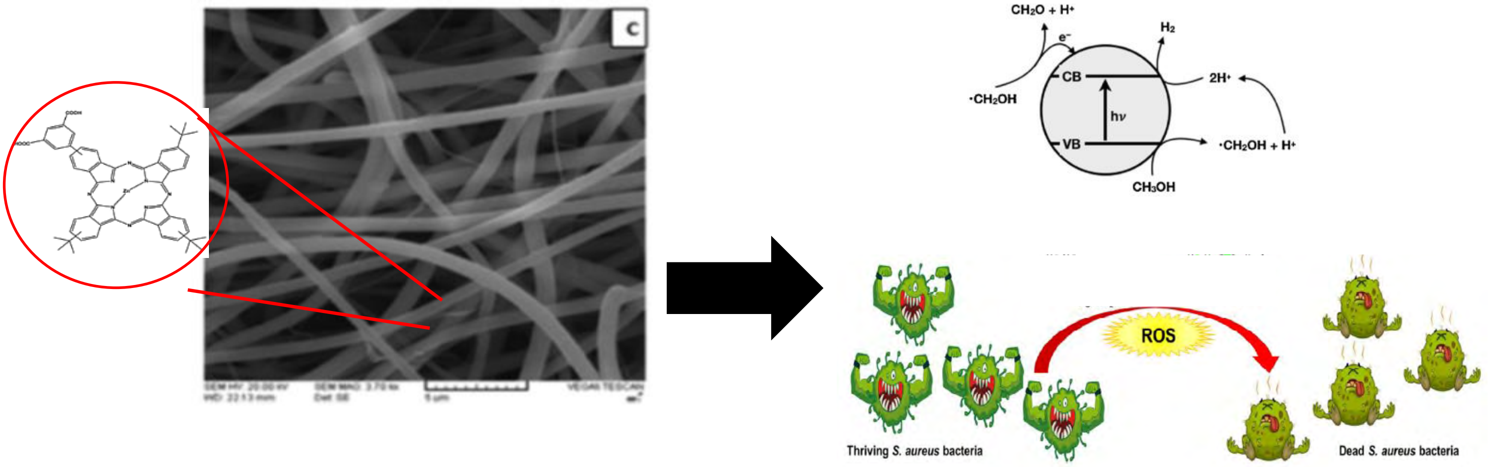
Electrospun fibers provide decent scaffolding support for other reactive chemicals structures, such as phthalocyanines, to be bound onto. Due to this the fibers can be modified to possess a variety of useful properties. In addition to this, the final fibers formed through electrospinning may also themselves be made from compounds with interesting properties.

In this presentation we'll be reporting on the formation of both polymer and metal oxide fibers via electrospinning and the subsequent modification of them with different phthalocyanines and metal clusters. These modified fibers are then tested for their ability to degrade pollutants [1-3], generate hydrogen [2] and their antimicrobial activity [4], and these modified fibers displayed improved behaviour in all of these tested areas.



REFERENCES

1. Ben Jones, Donovan Mafukidze and Tebello Nyokong, *Journal of Molecular Structure* 1213 (2020) 128191
2. Sivuyisiwe Mapukata, Andrew S. Hainer, Anabel E. Lanterna, Juan C. Scaiano and Tebello Nyokong, *Journal of Photochemistry & Photobiology A: Chemistry* 388 (2020) 112185
3. Sivuyisiwe Mapukata and Tebello Nyokong, *New J. Chem.*, 2020, 44, 16340--16350
4. Sivuyisiwe Mapukata, Jonathan Britton, Olawale L. Osifeko and Tebello Nyokong, *Photodiagnosis and Photodynamic Therapy* 33 (2021) 102100

Engineering of directly liked metalloporphyrin conjugated polymers via halogenated substituents: Impact on the optoelectronic properties and catalytic performance.

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Directly linked metalloporphyrin conjugated polymers are excellent candidates for electro- and photocatalytic chemical transformations, –including solar-assisted water splitting for clean hydrogen production– due to their enhanced optoelectronic properties resulting from the direct fusion of multiple porphyrins units. [1] Additionally, fused-metalloporphyrins can be engineered by the selection of the metal cation chelated at the porphyrin core, to be able to act as catalytic active sites towards specific chemical reactions. [2] Despite their promising properties, the incorporation of fused-metalloporphyrin conjugated polymers into functional devices is often hampered by processability limitations through wet synthesis routes. In this scenario, the oxidative chemical vapor deposition (oCVD) has emerged as a suitable alternative enabling the simultaneous synthesis and deposition of fused-metalloporphyrin thin films in a wide variety of substates. [3-4] Moreover, the oCVD approach provides an attractive solution to the engineering of the frontier energy levels of fused-metalloporphyrin conjugated polymers, allowing to explore a wide variety of porphyrins monomers affording metal cations and substituents of different classes.

Previous studies in our group revealed the strong influence of the chelated cation on the regioselectivity for the C-C coupling reaction, as well as on the occurrence of side reactions, and therefore, on the optoelectronic properties of the resulting conjugated metalloporphyrin films. [2] Herein, we investigate the impact of *meso-* substituents in the constitution and optoelectronic properties of cobalt (II) *5,15*-disubstituted porphyrins bearing halogenated substituents: 4-triflouromethyl phenyl (4-CF3P), 4-bromo phenyl (4-BrP), 4-flouro phenyl (4-FP), and pentafluoro phenyl (PFP). In-depth physicochemical characterization by ultraviolet-visible-near infrared spectroscopy and laser desorption ionization coupled to high resolution mass spectrometry analysis of the resulting films confirmed the formation of directly liked metalloporphyrin conjugated polymers resulting from the dehydrogenative coupling reaction. However, the efficiency of the coupling reaction, as well as the occurrence of side reactions, was found to be strongly dependent on the nature of the substituent. The characteristic oCVD reaction of each fused metalloporphyrin according to the substituent were reflected on the optoelectronic properties and catalytic performance of the resulting films toward the hydrogen evolution reaction. For a deeper understanding of the relation between the nature of the substituent with the conjugated metalloporphyrins conformation, and their further optoelectronic properties and catalytic performance, density functional theory calculations were carried out, providing a correlation between the molecular orbitals' distribution and the energy levels arrangement with the fusing degree. This work provides new insights for the engineering of functional devices based on fused-metalloporphyrin thin films, and their further implementation into clean hydrogen production approaches.

REFERENCES

1. T. Tanaka *et al. Chem. Eur. J.* **2011**, 17, 14400–14412.
2. D. Cardenas-Morcoso *et al. J Mat Chem C* 10, 2194 - 2204
3. G. Bengasi, *et al. Angew. Chem. Int*. Ed. **2019**, 58, 2103–2108.
4. G. Bengasi, *et al. Eur. J. Inorg. Chem*. **2020**, 1–9

Induction and Rationalization of Supramolecular Chirality using Urea-bridged Metalloporphyrin *tweezers*: A Structure-Function Correlation

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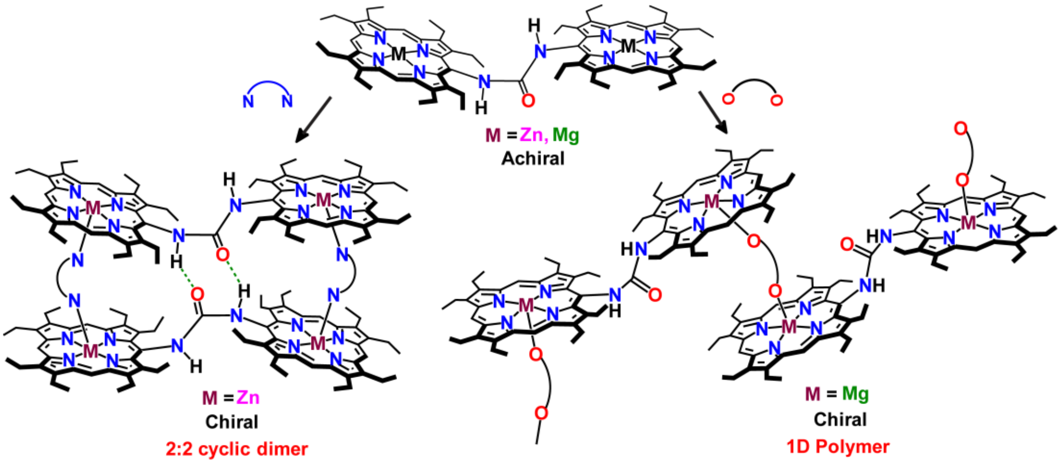
Inspired by the complexity and functionality of chirogenic systems existed in living organisms, supramolecular chirogenesis has become an important way to create symmetry breaking in artificial systems. A comprehensive and rigorous understanding of such phenomenon is necessary to have a clear insight into the fundamental mechanisms and the several controlling factors for a wide range of applications of chiral supramolecular science. Herein a clear and unambiguous rationalization of chirality transfer processes has been demonstrated using a flexible achiral urea-bridged porphyrin dimer (host) and a series of chiral diols and diamines (guests). Mg(II)-porphyrin dimer on complexation with chiral diols demonstrates chirality induction, amplification, and subsequent inversion upon formation of a 1:1 polymer and 1:2 monomer via intermolecular assembling and disassembling processes, whereas in case of Zn analogue, stepwise formation of 2:2 cyclic dimer and 1:2 monomeric complex with chiral diamines have been observed. Interestingly higher CD amplitudes have been observed for the 2:2 cyclic dimer as compared to the linear 1:1 polymer. Also, strong intermolecular H-bonding interactions generate additional stability in the more confined cyclic structure over the linear polymer. The present study opened up new avenues towards understanding of various controlling factors regulating supramolecular chirogenesis [1-5].



REFERENCES

1. B. Saha, D. Chandel, S. P. Rath *Inorg. Chem.* **2022**, *61*, 0000.
2. A. Dhamija, B. Saha, D. Chandel, H. Malik S. P. Rath *Inorg. Chem.* **2020**, *59*, 801.
3. B. Saha, S. A. Ikbal, S. P. Rath *Inorg. Chem.* **2020**, *59*, 7795.
4. A. Dhamija, P. Mondal, B. Saha, S. P. Rath *Dalton Trans.* **2020**, *49*, 10679.
5. A. Dhamija, B. Saha, S. P. Rath *Inorg. Chem.* **2017**, *56*, 15203.

Correlation between the charge transfer kinetics and CO_2 reduction catalytic performance of metal oxide-metalloporphyrin based hybrid catalysts

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Electro and photocatalytic CO_2 reduction is the quintessence of modern-day sustainable and catalysis research. Ideal CO_2 reduction reaction (CO_2RR) catalyst should avoid competitive H_2 evolution reaction (HER), maintain good C1 or C2 products selectivity, and work in water medium with low overpotential [1, 2]. Fe and Co-porphyrin-based molecular catalysts showed efficient electro, and photochemical CO_2RR performance and catalytic pathways often involved metal center-based multi-redox reactions [3]. However, they suffer long-term stability and deactivation. To overcome these shortcomings, we developed hybrid catalyst systems supported on FTO coated glass material by combining mesoporous metal oxide (TiO_2, SnO_2, etc.) anchored with the metalloporphyrins. During photoelectrochemical CO_2RR using hybrid catalysts, electron transfer takes place at the interface of the metal oxide-metalloporphyrin system [4]. In our present study, we have studied transient absorption spectroscopy and spectroelectrochemical techniques to monitor the kinetics of the photoinduced electron transfer from metal oxide to metalloporphyrin unit, possible recombination processes, and correlate the efficiency of the electron transfer process with their CO_2RR/ HER catalytic reaction performances.

REFERENCES

1. Kumaravel, V., Bartlett, J., Pillai, S. C. *ACS Energy Lett*. 2020, *5*, 486−519.
2. Chatterjee, T., Boutin, E., Robert, M. *Dalton Trans*, 2020, *49*, 4257-4265.
3. Amanullah, SK., Saha, P., Nayek, A., Ahmed, Md. E., Dey, A. *Chem. Soc. Rev.*, 2021, *50*, 3755–3823.
4. Kandoth, N., Hernández, J.P., Palomares, E., Lloret-Fillol. J., *Sustainable Energy Fuels*, 2021, *5*, 638–665.

Erosion of the graded (and surprising) aromaticity of β-trioxopyrrocorphins upon reduction

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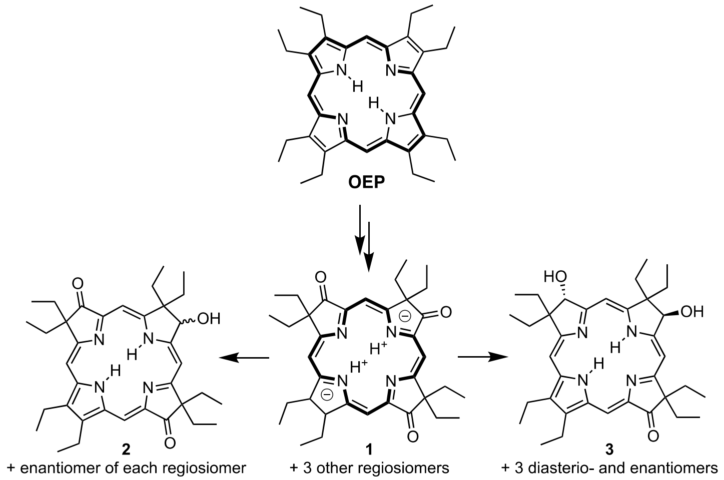
Octaethyltrioxopyrrocorphins, prepared by H_2O_2/sulfuric acid oxidation of octaethylporphyrin **OEP** (Scheme 1) [1], unexpectedly show macrocycle-aromatic properties, even though they contain the macrocyclic π-system of the non-aromatic pyrrocorphins (hexahydroporphyrins) [2]. All four regioisomers possess unique electronic properties, including broadly varying degrees of diatropicity that were experimentally determined using ^{1}H NMR spectroscopy and were computationally verified. In addition, the unusual halochromic properties of the triketones were also taken to support the proposed 16-membered, 18 π-electron aromatic ring-current [2].

The diatropic ring current of the triketones gets drastically reduced upon chemical reduction of one (forming alcohols **2**) and particularly two ketone moieties (forming diols **3**) [3]. With increasing reduction, the chromophores containing one pyrrole, one/two pyrrolinone, and one/two pyrrolines, respectively, become more like regular, non-macrocycle-aromatic pyrrocorphins [4]. Their weak diatropic ring currents, as assessed by ^{1}H NMR spectroscopy, showed them to possess largely non-aromatic π-systems. Computations were able to reproduce the experimental trends of the diatropic ring currents and to fill in data for the regio-isomers that could not be experimentally accessed.

The work conceptually expands the understanding of tris-modified hydroporphyrinoid analogues and further highlights the electronic influence of the β-oxo-substituents.



Scheme 1

REFERENCES

1. (a) Inhoffen, H. H.; Nolte, W. *Justus Liebigs Ann. Chem.* **1969**, *725*, 167–176. (b) Chang, C. K. *Biochemistry* **1980**, *19*, 1971-1976. (c) Brückner, C.; Chaudhri, N.; Nevonen, D. E.; Bhattacharya, S.; Graf, A.; Kaesmann, E.; Li, R.; Guberman-Pfeffer, M. J.; Mani, T.; Nimthong-Roldán, A.; Zeller, M.; Chauvet, A. A. P.; Nemykin, V., *Chem.—Eur. J.* **2021**, *27*, 16189–16203.
2. Chaudhri, N.; Guberman-Pfeffer, M. J.; Li, R.; Zeller, M.; Brückner, C. *Chem. Sci.* **2021**, *12*, 12292–12301.
3. Chaudhri, N.; Guberman-Pfeffer, M. J.; Zeller, M.; Brückner, C. **2022**, *submitted for publication*.
4. (a) Schwesinger, R.; Waditschatka, R.; Rigby, J.; Nordmann, R.; Schweizer, W. B.; Zass, E.; Eschenmoser, A. *Helv. Chim. Acta* **1982**, *65*, 600-610; (b) Peters, M. K.; Röhricht, F.; Näther, C.; Herges, R. *Org. Lett.* **2018**, *20*, 7879–7883.

Targeted Theranostic 111In/Lu-Nanotexaphyrin for SPECT Imaging and Photodynamic Therapy

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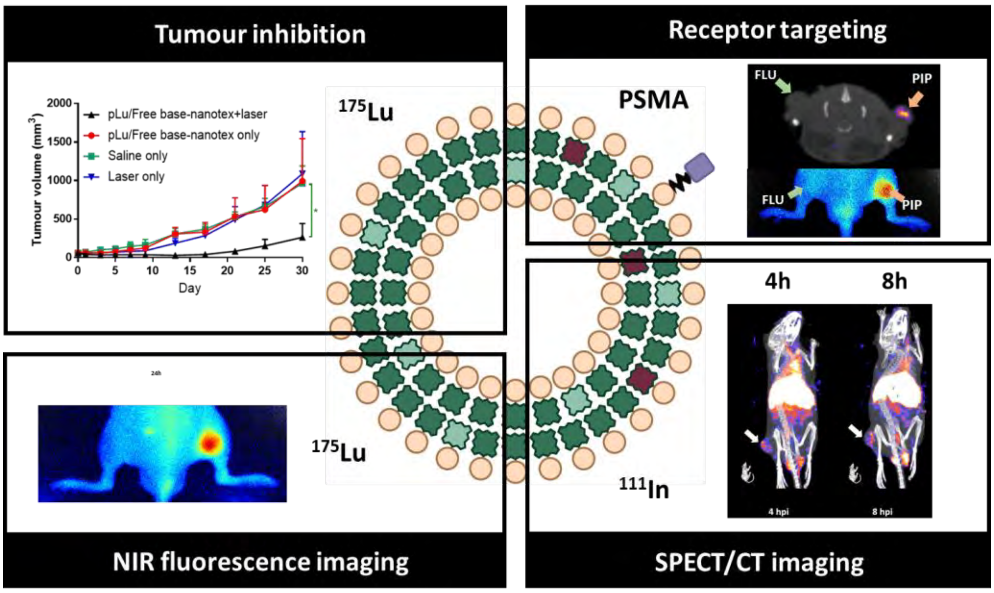

Theranostic nanoparticles aim integrate diagnostic imaging and therapy to facilitate image-guided treatment protocols. Herein, we present a theranostic nanotexaphyrin for prostate-specific membrane antigen (PSMA)-targeted radionuclide imaging and focal photodynamic therapy (PDT) accomplished through the chelation of metal isotopes (In, Lu). To realize nanotexaphyrin's theranostic properties we developed a rapid and robust ^{111}In/Lu-nanotexaphyrin radiolabeling method using a microfluidic system that achieved a high radiochemical yield (>90%). The optimized metallated nanotexaphyrin displayed excellent chemical, photo, and colloidal stabilities, potent singlet oxygen generation and favorable plasma circulation half-life *in vivo* ($t_{1/2}$ = 6.6 h). Biodistribution, including tumour accumulation was characterized by NIR fluorescence, SPECT/CT imaging and gamma counting. Inclusion of the PSMA targeting ligand enabled preferential accumulation of 111In/Lu-nanotexaphyrin in PSMA-positive prostate tumours (3.0 ± 0.3 %ID/g) at 48 h with tumour vs prostate in a 2.7:1 ratio. In combination with light irradiation, the PSMA targeting nanotexaphyrin showed a potent PDT effect and successfully inhibited PSMA+ tumour growth in a subcutaneous xenograft model. To the best of our knowledge, this study is the first demonstration of the inherent metal chelation-driven theranostic capabilities of texaphyrin nanoparticles, which in combination with PSMA targeting enabled prostate cancer imaging and therapy.

Development of new antimicrobial materials based on porphyrinoids

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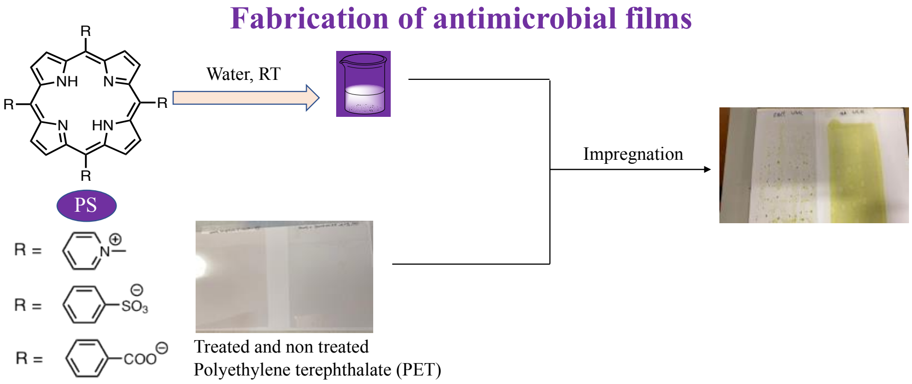
In France, each year more than 150.000 peoples suffer from infections caused by multi-resistant bacteria. Huge efforts have been dedicated to find alternative treatment methods to conventional antibiotics and Photodynamic Inactivation (PDI)[1,2] is considered as a promising one. PDI[3] is an innovative technique that is highly efficient against both gram-positive and gram-negative bacteria. Another advantage of this technique is that bacteria are not developing resistance against it. PDI is the combination of a photosensitizer (PS) and light in presence of oxygen to generate cytotoxic reactive oxygen species (ROS) that kill bacteria but also viruses, fungi and parasites. In this project, we were interested in the development of new antimicrobial films, based on porphyrinoids (porphyrins, chlorins and phthalocyanines) for PDI applications mainly in hygiene and food safety. These films could be used on different surfaces in order to kill bacteria and ~~to~~ prevent their growth. These antimicrobial materials could also prevent surface contamination.



REFERENCES

1. E. Tsuchida, H. Nishide, M. Ohyanagi, *J. Macromol. Sci.-Chem. A*, 1988, **25**, 1327-1338.
2. T. Hasobe, *J. Physical Chem. Lett.,* 2013, **4**, 1771-1780.
3. B. Habermeyer, T. Chilingaryan, R. Guilard, Bacterial Efficiency of Porphyrin Systems, *J. Porphyrins Phthalocyanines*, 2021, **25**, 359-381.

Heme *B* as catalyst for the green synthesis of the conductive emeraldine salt form of polyaniline

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In previous studies, the template-directed enzyme-catalyzed chemical oxidation leading to oligomeric/polymeric products resembling the emeraldine salt form of polyaniline (PANI-ES) was demonstrated. Aniline [1-4] or the linear aniline dimer, *p*-aminodiphenylamine (PADPA) [5], were used as starting materials in the presence of polymolecular anionic self-assembled structures. Such structures in the form of micelles or vesicles [1, 6] were used as templates [4, 7-9] to guide the reaction towards the formation of PANI-ES type products. One of the enzymes used in previous work was horseradish peroxidase (HRP) [1, 5, 10], with H_2O_2 as terminal oxidant.

In this work, we investigated whether HRP can be replaced by its prosthetic group, heme *B*, for the oxidative oligomerization of PADPA using SDBS (sodium dodecylbenzenesulfonate) micelles as molecular templates and hosts of heme *B*. How successfully HRP can be replaced by heme *B* has been assessed by spectroscopic analysis (UV/vis/NIR, EPR, and Raman) of the products obtained in aqueous media at pH = 4.3 and room temperature.

Criteria were set in terms of desired properties the product should possess: (i) presence of spectroscopic features that are typical for PANI-ES, (ii) high amounts of PANI-ES motifs, (iii) high quality of product, meaning, high fraction of favorable PANI-ES type units compared to unfavorable products containing branches or phenazine-type units, and (iv) no product precipitation.

Based on the results obtained, we conclude that HRP can be replaced successfully by heme *B* for the formation of PANI-ES type products with PADPA as starting monomer, although heme *B* is catalytically much less active than HRP. For production of the same amount of PANI-ES type materials, however, catalyst costs in the case of heme *B* are considerably lower than for the reaction with HRP.

REFERENCES

1. Junker, K., G. Zandomeneghi, Z. Guo, R. Kissner, T. Ishikawa, J. Kohlbrecher, and P. Walde. *RSC Advances*, 2012. **2**(16): p. 6478-6495.
2. Wang, R. and X. Huang. *ACS Omega*, 2021. **6**(31): p. 20699-20709.
3. Rumbau, V., J.A. Pomposo, A. Eleta, J. Rodriguez, H. Grande, D. Mecerreyes, and E. Ochoteco. *Biomacromolecules*, 2007. **8**(2): p. 315-317.
4. Liu, W., A.L. Cholli, R. Nagarajan, J. Kumar, S. Tripathy, F.F. Bruno, and L. Samuelson. *Journal of the American Chemical Society*, 1999. **121**(49): p. 11345-11355.
5. Luginbühl, S., M. Milojević-Rakić, K. Junker, D. Bajuk-Bogdanović, I. Pašti, R. Kissner, G. Ćirić-Marjanović, and P. Walde. *Synthetic Metals,* 2017. **226**: p. 89-103.
6. Liu, W., J. Kumar, S. Tripathy, and L.A. Samuelson. *Langmuir*, 2002. **18**(25): p. 9696-9704.
7. Zhang, Y., S. Serrano-Luginbühl, R. Kissner, M. Milojević-Rakić, D. Bajuk-Bogdanović, G. Ćirić-Marjanović, Q. Wang, and P. Walde. *Langmuir*, 2018. **34**(31): p. 9153-9166.
8. Walde, P. and Z. Guo. *Soft Matter*, 2011. **7**(2): p. 316-331.
9. Otrokhov, G.V., O.V. Morozova, I.S. Vasil'eva, G.P. Shumakovich, E.A. Zaitseva, M.E. Khlupova, and A.I. Yaropolov. *Biochemistry (Moscow)*, 2013. **78**(13): p. 1539-1553.
10. Kurisu, M., H. Aoki, T. Jimbo, Y. Sakuma, M. Imai, S. Serrano-Luginbühl, and P. Walde. *Communications Chemistry*, 2019. **2**(1): p. 117.

Photodynamic Immunotherapy with Bacteriochlorins: Mechanisms and Applications

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Bacterichlorins possess a characteristic intense electronic absorption in the near-infrared (NIR) from 700 nm up to 900 nm, where endogenous chromophores do not absorb and which allows deep penetration through tissues. Although naturally-occurring metal complexes derived from bacteriochlorophylls are unstable and their use is limited, it is currently possible to obtain large-scale libraries of photostable synthetic compounds belonging to the bacteriochlorin family. The first part of the work presents an up-to-date overview of the most significant studies on the synthesis, spectroscopic, photochemical, and electrochemical characteristics as well as various potential applications of bacteriochlorins in our laboratories [1-4].

The role of photodynamic-immunotherapy has become increasingly important compared to conventional treatments. One of the strategies is based on molecular targeting of immune checkpoints - a group of costimulatory molecules negatively regulating the immune system. Programmed death-1 (PD-1) and its ligand PD-L1 play a key role in tumor immune escape and formation of tumor microenvironment, closely related with tumor progression and invasiveness. Here, we present the design of combining anticancer modality based on PDT with checkpoint blockade immunotherapy. We developed novel PD-1/PD-L1-targeting molecules and present their therapeutic potential in combination with Redaporfin-PDT. We also compare the results with those obtained with anti-PD-1/PD-L1 mAbs. After comprehensive *in vitro* screening, we performed PDT augmented by systemic PD-1/PD-L1 inhibition *in vivo*. Using the multitarget approach it was possible to evaluate whether modulation of inflammatory response induced by PDT affect the tumor microenvironment and determine the susceptibility to systemic PD-1/PD-L1 inhibition including effects on primary tumor control as well as prevention of metastasis in a preclinical model. In summary, our data provide evidence for the role of PDT for local immune modulation, and that the combination with PD-1/PD-L1 axis inhibition is a promising strategy in the therapy of more resistant tumors [5-6].

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REFERENCES

1. B. Pucelik, A. Sułek, J.M. Dąbrowski, *Coord. Chem. Rev.* (2020) 416, 213340.
2. J.M. Dąbrowski, *Advances in Inorganic Chemistry* (2017) 70, 343-394.
3. B. Pucelik, A. Sułek, A. Barzowska, J.M. Dąbrowski *Cancer Letters* (2020) 492, 116-135.
4. B. Pucelik, LG Arnaut, JM Dąbrowski, *Journal of Clinical Medicine* (2020) 9, 8.
5. M. Karwicka, B. Pucelik, M. Gonet, M. Elas, J.M. Dąbrowski (2019) *Scientific Reports* 9, 1-15.
6. B. Pucelik, L.G. Arnaut, J.M. Dabrowski *ACS Appl. Mat. Interfaces* (2016) 8 (34), 22039-22055.

Porphyrin@CC: from laundry sheets to low-cost optical sensors and photocatalysts

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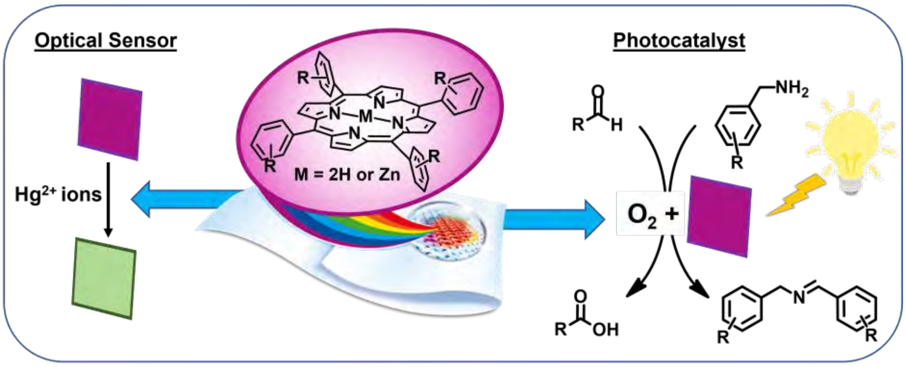
The easy synthetic access to *meso*-substituted porphyrins and their well-known photophysical properties makes these macrocycles very attractive for a broad range of applications as optical sensors [1] and photocatalysts [2]. However, the increasing demand for more sustainable, low-cost, and reusable systems has stimulated the scientific research to optimize the heterogenization of porphyrin-based compounds onto eco-compatible, readily available and inexpensive solid supports.

Thus, we studied an easy anchoring procedure to immobilize the porphyrin on the low-cost and commercially available Colour Catcher®(**CC**), a cellulose-based laundry sheet that is commonly used to absorb and trap colours released during the wash. By applying an ion-exchange strategy, we obtained the two solid-supported **TCPPH₂@CC** and **ZnClick@CC** porphyrins that revealed very good activity in sensing and photocatalytic applications, respectively (scheme 1).

The metal-free **TCPPH₂@CC** was an excellent and selective sensor for detecting mercury ions in aqueous solutions thanks to the eye-visible colour change of the sheet from purple to green that allows detecting concentrations of Hg^{2+} ions up to 1×10^{-8} M (below the limit value legally allowed in drinking water). The rapid response, combined with the high selectivity, makes **CC@TCPPH₂** perfectly suited to *in situ* monitoring of natural water sources or industrial discharges [3]. On the other hand, the **ZnClick@CC**, that contains a zinc(II) florurated porphyrin, showed a very good activity in the photo-oxidation of organic substrates, such as aldehydes and benzylamines [4]. The high activity and selectivity of **ZnClick@CC**, combined with its low-cost and recyclability, makes this heterogenous catalyst very interesting for large application in photocatalysis.



Scheme 1: Applications of **Porphyrin@CC** heterogenous systems.

REFERENCES

1. R. Paolesse, S. Nardis, D. Monti, M. Stefanelli and C. Di Natale, *Chem. Rev*. **2017**, 117, 2517-2583.
2. T. Costa e Silva, L. O. da Silva, A. de Andrade Bartolomeu, T. J. Brocksom and K. T. de Oliveira, *Beilstein J. Org. Chem.* **2020,** 16*,* 917–955.
3. F. Caroleo, G. Magna, C. Damiano, M. Cavalleri, E. Gallo, C. Di Natale, R. Paolesse. *Submitted*
4. *Manuscript in preparation*.

Elucidation of Powering the Artificial Photosynthesis by Charge Separated CdTe@CdS/Co-Porphyrin Materials

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Limiting fossils fuels and increasing global warming have dragged the attention of researchers for capturing and converting CO_2 to carbon-based fuel.[1] It can be done by solar energy through the photocatalysis in presence of water in a process called artificial photosynthesis (AP).[2] The reduction of CO_2 in presence of H_2O is very competitive with the oxidation of H_2O, where H_2O oxidation is a more feasible process than CO_2 reduction.[3] Semiconductor quantum dots (QDs) where an electron-hole (e-h) pair can be generated by a photon is one of the best materials for CO_2 reduction.[4] Metal-porphyrins can be coupled with QDs for better photocatalytic performance, employing the metal-porphyrin is an electron acceptor from NCs and an excellent catalyst for CO_2 reduction with quite good stability.[3, 4] However, the photochemistry of these composite systems is still unclear. The final products of the AP can be HCOOH, CH_4, CO, CH_3OH, etc, which is also ambiguous.[5] For boosting up the efficiency and selectivity of the CO_2 reduction, we have chosen CdTe and CdTe@CdS core-shell with metal-porphyrin composite systems where QDs and metal-porphyrin molecule act as photo sensitizer and catalyst, respectively. Here we studied the charge transfer and charge separation in CdTe/Co-porphyrin and CdTe@CdS/Co-porphyrin systems for CO_2 reduction by femtosecond transient absorption (TA) spectroscopy. Slower TA bleach dynamics of CdTe@CdS relative to CdTe core itself attributes to the long-lived charge separation in this type II materials.[6] Luminescence quenching of CdTe and CdTe@CdS in presence of Co-porphyrin molecule depicts either electron transfer or energy transfer from CdTe and CdTe@CdS to the Co-porphyrin molecule. The TA spectroscopy unveils the electron transfer from core and core shell to Co-porphyrin molecule. This charge transfer and charge separation in this CdTe@CdS/Co-porphyrin system can boost up the CO_2 reduction efficiency.

REFERENCES

1. Lewis, N. S. et. al. *Proc. Natl. Acad. Sci. U. S. A.* 2006, **103**, 15729−15735.
2. Smith P. et al. *Acc. Chem. Res.* 2020, **53**, 575−587.
3. Lian S. et.al. *J. Am. Chem. Soc.* 2017, **139**, 8931−8938.
4. Arcudi F. et al. *J. Am. Chem. Soc.* 2021, **143**, 18131–18138.
5. Yan Y. et.at. *J. Phys. Chem. C* 2011, **115**, 22717–22728.
6. Schops O. et. al. *J. Phys. Chem. B* 2006, **110**, 2074-2079.

A Mechanically Interlocked Jail for C$_{60}$ Fullerene

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Fullerenes and their derivatives present a wide range of applications highlighting their use in solar cells,[1]or biological applications.[2] However, their synthesis and purification is difficult and expensive. Functional systems formed from two or more porphyrin units, such as molecular tweezers, macrocycles or molecular cages, have been widely employed as supramolecular receptors for fullerenes.[3]

Here, we present a self-assembled molecular cage, formed by two porphyrin units tetra-functionalized and connected through molecular linkers (see Figure 1), which has the ability to host fullerene C60 into its inner cavity upon external stimulus. The mechanically interlocked nature of the jail was demonstrated, since fullerene C60 only can be released from the molecular cage by breaking (some of) its covalent structure.

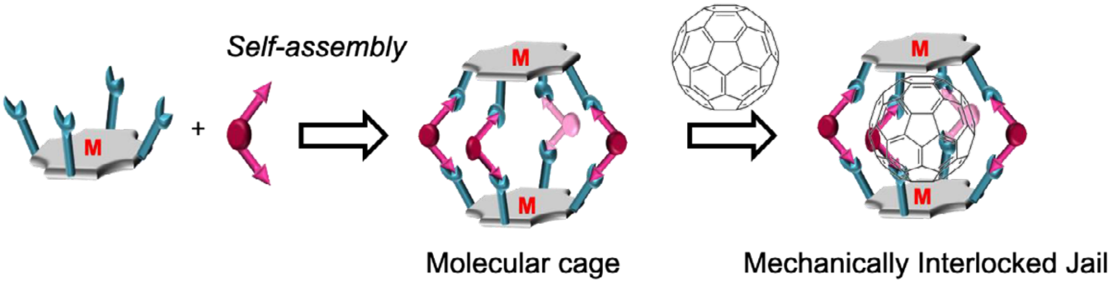

Figure 1. Schematic representation of the metalloporphyrin cage assembly and the mechanical jail for fullerene.

REFERENCES

1. J. M. J. Frochet et. al., *Angew.Chem.Int.Ed.,* **2008**, *47*, 58-77.
2. I. Rasovic, *Materials Science and Technology*, **2017**, *33*, 777-794.
3. a) X. Ribas, et. al., *Chem. Soc. Rev.*, 2016, 45, 40-62, b) S. Li, et. Al., *J. Porphyrins Phthalocyanines,* **2018**, *22*, 2-13.
4. A. de Juan, F. G. Guijarro, A. Martínez, M. García-Iglesias, D. González-Rodríguez, *manuscript in preparation.*

Tuning the Nonlinear Optical Contrast of Modified Hexaphyrin-based Molecular Switches using Inverse Design

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The search for efficient molecular electronic devices has recently intensified, motivated by their potential as a replacement of the omnipresent silicon-based technologies [1]. Due to their amazing tuneable chemical and photophysical properties, porphyrins and their expanded analogues are put forward as new test candidates for multiple applications ranging from medicine and photosensitizers to new materials such as nonlinear optical (NLO) materials [2,3]. The introduction of *meso*-substituents and core-modifications into these expanded porphyrins lead to enhanced values in the nonlinear optical properties and their corresponding NLO contrasts [4,5]. However, the influence of the *meso*-substituted structures on their respective structural parameters and nonlinear optical properties have been scarcely investigated. In this work, we aim to grasp the underlying concepts pivotal for the fine-tuning of the NLO contrasts of hexaphyrin-based molecular switches with Density Functional Theory (DFT) and an inverse design algorithm [6]. Starting from the unsubstituted hexaphyrins with different topologies and number of π-electrons, structure property relationships are established based on different structural parameters, aromaticity descriptors and first-hyperpolarizabilities related to the Hyper-Rayleigh Scattering (β_{HRS}). Comparing the unsubstituted to the modified hexaphyrin structures allowed us to retrieve variations in electronic, spectroscopic and NLO properties. By applying of the Best-First Search (BFS) algorithm on the most promising switches, we explored the combinatorial chemical compound space of hexaphyrin-based molecular switches with high NLO contrasts. Several *meso*-substitution patterns including both electron-donating and electron-withdrawing groups are identified increasing the NLO contrast. We concluded that both molecular symmetry as well as the electronic nature of the substituents are key players in tuning the β_{HRS} contrast of the hexaphyrin-based switches.

REFERENCES

1. B. L. Feringa, *Angew. Chem. Int. Ed.* **2017**, 56, 11060.
2. H. Imahori, *J. Phys. Chem. B* **2004**, 108, 6130.
3. T. Stuyver, M. Perrin, P. Geerlings, F. De Proft and M. Alonso, *J. Am. Chem. Soc.* **2018**, 104, 1313.
4. T. Tanaka and A. Osuka, *Chem. Rev.* **2017**, 117, 2584
5. T. Woller P. Geerlings, F. De Proft, B. Champagne and M. Alonso, *J. Phys. Chem C* **2019**, 123, 7318.
6. E. Desmedt, T. Woller, J. L. Teunissen, F. De Vleeschouwer, M. Alonso, *Front. Chem.* **2021**, 9, 786036.

Novel π-functional materials based on conjugated BODIPY-anthracenes

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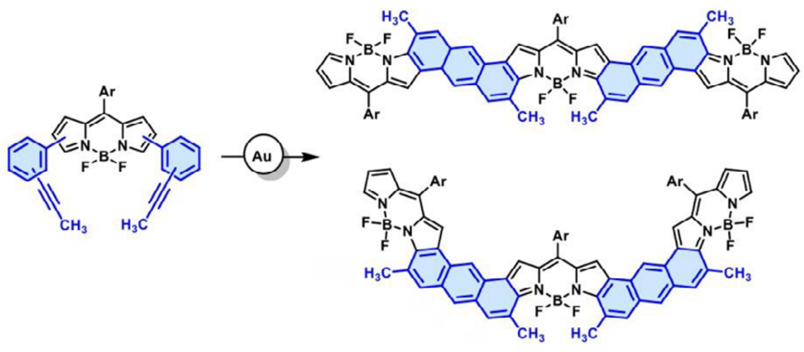
π-Conjugated polycyclic aromatic hydrocarbons (PAHs) have attracted increasing attention from the synthetic community due to their use in pharmaceuticals and materials [1] as well as their potential for the bottom-up construction of structurally uniform graphenes.[2] In this context, the fusion of dyes to the π-scaffold to boost the applications of PAHs constitutes a very promising but still unexplored approach. For this reason, the search for "dye-doping" alternatives would be highly desirable as it would enable the further development of this field and, thus, the design of novel doped π-functional materials.

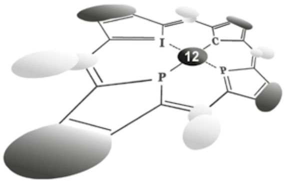
Nowadays, one of the widely used fluorophores in the field of biophotonic materials is the boron dipyrromethenes (BODIPYs) due to their advantageous photophysical properties, which include photostability, high extinction coefficients, and high luminescence efficiency.[3] Despite these advantages, the use of BODIPYs to dope carbon π-nanostructures has not been reported so far.

Considering the above mentioned, here we report the synthesis and study of novel BODIPY-anthracene hybrids (Scheme), with the aim of understanding the impact of incorporating BODIPYs in PAHs in terms of length and geometry of the π-conjugated structure. The synthesis of these derivatives is conducted through a straightforward synthesis involving Suzuki-Miyaura cross-couplings followed by Au(I)-catalyzed cyclizations. These derivatives offer valuable properties for technological applications, such as face-to-face supramolecular organization, NIR absorption and emission, and strong acceptor characters.



REFERENCES

1. Georgakilas, V., Perman, J.A., Tucek, J., Zboril, R., *Chem. Rev.* **2015**, *115*, 4744–4822.
2. Hoheisel, T.N., Schrettl, S., Szilluweit, T., Frauenrath, H., *Angew. Chem. Int. Ed.* **2010**, *49*, 6496–6515.
3. Loudet, A., Burgess, K., *Chem. Rev.* **2007**, *107*, 4891−4932.



Overcoming energy barriers to achieve complex ensembles in the self-assembly of metalloporphyrin binding peptides.

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Nature utilizes supramolecular, macrocycle binding, protein ensembles to afford many energy relevant processes including photosynthesis and long range electron transport in anaerobic cellular respiration. Over the past decade, we have synthesized a number of metalloporphyrin binding peptides that self-assemble into 0D, 1D, and 2D nanostructures in an attempt to replicate natural energetic processes or discover new energetic phenomena. Too often when developing these peptide structures, a pH trigger was deployed to initiate self-assembly. As a result, many earlier works were performed at high pH to overcome a buried polar amino acid, histidine, critical for binding metalloporphyrins. Recently, we have explored overcoming this energetic barrier of burying a polar amino acid within a peptide material through careful molecular design. Every peptide we have synthesized for metalloporphyrin binding is comprised of four main regions in our peptide design process: (1) the aliphatic tail, (2) the metalloporphyrin binding site, (3) the structural/β-sheet forming region, and (4) the polar head group. Here, we take two approaches to overcome the energetic barrier of burying a polar amino acid. First, we manipulate the β-sheet region to explore the impact that employing higher β-sheet propensity amino acids to ensure greater intermolecular packing that yields metalloporphyrin binding sites. Second, we create electrostatic peptide pairs to yield a 1D ensemble. As a result of these two studies, we begin to approach more complicated architectures where we can create stable 0D light harvesting antennae that can be coupled to 1D reaction centers thus achieving complex architectures from simple synthetic precursors.

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SubPcs - Peryleneimides for Optoelectronical Applications

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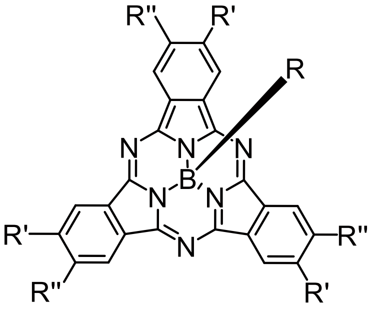
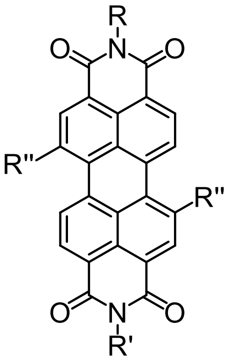
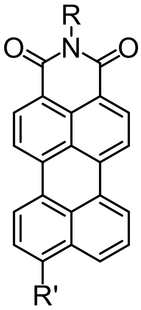
SubPcs are usually modified with different highly conjugated structures in order to improve their general properties. Their derivatization with bulky and/or fluorescent molecules changes characteristics such as their absorption, band gap, stacking or stability; which are directly related to their applications in, for example, the design of organic solar cells.

Years ago, the group worked in the synthesis of several perylenediimide (PDI) – subphthalocyanine derivatives. Then, it was demonstrated an ultrafast photoinduced electron transfer whenever the PDIs are introduced in axial position of the SubPc [1]. However, this is a field with a lot of potential and not fully explored; different derivatives could be studied by introducing PDIs and PMIs into the axial- [2] or para- [3] positions of the SubPc; finding a straightforward relation with the electronical properties and intramolecular interactions. Here, we are working in new ways to combine SubPcs+PDIs or SubPcs+PMIs to study these phenomena.







REFERENCES

1. Romero-Nieto, C.; Guilleme, J.; Fernández-Ariza, J.; Rodríguez-Morgade, M. S.; González-Rodríguez, D.; Torres, T.; Guldi, D. M. Ultrafast Photoinduced Processes in Subphthalocyanine Electron Donor–Acceptor Conjugates Linked by a Single B–N Bond. *Org. Lett.* **2012**, *14*, 5656–5659.
2. Kasi Viswanath, L. C.; Shirtcliff, L. D.; Krishnan, S.; Handa, N. V.; Darrell Berlin, K. Synthesis, Photophysical and Electrochemical Properties of Bay-Axial Perylene Diimide–Subphthalocyanine Dyads. *Tetrahedron Letters* **2014**, *55*, 4199–4202.
3. Hang, H.; Zhang, Z.; Wu, X.; Chen, Y.; Li, H.; Wang, W.; Tong, H.; Wang, L. Subphthalocyanine-Cored Star-Shaped Electron Acceptors with Perylene Diimide Wings for Non-Fullerene Solar Cells. *J. Mater. Chem. C* **2018**, *6*, 7141–7148.

Photoinduced proton-coupled electron transfer processes in bioinspired systems

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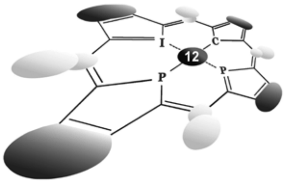
To study a photoinduced proton-coupled electron transfer (PCET) process, we covalently attached a benzimidazole–phenol (BIP) unit to a tripentafluorophenylporphyrin (PF$_{15}$).[1] The BIP system has been used to illustrate an E1PT process, where one-electron oxidation of the phenol is accompanied by the transfer of its proton to the attached benzimidazole. IR spectroelectrochemistry (IRSEC) of BIP–PF$_{15}$ showed that upon electrochemical oxidation a new band at 1552 cm^{-1} appeared, corresponding to the formation of the benzimidazolium cation following intramolecular proton transfer from the phenol to the attached benzimidazole. Upon electrochemical reduction of BIP–PF$_{15}$, a new band characteristic of the porphyrin radical anion formation was observed at 1593 cm^{-1}. Based on these IR signatures, a detailed study of the dynamics of the photoinduced E1PT process was investigated by transient IR and two-dimensional electronic–vibrational (2DEV) spectroscopies, along with calculations using long-range-corrected hybrid density functionals. Excitation of the porphyrin unit of BIP–PF$_{15}$ results in processes that take place on two-time scales: 1) an ultrafast process from the initially prepared, unrelaxed excited level, and 2) a slower process on the time scale of a few hundred picoseconds arising from the relaxed lowest excited singlet state of PF$_{15}$. The ultrafast process is not the dominant pathway, but it enables observations which we interpret as the evolution of an initial, partly charge transferred state to full charge separation on the 120 fs time scale. This interpretation is supported by a theoretically predicted dipole moment arising from dihedral twisting between the BIP and the plane of the PF$_{15}$ macrocycle.[2] Substitutions on the BIP in BIP–PF$_{15}$ dyads to include proton-accepting groups with sufficiently high pK_a predispose the system for a photoinduced one-electron two-proton transfer (E2PT) process. Pyridine or substituted pyridines have been shown to have the required pK_a's for acting as a secondary or terminal proton acceptor.[3,4] Upon protonation, the resulting pyridinium cations display distinctive IR absorptions which differ from the neutral pyridyl state. Preliminary analysis of 2DEV results indicates the electron and protons translocation occur within a few hundred fs via a concerted process. These bioinspired dyads enable exploration of the differences in the dynamics of photoinitiated E1PT and E2PT processes. Further elaboration of these systems is planned with the objective of constructing molecular proton wires or circuits over which protons are translocated, as a consequence of a photoinduced electron transfer process, over long (~ 30Å) distances by a Grotthuss-type mechanism.

REFERENCES

1. Mora, S. J.; Heredia, D. A.; Odella, E.; Vrudhula, U.; Gust, D.; Moore, T. A.; Moore, A. L. JPP 2019, 23, 1336-1345.
2. Yoneda, Y.; Mora, S. J.; Shee, J.; Wadsworth, B. L.; Arsenault, E. A.; Hait, D.; Kodis, G.; Gust, D.; Moore, G. F.; Moore, A. L.; Head-Gordon, M.; Moore, T. A.; Fleming, G. R. J. Am. Chem. Soc. 2021, 143, 3104-3112.
3. Guerra, W. D.; Odella, E.; Secor, M.; Goings, J. J.; Urrutia, M. N.; Wadsworth, B. L.; Gervaldo, M.; Sereno, L. E.; Moore, T. A.; Moore, G. F.; Hammes-Schiffer, S.; Moore, A. L. J. Am. Chem. Soc. 2020, 142, 21842-21851.



Triphenylamine substituted copper and zinc phthalocyanines as alternative hole-transporting materials for solution-processed perovskite solar cells

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Perovskite solar cells (PSCs) are promising for use as a renewable energy source due to their high mobility, unique optoelectronic properties, and simple fabrication by solution-processing methods. Although perovskites were started to be studied with a power conversion of 3.8% in 2009, today the power conversion values have reached 25% [1]. However, the instability problem observed in many PSCs under normal operating conditions (under 1 sun illumination at 27 °C and without UV filtration) is one of the main barriers to the successful commercialization of such devices. More recently, it was shown that the stability of the PSCs can be improved by different strategies such as by selecting an appropriate hole transport material (HTM), by choosing electron transport layer, by solvent engineering, and optimizing the PSCs encapsulation process. As one strategy for cost-effectiveness, choosing a suitable hole transport layer seems to be the most effective way to solve the instability problem in PSCs [2, 3].

In this work, the Pc ring was molecularly tailored by adding four triphenylamine (TPA) groups on peripheral position through the oxygen atoms. To improve the solubility in common solvents as well as the hydrophobic quality was appended *tert*-butyl unit as an alkyl group to TPA. In this respect, tetra-4-(bis(4-*tert*-butylphenyl)amino)phenoxy-substituted Cu and ZnPc derivatives (**p-ZnPc** and **p-CuPc**), were synthesized. The optical and electrochemical properties of these compounds were characterized. The purpose of this study is to examine the effect of the **p-ZnPc**, and **p-CuPc** as HTM on the long-term stability of PSCs under real operating conditions. For this purpose, PSCs were fabricated with and without HTM to analyse the role of HTM and explore the effect of using different materials on the long-term stability of the perovskite solar cells.

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REFERENCES

1. Chen W, Wu Y, Yue Y, Liu J, Zhang W, Yang X, et al. *Science*, 2015;350:944–8.
2. Sathiyan G, Syed AA, Chen C, Wu C, Tao L, Ding X, et al. *Nano Energy* 2020;72:10467.
3. Feng Y, Hu Q, Rezaee E, Li M, Xu ZX, Lorenzoni A, et al. *Adv Energy Mater* 2019;9:190101.

Oxidation-State Tuning and Supramolecular Mixed-Valence Phases: Nickel(II) Porphyrin and Nickel(II) Corrole on Different Metal Surfaces

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Nickel tetrapyrrole complexes whose structure is related to biologically relevant molecules (e.g., F430 cofactor, tunichlorin and nibalamine) are promising precursors for novel functional surfaces in which the active sites are anchored in a highly ordered nanostructure. Here, we cover different strategies to specifically modify the properties of the nickel centers in a monomolecular layer by tuning the interactions between the complexes and the underlying substrate.

First, we report on the influence of the interaction at the metal/organic interface on the electronic structure of a nickel porphyrin (Ni(OEP)) monolayer. This was studied on different coinage metal surfaces by X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), scanning tunnelling microscopy (STM), near edge X-ray absorption fine structure (NEXAFS) and low-energy electron diffraction (LEED). On Ag(111), Ni(OEP) forms a mixed-valent adsorbate structure in which the Ni centers occur in different oxidation states. The two separate peaks in the Ni 2p XP spectrum indicate that about 40% of the Ni centers are reduced. STM and LEED show an incommensurate superstructure with an ordered arrangement of the metal centers in different oxidation states. Further insights into the valence electronic structure were obtained by UPS and NEXAFS. On the more reactive Cu(111) surface, Ni(OEP) forms a long-range ordered structure in which nickel centers are uniformly reduced. In contrast, on the least reactive Au(111) surface, the oxidation state of the Ni centers remains unaffected by adsorbate/substrate interactions. By comparing the characteristics of Ni(OEP) on differently terminated single crystal surfaces (Ag(111), Ag(100), Ag(110)), the influence of the substrate lattice on the electronic state of the Ni centers is further investigated.

Finally, we show how the oxidation state of the central atom and the interaction of a nickel tetrapyrrole can be influenced by a modification of the ligand skeleton, i.e., using a nickel corrole complex. The investigated corrole complex (Ni(HEDMC)) retains the nickel(II) oxidation state[1] even on the reactive Cu(111) surface, as shown by XPS. This is accompanied by an integer charge transfer from the metal surface into the former singly occupied orbital. Thus, nickel corrole complexes are substantially different from corresponding porphyrin complexes, in which the nickel centers are uniformly reduced.

REFERENCES

1. J. Herritsch, J.-N. Luy, S. Rohlf, M. Gruber, B. P. Klein, M. Kalläne, P. Schweyen, M. Bröring, K. Rossnagel, R. Tonner, J. M. Gottfried, *Influence of ring contraction on the electronic structure of nickel tetrapyrrole complexes: corrole vs porphyrin*, *ECS J. Solid State Sci. Technol.* 9 (2020), 061005, https://doi.org/10.1149/2162-8777/ab9e18.

Novel next-generation porphysome nanoplatform for photodynamic therapy applications

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Porphysomes (PS) are non-toxic, liposome-like nanoparticles self-assembled and composed of porphyrin-lipid conjugates [1]. The high packing density of porphyrins in PS (>80 000 porphyrins per particle) enables the use of PS for both photonic-based therapy and imaging applications [1]. One such application is their use as photodynamic therapy (PDT) agents, where porphyrin irradiation with light generates cytotoxic reactive oxygen species for local cancer cell and tissue destruction. However, PS suffer from limited uptake in cancer cells, which has greatly hampered its PDT application [2-3]. We have recently developed a new generation of porphysome nanoparticles (NPS) which utilize a novel EDTA-nanoparticle mediated strategy to overcome the current limitations of PS. We found that NPS was able to significantly enhance the intracellular accumulation of PS in KB cervical cancer cells after 6 hours of incubation. Herein, we present the results of the most suitable NPS formulation we discovered to date for *in vivo* applications due to its higher serum stability and pharmacokinetics. NPS was found to remain over 85% quenched in 50 v/v% fetal bovine serum over a period of 24 hours and possessed an elimination half-life of 7.5 ± 0.8 hours. NPS exhibited significant photocytotoxicity compared to PS after a short 3-hour incubation in KB cells when irradiated with a 660 nm BioTable light box and displayed minimal dark toxicity. A recent *in vivo* PDT efficacy study in KB subcutaneous tumour-bearing mice demonstrated the ability of NPS to significantly suppress tumour growth with a higher rate of tumor eradication and increased survival rate with a 3-, 6-, and 24-hour drug-light-interval (DLI) compared to PS with a 24-hour DLI. This work aims to introduce our novel NPS as a promising nanoplatform for cancer PDT. Our results encourage further investigation into understanding the underlying mechanism and application of this EDTA-nanoparticle approach to improve current nanomedicine formulations that are hindered by poor cellular uptake.

REFERENCES

1. J. F. Lovell, S. Jin, E. Huynh, H. Jin, C. Kim, J. L. Rubinstein, W. C. Chan, W. Cao, L. V. Wang and G. Zheng, "Porphysome nanovesicles generated by porphyrin bilayers for use as multimodal biophotonic contrast agents," *Nature Materials*, vol. 10, pp. 324-332, 2011.
2. C. S. Jin, L. Cui, F. Wang, J. Chen and G. Zheng, "Targeting-triggered porphysome nanostructure disruption for activatable photodynamic therapy," *Adv Healthc Mater*, vol. 3, no. 8, pp. 1240-9, 2014.
3. K. K. Ng, M. Takada, C. S. Jin and G. Zheng, "Self-Sensing Porphysomes for Fluorescence-Guided Photothermal Therapy," *Bioconjugate Chem*, vol. 26, no. 2, pp. 345-351, 2015.

Verteporfin Photodynamic Therapy: An Enabling Technology to Improve Brain Drug Delivery and Tumor Control

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Most primary brain tumors are managed by maximal safe resection followed by adjuvant chemoradiation to treat residual and potentially infiltrative tumor cells [1]. However, these adjuvant approaches do not effectively treat the tumor-invaded brain regions due to an intact blood-brain barrier (BBB) that restricts drug penetration or a high risk of toxicity to nearby neural structures [2]. The strength of the BBB in protecting brain tumors from exposure to circulating drugs is maintained by not only the intact endothelial tight junctions, but also a range of ATP-binding cassette (ABC) drug efflux transporters on endothelial and cancer cells [3]. My research program is interested in using verteporfin-based photodynamic therapy (PDT) to open the BBB tight junctions and shut down ABC transporters without damaging normal tissues [4, 5, 6]. This approach offers a more specific and less disruptive strategy to deliver drugs to recurrent or residual brain tumors effectively. Furthermore, we will discuss a surfactant-free approach to prepare novel amorphous verteporfin nanosuspensions. The verteporfin nanosuspensions can be activated upon cancer cell uptake, enabling PDT and fluorescence imaging of tumors in vivo. We demonstrate up to a 10-fold increase in anti-cancer efficacy of the verteporfin nanosuspensions in glioblastoma cells and animal models, compared to the clinically used liposomal verteporfin formulation. We will also discuss the planning of a clinical trial to evaluate verteporfin nanosuspensions for PDT of brain cancer.

REFERENCES

1. Di Carlo DT, Cagnazzo F, Benedetto N, Morganti R, Perrini P. Multiple high-grade gliomas: epidemiology, management, and outcome. A systematic review and meta-analysis. Neurosurgical Review. 2019;42(2):263-75. doi: 10.1007/s10143-017-0928-7. PubMed PMID: 29138949
2. Sarkaria JN, Hu LS, Parney IF, Pafundi DH, Brinkmann DH, Laack NN, Giannini C, Burns TC, Kizilbash SH, Laramy JK, Swanson KR, Kaufmann TJ, Brown PD, Agar NYR, Galanis E, Buckner JC, Elmquist WF. Is the blood-brain barrier really disrupted in all glioblastomas? A critical assessment of existing clinical data. Neuro Oncol. 2018;20(2):184-91. doi: 10.1093/neuonc/nox175. PubMed PMID: 29016900; PMCID: PMC5777482.
3. Eisenblatter T, Huwel S, Galla HJ. Characterisation of the brain multidrug resistance protein (BMDP/ABCG2/BCRP) expressed at the blood-brain barrier. Brain research. 2003;971(2):221-31. PubMed PMID: 12706238.
4. Inglut CT, Baglo Y, Liang BJ, Cheema Y, Stabile J, Woodworth GF, Huang H-C. Systematic Evaluation of Light-Activatable Biohybrids for Anti-Glioma Photodynamic Therapy. Journal of Clinical Medicine. 2019;8(9). doi: 10.3390/jcm8091269. PubMed PMID: 31438568.
5. Baglo Y, Liang BJ, Robey RW, Ambudkar SV, Gottesman MM, Huang H-C. Porphyrin-lipid assemblies and nanovesicles overcome ABC transporter-mediated photodynamic therapy resistance in cancer cells. Cancer Letters. 2019;457:110-8. doi: 10.1016/j.canlet.2019.04.037. PubMed PMID: 31071369; PMCID: PMC6690745.
6. Liang BJ, Lusvarghi S, Ambudkar SV, Huang H-C. Mechanistic Insights into Photodynamic Regulation of Adenosine 5′-Triphosphate-Binding Cassette Drug Transporters. ACS Pharmacology & Translational Science. 2021;4(5):1578–1587. doi.org/10.1021/acsptsci.1c00138.

An unexpected way to 1,4-diketones – site-selective C(sp^3)–H oxidation of arylalkanes

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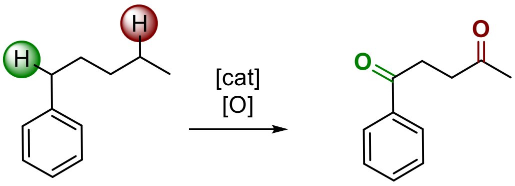
C–H functionalization represents a powerful approach to the synthesis of complex molecules [1]. Previous studies showed metalloporphyrins as effective catalysts in such reactions [2]. The activity and selectivity of these complexes strongly depend on the central metal, and on stereo-electronic features of porphyrin ligands. Under the current protocols, specific substrates bearing one inherently most reactive C–H bond react with high selectivity, while other substrates typically react unselectively, leading to a mixture of products. The control of regioselectivity for such unactivated substrates remains challenging, partially due to the relatively low reactivity of current catalysts, which require high temperatures to operate [3-5].



One of an interesting class of compounds, to which so far no direct way, when starting from alkanes/arylalkanes, has been reported are 1,4-dicarbonyl compounds. 1,4-dicarbonyls are common synthetic precursors for bioactive 5-membered heterocycles such as furans, thiophenes, pyrroles and cyclopentenones [6].

We have development a complete methodology for one-pot oxidation of arylalkanes to obtain 1,4-diketones under mild conditions with high site-selectivity and using water, as a main solvent.

REFERENCES

1. Bietti, M., *Angew. Chem. In. Ed.* **2018**, *57*, 16618.
2. Liu, W.; Ren, Z.; Bosse, A. T.; Liao, K.; Goldstein, E. L.; Bacsa, J.; Musaev, D. G.; Stoltz, B. M.; Davies, H. M. L., *J. Am. Chem. Soc.* **2018**, *140*, 12247.
3. Liao, K.; Negretti, S.; Musaev, D. G.; Bacsa, J.; Davies, H. M. L., *Nature* **2016**, *533*, 230.
4. Liao, K.; Pickel, T. C.; Boyarskikh, V.; Bacsa, J.; Musaev, D. G.; Davies, H. M. L., *Nature* **2017,** *551*, 609.
5. Che, C.-M.; Lo, V. K.-Y.; Zhou, C.-Y.; Huang, J.-S., *Chem. Soc. Rev.* **2011**, *40*, 1950.
6. Ma, X.; Dewez, D. F.; Du, L.; Luo, X.; Markó, I. E.; Lam, K., *J. Org. Chem.* **2018**, *83*, 12044.

Straightforward access to functional porphyrins from meso-poly-halogeno-alkyl-dipyrromethanes

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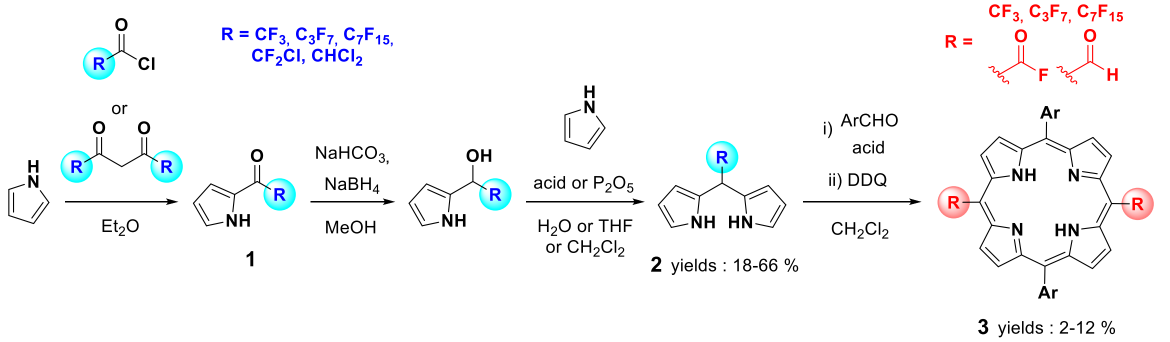
Although porphyrins and their derivatives have been studied for over a century, only very few examples of *meso*-poly-halogeno-alkyl porphyrinoïds have been brought up to light [1]. These substituents are unique because i) they increase the lipophilicity and/or the metabolic stability of the macrocycles, ii) they can induce non planar distortion or photo-stability leading to numerous possible applications [2]. Porphyrinoïds are also widely used as catalysts whose activity can be enhanced by adding electron withdrawing groups on *meso* positions [3]. This presentation will focus on original synthetic pathways to access poly-halogeno-alkyl-dipyrromethanes **2** from acylpyrroles **1**, and their use in the preparation of unprecedented A_2B_2-porphyrins **3** bearing either two perfluoroalkyl chains, two formyl groups or two rarely observed fluoro acyl moieties [4]. Those dipyrromethanes can also be used in the preparation of innovative A_2B corroles *via* a bilane intermediate. A physico-chemical characterization of porphyrins **3** will be also enlightened by their distinctive electrochemical and photophysical properties that vary significantly with the nature of the functional substituents.



REFERENCES

1. a) Wijesekera T. P., *Can. J. Chem.* **1996**, *74*, 1868; b) Nishino N., Wagner R. W., Lindsey J. S., *J. Org. Chem.* **1996**, *61*, 7534.
2. a) Smart B. E., *J. Fluorine Chem.* **2001**, *109*, 3; b) Rivkin A., Biswas K., Chou T.-C., Danishefsky S. J., *Org. Lett.* **2002**, *4*, 4081; c) DiMagno S. G., Williams R. A., Therien M. J., *J. Org. Chem.* **1994**, *59*, 6943; d) DiMagno S. G., Wertsching A. K., Ross C. R., *J. Am. Chem. Soc.* **1995**, *117*, 8279; e) Thomas K. E., Conradie J., Hansen L. K., Ghosh A., *Inorg. Chem.* **2011**, *50*, 3247.
3. a) DiMagno S. G., Dussault P. H., Schultz J. A., *J. Am. Chem. Soc.* **1996**, *118*, 5312; b) Zhang W., Lai W., Cao R., *Chem. Rev.* **2017**, *117*, 3717.
4. Julliard P. G., Pascal S., Siri O., Cortés-Arriagada D., Sanhueza L., Canard G., *Comptes Rendus. Chimie* **2021**, *24*, 27.

Nonlinear Optical Properties of Metal Free Thio Alkyl and Tert-butyl Phenoxy Phthalocyanines

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NLO limiting materials, such as phthalocyanines, are of interest due to the need to protect sensitive optical devices, especially human eyes, from high intensity light sources such as lasers. These materials show considerable nonlinear optical responses to a high intensity light [1]. NLO materials also provide a non-mechanical method of controlling light intensity. These responses are typically as a result of the atomic or molecular structure of the material [2]. This work reports on the nonlinear optical properties of tetra - and octa substituted phthalocyanines (Pcs) utilising pentane thiol and 4-tertbutyl phenol as substituents. Their nonlinear absorption coefficient (β) and absorption cross sections were determined using the Z-scan technique with a 10 ns pulse laser at 532 nm. The molecular second order hyperpolarizability Im[γ] was observed and the following Im[γ] trend was obtained for α- $H_2Pc(SC_5H_{11})_4$ isomers, 5.93×10^{-31} (C_s) 2.24×10^{-32}(D_{2h}) > 1.21×10^{-32}(C_{4h}) > 1.05×10^{-32} (C_{2v}) esu, respectively, in chloroform. Symmetry was observed to have an effect on the reverse saturable absorption (RSA) response. When the alkyl thio substituent is replaced with tertbutylphenoxy substituent at the β position, 10-fold improvement in Im[γ] value was observed.

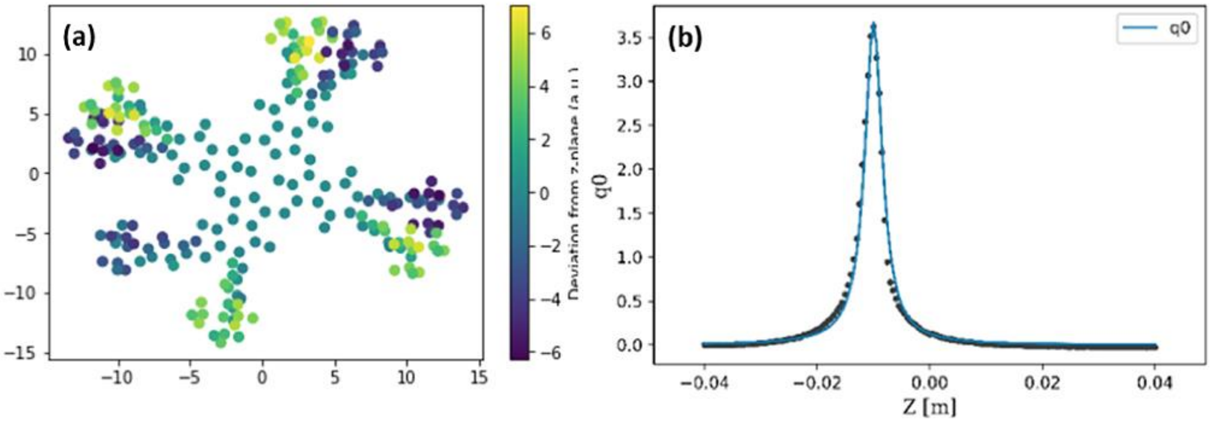

Figure 1:(a) Geometrically optimised phthalocyanine model of $\boldsymbol{\beta}$-$H_2Pc(tert\text{-}BPh)_8$ and **(b)** Open aperture nonlinear fit z-scan curve

REFERENCES

1. Britton, J., Martynov, A. G., Oluwole, D. O., Gorbunova, Y. G., Tsivadze, A. Y., & Nyokong, T., Journal of Porphyrins and Phthalocyanines,2016, 1296-1305.
2. Ying Xie, Fei Liang, Bo Zhang, Binghui Ge, Haohai Yu, Zheshuai Lin, Z., & Wang, Huaijin Zhang, Baibiao Huang, J. W., ACS Omega, 2019, 4, 1045–1052.

Synthesis and studies of NIR-absorbing porphyrin−ryleneimide hybrids and donor–acceptor heterodimer *via* trifunctional completive self-sorting

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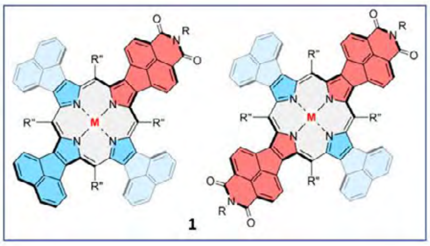
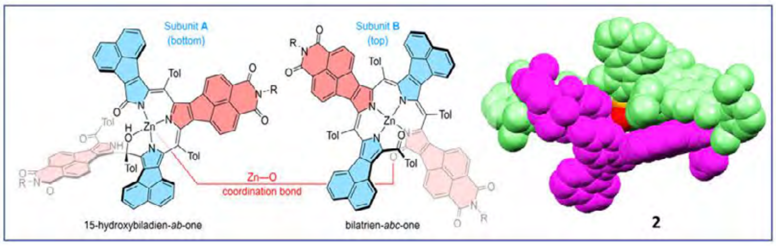
Ryleneimides, most notably perylenediimides (PDIs), are one of the most important classes of organic dyes, with an exceptional scope of industrial and research applications.[1] The development of unsymmetrically fused porphyrins **1**[2] containing one or two naphthalimide subunits in modular syntheses relying on electron-rich and electron-poor pyrrole building blocks. These new chromophores show progressive changes of their electron-deficient character while retaining comparably small optical and electrochemical bandgaps. The electronic band gap is significantly affected when NMI moieties added to the chromophores, the smallest gap is observed for the tD_2A_2 porphyrin, which is highly attractive as an NIR-absorbing. Photocleavage of a donor–acceptor porphyrin complex was found to produce an unprecedented heterodimeric **2**[3] structure with surprising selectivity. The system forms via a multi-step sequence that starts with an oxidative ring opening, which produces an equimolar mixture of two isomeric zinc(II) bilatrien-abc-ones (BTOs). The two isomers are susceptible to water addition, yielding the corresponding zinc(II) 15-hydroxybiladien-ab-ones (HBDOs). However, in the photocleavage experiment only one HBDO isomer was formed, and it quantitatively combined with the remaining BTO isomer. The resulting heterodimer was characterized in the solid state and in solution, and found to be stabilized by a Zn–O coordination bond and extended dispersion interactions between the overlapping π-surfaces of the monomers. The observed selectivity, which was explored in detail using chemical and computational methods, can be seen as a case of completive self-sorting, driven by three types of complementary interactions make them of interest as mono- and difunctional components of multichromophoric assemblies.





REFERENCES

1. Würthner, F.; Saha-Möller, C. R.; Fimmel, B.; Ogi, S.; Leowanawat, P.; Schmidt, D. *Chem. Rev.* **2016**, 116 , 962-1052.
2. Kumar, S.; Maurya, Y. K.; Kang, S.; Chmielewski, P.; Lis, T.; Cybińska, J.; Kim, D.; Stępień, M. *Org. Lett.* **2020**, 7202-7207.
3. Kumar, S.; Maurya, Y. K.; Lis, T.; Stępień, M. *Manuscript submitted.*

New avenues in the fabrication of SubPc-based molecular materials: Chirality, *C-H* activation, and supramolecular organization

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By virtue of their outstanding structural and photophysical properties (*i.e.*, intense absorption and/or emission in the UV-vis and near-infrared (NIR) region, excellent charge transport properties, and a wide chemical versatility), **Subphthalocyanines** (**SubPcs**; Figure 1) actually hold a privileged position among the most exploited and versatile porphyrinoids [1]. These aromatic macrocycles, with their singular non-planar structure, have demonstrated a great potential in many state-of-art applications, including the fabrication of polar superstructures, thermotropic and lyotropic liquid crystals, non-fullerene acceptors and singlet fission materials [2].

Herein we disclose particular aspects within the SubPc chemistry which could open a new dimension in the design, synthesis, and application of SubPcs. First, we analyze the impact of the intrinsic chirality of SubPcs on aspects as fundamental as the supramolecular organization, the behavior in contact with metallic surfaces, or the reactivity (Figure 1a). Next, we described novel methodologies to prepare complex SubPcs from very simple substrates *via* novel *C-H* activation reactions (Figure 1b). Finally, we report the synthesis and characterization of SubPc columnar materials which, depending on the molecular design, behave as lyotropic or thermotropic liquid crystals, form columnar polymers in solution or organize into polar assemblies in the solid state (Figure 1 c). The factors that govern such unusual behaviours are discussed by a combination of several experimental techniques and theoretical calculations.

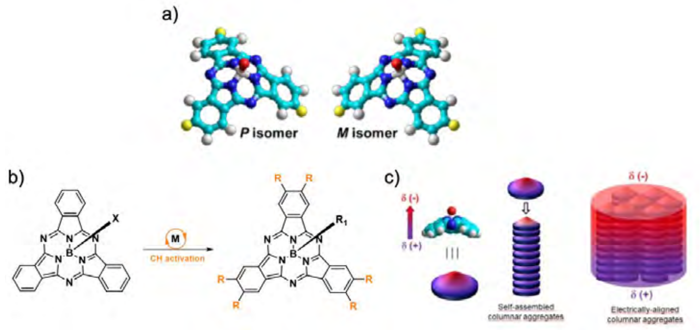

Figure 1. a) Molecular structure of SubPc enantiomers. b) Representation of peripheral functionalization of SubPcs via C-H activation. c) Columnar structures resulting from the assembly of SubPc molecules.

REFERENCES

1. Claessens, C. G. et al., Chem. Rev. 2014, 114, 2192-2277.
2. a) Guilleme, J. et al., J. Mater. Chem. C 2015, 3, 985-989. b) Guilleme, J. et al., Adv. Mater. 2015, 27, 4280-4284. c) Mayoral, M.J. et al., J. Am. Chem. Soc. 2020, 142, 21017-21031. d) Duan, C. et al., Angew. Chem. Int. Ed. 2017, 56, 148-152. e) Labella, J. et al. J. Mater. Chem. C, 2021,9, 16298-16303. f) Lavarda, et al. G., Angew. Chem. Int. Ed. 2018, 57, 16291-16295.

On-surface synthesis of fused anthracenyl porphyrin derivatives

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For the last fifteen years, on-surface synthesis became an extremely popular and powerful method to fabricate nanostructures which otherwise would not have been accessible by conventional wet organic syntheses. The syntheses, realized in the chamber of high vacuum scanning tunneling microscope (STM), permitted the fabrication and the characterization of atomically defined nanostructures such as polycyclic aromatic hydrocarbons (PAH), graphene nanoribbons or 2D covalent networks.[1] Among the organic molecules studied by STM, porphyrins are of particular importance because of their electronic and optical properties. Initial studies were mainly devoted to the supramolecular organization of porphyrins and porphyrin derivatives on surface and it is only in 2004 that noble metal surfaces were used as catalytic surface to perform reactions on the porphyrin cores.[2] Since then, examples of open-shell porphyrin derivatives [3] and conjugated oligomers [4] were reported.

While the synthesis of fused bis- and tetra-4,5-bis-(2,4,6-trimethylphenoxy)anthracen-9-yl porphyrins containing Ni(II) was reported by Anderson about 10 years ago,[5] the formation π-extended porphyrin bearing unsubstituted anthracenyl moieties were never achieved. The formation of such compounds became possible by on-surface synthesis. Herein, we report on the synthesis of fused bis- and tetra-anthracenylporphyrin derivatives via the cyclodehydrogenation the parent meso-substituted molecules on a catalytic Au(111) surface.[6] Depending on the annealing temperature, anthracenylporphyrins with the four anthracene fully linked to the porphyrin core or over-oxidized porphyrin in which the anthracene are connected two by two in 2-2' position were observed by STM (Figure 1).

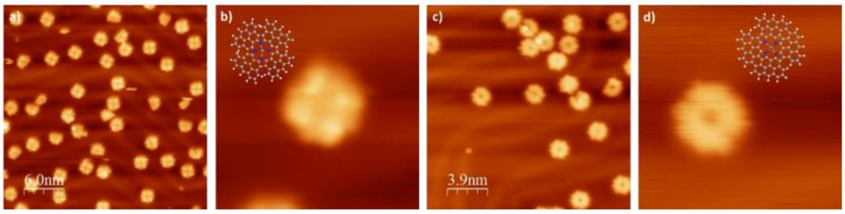

Figure 1. STM images of the fused tetra-anthracenylporphyrins and related porphyrin structures

REFERENCES

1. Clair, S.; de Oteyza, D. G. Chem. Rev. 2019, 119, 4717-4776.
2. Fox, S.; Boyle, R. W. Chem. Commun. 2004, 1322-1323.
3. a) Sun, Q.; Mateo, L. M.; Robles, R.; Ruffieux, P.; Lorente, N.; Bottari, G.; Torres, T.; Fasel, R. J. Am. Chem. Soc. 2020, 142, 18109-18117; b) Zhao, Y.; Jiang, K.; Li, C.; Liu, Y.; Xu, C.; Zheng, W.; Guan, D.; Li, Y.; Zheng, H.; Liu, C.; Luo, W.; Jia, J.; Zhuang, X.; Wang, S. J. Am. Chem. Soc. 2020, 142, 18532-18540
4. a) Mateo, L. M.; Sun, Q.; Liu, S.-X.; Bergkamp, J. J.; Eimre, K.; Pignedoli, C. A.; Ruffieux, P.; Decurtins, S.; Bottari, G.; Fasel, R.; Torres, T. Angew. Chem., Int. Ed. 2020, 59, 1334-1339; b) Mateo, L. M.; Sun, Q.; Eimre, K.; Pignedoli, C. A.; Torres, T.; Fasel, R.; Bottari, G. Chem. Sci. 2021, 12, 247-252.
5. a) Davis, N. K. S.; Thompson, A. L.; Anderson, H. L. Org. Lett. 2010, 12, 2124-2127; b) Davis, N. K. S.; Thompson, A. L.; Anderson, H. L. J. Am. Chem. Soc. 2011, 133, 30-31.
6. Baljozović, M. et al., in preparation

Parent Corrphycene - Synthesis and Properties

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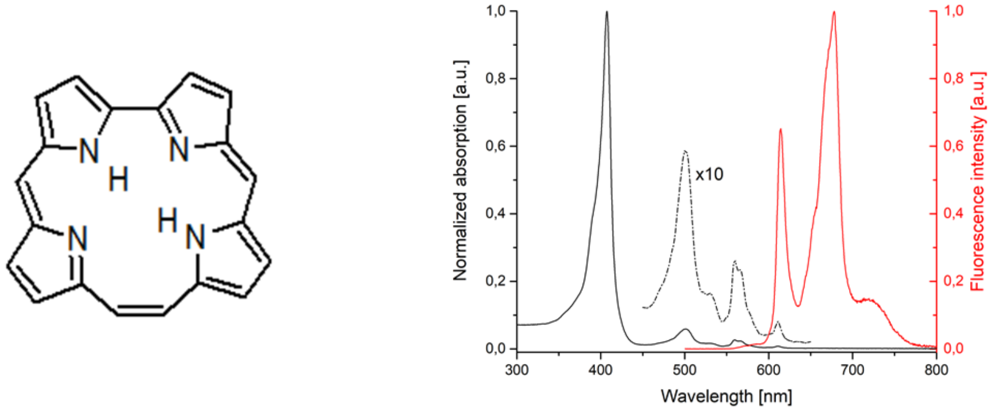
Corrphycene is one of the four structural isomers of porphyrin obtained so far [1,2] in which all four nitrogen atoms are directed towards the interior of the ring formed by the pyrrole subunits and the carbon atoms connecting them. The structure of this compound implicates that, unlike the much more well-known porphycene, corrphycene belongs to the group of soft chromophores. This means that even slight changes in the substitution pattern of corrphycene can significantly affect its spectroscopic properties, as well as the energy of its tautomeric forms [3]. The number of tautomeric forms is larger than in porphyrin and porphycene, but smaller than in hemiporphycene. This is one of the reasons why it is so important to test this compound in its unsubstituted form. Unfortunately, although 28 years have passed since the first synthesis of the corrphycene was published [4], and the synthesis of such compounds continues to be of interest [5], the synthesis of parent corrphycene has not been reported yet. This encouraged us to develop a convenient method for obtaining unsubstituted corrphycene. In addition to typical photophysical measurements, it will also be possible to learn about the reactivity of this compound, and the corrphycene derivatives obtained in this way can serve as models to understand the nature of the intramolecular hydrogen transfer, possibly involving vibrationally mode-selective tunnelling.



Parent corrphycene and its absorption (black) and emission (red, excitation at 407 nm) spectra in CH_2Cl_2.

REFERENCES

1. J. Waluk, J. Michl, *J. Org. Chem*., **1991**, *56*, 2729−2735.
2. G. Anguera, D. Sánchez-García, *Chem. Rev*., **2017**, *117*, 2481−2516.
3. A. Gorski, B. Leśniewska, G. Orzanowska, J. Waluk, *J. Porphyrins Phthalocyanines*, **2016**, *20*, 3–11.
4. J. L. Sessler, E. A. Brucker, S. J. Weghorn, M. Kisters, M. Schafer, J. Lex, E. Vogel, *Angew. Chem. Int. Ed. Engl*., **1994**, *33*, 2308-2312; M. A. Aukauloo, R. Guilard, *New J. Chem*., **1994**, *18*, 1205−1207.
5. R. Nozawa, H. Shinokubo, *Org. Lett*., **2017**, *19*, 4928−4931.

Nanoparticles of vitamin B_{12} hydrophobic derivative. Formation and gas sensor properties

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First nanoparticles of a hydrophobic derivative of vitamin B_{12} – aquacyanocobyrinic acid heptabutyl ester (fig. 1a) in the layers at air-water interface and Langmuir-Schaefer (LS) films were formed. Characteristics of the structure and properties of 2D and 3D nanoaggregates in the layers were determined with the method of quantitative analysis of compression isotherms [1]. Gas sensor properties of nanostructured LS films were studied. The appearance (color) and UV-Vis spectrum of the films did not change when stored in air for one month, but in the presence of hydrogen cyanide gas there are rapid pronounced changes: the films become purple, new peaks appear in the spectrum at 369 and 588 nm. The initial state is restored when contaminated air is replaced by clean one. The color changes of the LS film could be repeated at least 10 times without reducing the brightness.

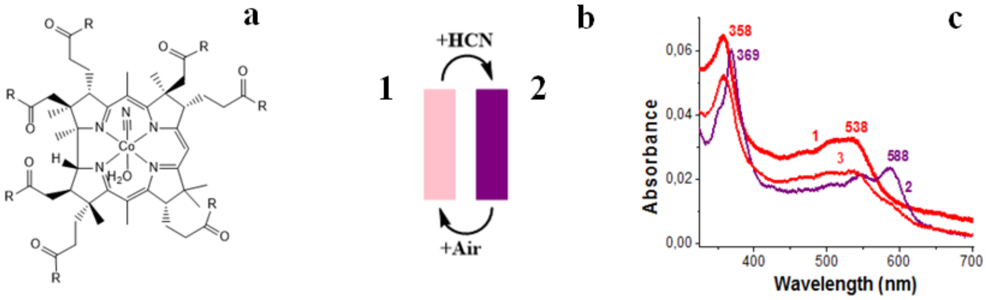

Figure 1. (a) Structure of aquacyanocobirinic acid heptabutyl ester (R – OC_4H_9), (b, c) Color and UV-Vis spectral changes of the LS film: 1 – in air, 2 – in the presence of hydrogen cyanide, HCN gas, 3 – after purging the setup with air.

The results make a prospect for developing more affordable and natural new chemical sensors purposed for medicine, food and chemical industries. They can be utilized for the determination of toxic HCN gas in air.

The work was financially supported by the grant of the RSF (20-12-00175, film formation and study), ISUCT, and Ministry of Science and Higher Education of the RF (FZZW-2020-0008, synthesis of the compounds).

REFERENCES

1. L.A. Maiorova et al. *ACS Langmuir* 2018, 34, 9322-93293; *Vu T.T. et al. Macroheterocycles* 2016, 9(1), 73-79; Valkova LA. Et al. *Bull. Russ. Acad. Sci.: Phys.* 1997, 61, 631; Maiorova LA. et al. *Prot.Met.Phys.Chem.* 2015, 51, 85-92; Kharitonova N.V. et al. *JPP* 2018, 22(6), 509-520.

Design of supramolecular assemblies based on phospholipid-porphyrin conjugates with photodynamic and photothermal properties to combat bacterial infections

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Phospholipid-porphyrin conjugates (Pl-Por) are amphiphilic scaffolds that consist of porphyrin derivatives grafted to a lysophosphatidylcholine backbone [1-4]. Owing to their structural similarities with phospholipids, several Pl-Por conjugates have shown to be able to self-assemble into liposome-like assemblies exhibiting unique photophysical properties compared to their monomeric counterparts. For these reasons Pl-Por conjugates are considered nowadays as versatile backbones to design supramolecular assemblies with multifunctional properties and thus their application in photodynamic therapy, photothermal therapy, photoacoustic imaging and photo-triggerable release properties [1-3]. However, little is known about the impact of their structure on their assembling properties, their optical properties as well as on their photothermal and photodynamic activities.

In this work, we synthesized six new Pl-Por conjugates exhibiting different alkyl chain lengths in the sn2 position of C16 Lysophosphatidylcholine and linked via peptidic bond to two types of porphyrin derivatives; either pheophorbide-a (Ph$_x$LPC) or pyropheophorbide-a (Pyr$_x$LPC) [5]. By combining a variety of experimental techniques with molecular dynamics simulations, we investigated the thermodynamic, the optical properties and the structure of the Pl-Por either self-assembled or when incorporated in lipid bilayer membranes which exhibit different fluidity. Finally, the photothermal and photodynamic efficiencies of these assemblies were assessed on planktonic bacteria and their biofilms.

Our results demonstrated that all of the conjugates can form supramolecular assemblies with bilayers structures and exhibit different photothermal and photodynamic activities against Gram + and Gram - bacterial planktonic cultures and their biofilms depending on their chemical structure of the Pl-Por conjugates.

REFERENCES

1. J.F. Lovell et al., Nat Mater, 10 (2011) 324-332.
2. J. Massiot et al., Biochimica et Biophysica Acta (BBA) - Biomembranes, 1864 (2022) 183812.
3. J. Massiot et al., Chemistry – A European Journal, 24 (2018) 19179-19194.
4. J. Massiot et al., Journal of Materials Chemistry B, 7 (2019) 1805-1823.
5. L.-G. Bronstein et al., J Colloid Interf Sci, 611 (2022) 441-450.

Photodynamic activity of novel 5-(pyridyl)-10-15-20-tris(4-bromophenyl) porphyrin conjugated to graphene quantum dots against *Staphylococcus aureus*

Bridged Ngwanabjala Magaela[a], Lekgowa Collen Makola[a], Muthumuni Managa[b] and Tebello Nyokong[a]

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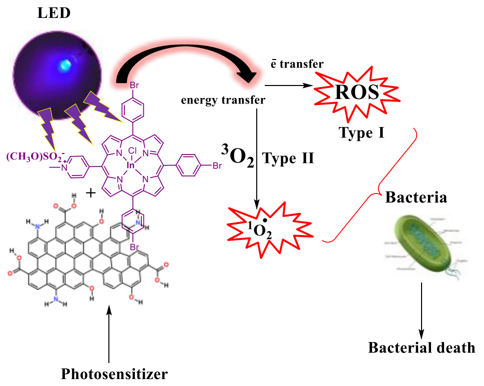
In the 21st century, microbe-related infections were reduced to a level where they no longer had a serious impact on human health because of availability of antibiotics. However, microorganisms have developed resistance against many antibiotics which were previously highly effective [**1**]. Methicillin-resistant Staphylococcus aureus (*S. aureus*) is causing much concern at present [**2**], it is among the top six most dangerous multidrug-resistant microorganisms according to the Infectious Diseases Society of America. Photodynamic antimicrobial chemotherapy (PACT) could be a potential antimicrobial therapy. PACT has already been shown to be effective in vitro against bacteria [**3**] and other microorganisms [**4**]. This work report on novel 5-(pyridyl)-10-15-20-tris(4-bromophenyl) porphyrin, the indium metal derivative and quaternized derivative conjugated to GQDs for PACT. Asymmetrical porphyrins are employed since asymmetry is known to result in high singlet oxygen quantum yield in porphyrins [**5**].



Representation of PACT

REFERENCES

1. G. Jori, S.B Brown, *Photochem. Photobiol. Sci.* 2004, 3, 403-405.
2. P. Dharmaratne, D. N. Sapugahawatte, B. Wang, C. L. Chan, K. M. Lau, C. BS Lau, K. P. Fung D. KP. Ng and M. IP. *Eur. J. Med. Chem.* 2020, 200, 112341-112367.
3. L. C. Makola, M. Managa, T. Nyokong, *Photodiagnosis Photodyn Ther.* 2020, 30, 101736-101748
4. R. F. Donnelly, P. A. McCarron, M. M. Tunney, *Microbiological Research*. 2008, 163, 1-12.
5. A.S. Oliveira, D. Licsandru, R. Boscencu, R. Socoteanu, V. Nacea, L. F. V. Ferreira, *Int. J. Photoenergy.* 2009, 1-10.

Silicon phthalocyanine compounds as organic linkers in MOF porous materials used as active material in optical resonators

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When an organic or inorganic compound is introduced into an optical cavity and interacts with light, electronic states of the molecular moieties can resonate with the eigenmodes of the cavity and give rise to new phenomena, being able to observe quantum-electro-dynamical (QED) events which affect different molecular properties (vibrational transitions, chemical reactivity landscapes, or electronic characteristics).[1] Metal-organic frameworks (MOFs) based on Silicon phthalocyanine (SiPc) chromophoric linkers, in connection with layer-by-layer (lbl) deposition methods, offer the possibility to fabricate well-defined and crystalline arrays of dye molecules, which serve as porous cavity materials in optical resonators.[2] The intrinsic porosity of these crystalline coordination networks allows to reversibly load guest species into the porous MOFs at high densities, and this particular property makes new applications possible, e.g., in the fields of optoelectronics, sensing, and catalysis.

In this communication, we will present the synthesis of new SiPc compounds, axially functionalized with carboxylic acid appends and peripherally substituted with electron donor (D) and electron withdrawing groups (D) (Figure 1), and the evaluation of their capability to generate, in combination with Zn atoms, MOF structures which are used as active material in optical cavities.

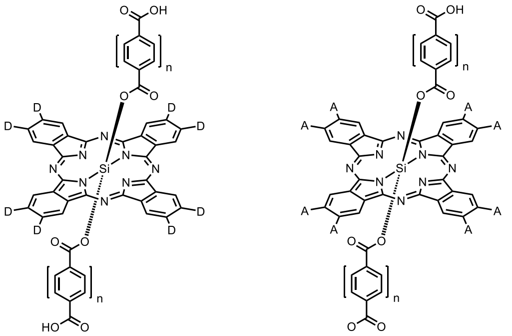

Figure 1. SiPc compounds, axially functionalized with carboxylic acid appends and peripherally substituted with electron donor (D) and electron withdrawing groups (D)

REFERENCES

1. A. Thomas, L. Lethuillier-Karl, K. Nagarajan, R. M. A. Vergauwe, J. George, T. Chervy, A. Shalabney, E. Devaux, C. Genet, J. Moran and T. W. Ebbesen, *Science*, **2019**, *363*, 615.
2. R. Haldar, Z. Fu, R. Joseph, D. Herrero, L. Martín-Gomis, B. S. Richards, I. A. Howard, A. Sastre-Santos, C. Wöll, *Chem. Sci*. **2020**, 11, 7972.
3. L. Martín-Gomis, V. Sobrino-Bastán, R. Haldar, C. Wöll, A. Sastre-Santos, *in preparation*

Metallophthalocyanines as electrocatalytic thin monolayer films for enhanced electrochemical (bio)sensing applications

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Fabrication of electrodes with stable thin monolayer films of metallophthalocyanines bearing pH sensitive functional groups and electroactive central metal ions still continues to be the subject of our research endevour. Various chemical modification strategies have been employed for the modification of gold electrode surfaces and for specific applications. The chemical strategies involved esterification [1], Schiff-base [2] and 'Click' chemistry [3a], and amide coupling [3b] reactions. The electrochemical and surface properties of the modified electrodes were investigated using state-of-the-art surface sensitive characterization techniques. Spectroscopic techniques were used for the characterization of metallophthalocyanine (MPc) complexes during the synthesis process. **Figure 1** shows the AFM images (2D, 3D and cross-section analysis) of the gold (Au) electrode modified with MPcs and single-walled carbon nanotubes (SWCNTs). **Figure 2** shows the X-ray Photoelectron Spectroscopy (XPS) spectra (i.e. survey and C 1s high-resolution) of Au-SWCNT-MPc surfaces. The MPc-SWCNT nanohybrids have been investigated for their electrocatalytic and electroanalytical properties. The modified electrodes were investigated for their potential applications in detecting various biomedical analytes. The method of modification investigated was specific for the analyte of interest. In this presentation, we will show the various methods of phthalocyanine synthesis and characterization, different chemical strategies for their fabrication as thin monolayer films onto gold electrodes, the characterization of thin monolayer films and finally their electrocatalytic properties.

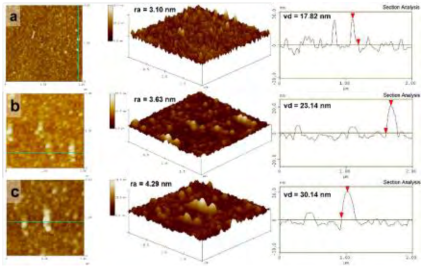

Figure 1: AFM images (2D, 3D and section analysis) of Au-MPc-SWCNT nanohybrids.

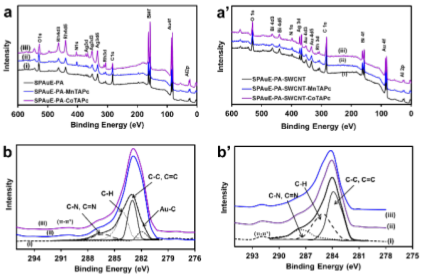

Figure 2: XPS spectra (a) survey and (b) C 1s high resolution of Au-MPc-SWCNT nanohybrids.

REFERENCES

1. (a) P. Mashazi, et. al, *Electrochimica Acta,* 52, **2006**, 177-186. (b) P. Mashazi, et. al, *Electrochimica Acta*, 53, **2007**, 1858-1869.
2. (a) P. Mashazi, T. Nyokong, *Microchim Acta*, 171, **2010**, 321–332. (b) P. Mashazi, et. al, *Talanta*, 85, **2011**, 2202-2211.
3. (a) D. Mwanza, et. al, *Electrochim. Acta*, 254, **2017**, 89 – 100. (b) K. Tshenkeng, P. Mashazi, *Electrochim. Acta, 360,* **2020**, 137015.

Phototransformation of dibenzothiphene using asymmetrical phthalocyanines covalently linked to metal tungstate nanoparticles

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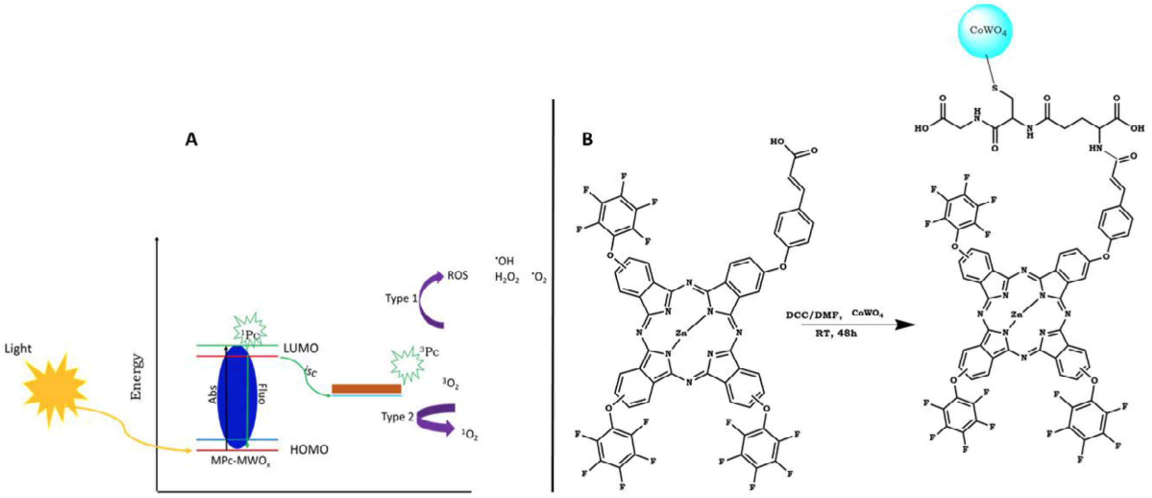
The high sulfur content of fuel is due to dibenzothiophenes (DBT) and its derivatives. In the petroleum refining industry, hydro-desulfurization (HDS) technique is now used to reduce sulfur concentration in fluel. Due to its limited effectiveness, the process has difficulties when it comes to removing sulfur from DBT. Photocatalysis-based advanced oxidation process (AOP) technology has been developed as an alternative. Photocatalysis takes advantage of reactive singlet oxygen species (ROS). Photosensitizers such as metallophthalocyanines (MPcs) are ideal due to their ability to generate ROS (Scheme 1A).. The existence of different functional groups in low symmetry Pcs (employed in this work) allow for the coexistence of several features in a molecule, and therefore an improvement in the MPc properties. Asymmetry is known to introduce distortion on the phthalocyanine macrocycle which affects the electronic states of the conjugated macrocycle ring, hence the physicochemical properties of the Pc. Semiconducting photocatalysts, on the other hand, have been employed for photocatalytic desulfurization of DBT[1]. Due to their wide variety of applications, metal tungstate semiconducting nanoparticles have attracted a lot of attention [2]. Their properties include high stability and appropriate narrow energy band gap which make them good photocatalysts. For the first time, metal tungstate nanoparticles and asymmetrical MPcs are combined (Scheme. 1B) in this study for application in desulfuration [3].



Scheme 1: (A) MPc generating ROSS. (B) MPc conjugation to functionalized nanoparticles [unpublished work]

REFERENCES

1. Y. Bi, S. Zeng, H. Nie, M. Li, Q. Yang, G. Xia, D. Li, Catal. *Commun.* 57 (2014) 5–8.
2. R. Karthiga, B. Kavitha, M. Rajarajan, A. Suganthi, *Mater. Sci. Semicond. Process.* 40 (2015) 123–129,
3. S.Mgidlana, N. Nwahara, T. Nyokong, *Polyhedron* 197 (2021) 115053-115068

TiO_2 electrospun nanofibers decorated with conjugates of porphyrin with graphitic carbon nitride quantum dots for photodegradation of organic pollutants.

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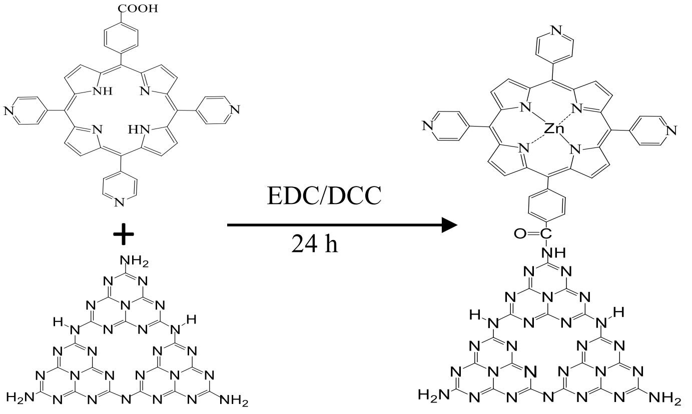
Water pollution prompted by the excessive use of the fertilizer and tennary products and improper disposal of industrial effluent containing organic compounds is the major global concern of the current century [1]. Hence, the development of the robust method for degradation of these compounds is highly necessary [2]. In this study we developed visible light driven photocatalytic method for degradation Rhodamine 6G and 2,4-dichlorophenol using TiO_2 electrospun nanofibers decorated with conjugates of Zn-5-p-carboxyphenyl-10,15,20-(tris-4-pyridyl)-porphyrin with graphitic carbon nitride quantum dots photocatalysts. The decoration of the TiO_2 with the porphyrin@g-C_3N_4 QDs conjugate resulted to an enhanced catalytic activity. The results demonstrate a prospective alternative for **2**@g-C_3N_4 QDs-TiO_2 fibers ternary hybrid catalyst to be used as novel catalyst for visible light driven photo-degradation of refractory organic water pollutants.



N,N'-Dicyclohexylcarbodiimide = DCC
Ethyl-3-(3-dimethylaminopropyl) carbodiimide = EDC

Figure 1. Synthesis of the conjugate porphyrin with graphitc carbon nitride quantum dots

REFFERENCES

1. P. V. Nidheesh and R. Gandhimathi. *RSC Advances*. 4 (2014) 27946–27954.
2. S. Mapukata, T. Nyokong. *New Journal of Chemistry*. 44 (2020) 16340-1350.

Porphyrin-based Lipid Nanoparticle Enhanced RNAi Endosomal Escape through Near-infrared Light

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RNA interference (RNAi) is a new therapeutic strategy to silence critical genes involved in cancer growth. To deliver intact RNA therapeutics to *in vivo* disease targets, lipid nanoparticle (LNP)-based delivery platform has been extensively developed and showed broad clinical successes in delivering siRNA [1], mRNA [2], and CRISPR gene editing tools [3]. However, even with the state-of-art LNPs, the endosomal escape efficiency of RNAi after LNP endocytosis remains extremely low (e.g. 1–2% for siRNA) [4], which dramatically impaired the efficacy of RNAi. Herein, we incorporated porphyrin-lipid into LNP and utilized it as a light trigger to improve RNAi endosomal escape efficiency. Formed porphyrin-based LNP (porphy-LNP) exhibited >95% siRNA encapsulation efficiency and excellent colloidal stability. We observed the reactive oxygen species (ROS) generated by porphyrin-lipid upon NIR light irradiation made endosomal membranes highly permeable, leading to sufficient siRNA release into cytosol in less than 1 min (Figure 1A). This effect has been verified in broad cancer cell lines and has shown over 2-fold enhancement in RNA knockdown efficacy (Figure 1B). *In vivo* light-assisted gene knockdown experiments have been performed on PC3-Luc6 tumor-bearing mice following intravenous administration of porphy-LNP. Overall, porphy-LNP provides a general solution to improve RNA endosomal escape efficiency and therapeutic efficacy for current LNP systems. Findings from our study can also be used in delivery of mRNA/ gene editing tools and fully boost the efficacy of RNA therapy.

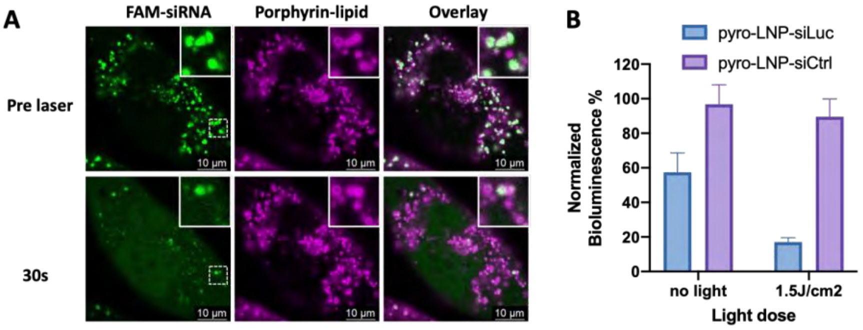

Figure 1 (A) siRNA endosomal escape induced by porphy-LNP upon light exposure. Inset showed porphyrin-lipid stayed on endosomal membranes **(B)** Decrease in bioluminescence intensity when PC3-Luc6 cells were treated by light

REFERENCES

1. Akinc, A. *et al.* The Onpattro story and the clinical translation of nanomedicines containing nucleic acid-based drugs. *Nature Nanotechnology* **14**, 1084–1087 (2019).
2. Polack, F. P. *et al.* Safety and Efficacy of the BNT162b2 mRNA Covid-19 Vaccine. *N Engl J Med* **383**, 2603–2615 (2020).
3. Gillmore, J. D. *et al.* CRISPR-Cas9 In Vivo Gene Editing for Transthyretin Amyloidosis. *The New England Journal of Medicine* 10 (2021) doi:10.1056/NEJMoa2107454.
4. Gilleron, J. *et al.* Image-based analysis of lipid nanoparticle–mediated siRNA delivery, intracellular trafficking and endosomal escape. *Nat Biotechnol* **31**, 638–646 (2013).

Light assisted electrodegradation of 4-acetamidophenol on fabricated phthalocyanine based electrode

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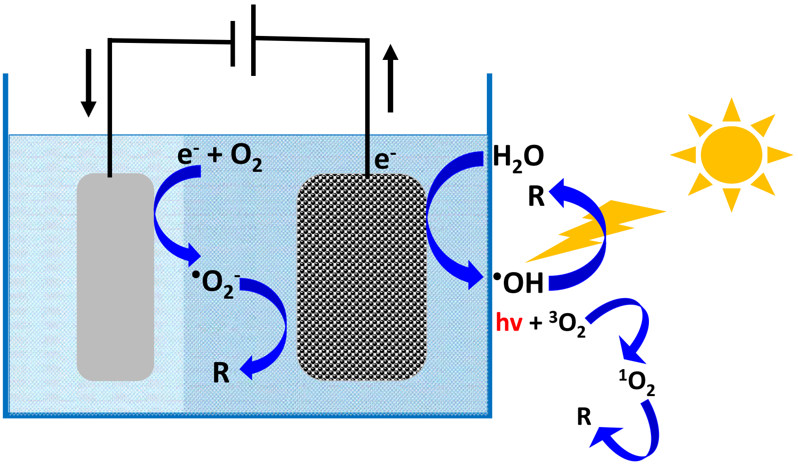
Access to clean water has been a challenge. Water pollution because of industrial effluents and domestic waste has serious implications on aquatic lives and the environment in general [1]. Recently, advanced oxidation process (AOP) has emerged as an efficient and effective method for the treatment of wastewaters since only oxygen is used and toxic by-products are avoided [2]. Photocatalysis is classified as AOP, and metallophthalocyanines (MPcs) [3], in this study MPcs were incorporated with exfoliated graphite and electrode fabricated, the degradation of 4-acetamidophenol (4-ACMP) was carried out in presence of light and current (Scheme 1). The advantages of fabricated electrode are 1; ease to recovery catalyst hence reusable 2; the tendency of electron and holes recombination is limited as electron are conducted via external circuit. The synergistic effect of light current was found to enhance degradation kinetics of 4-ACMP.



Scheme 1: Representation of electrophotodegradation experiment

REFERENCES

1. J. Mendez-Hernandez, F. Ramirez-Vives, M. Solis-Oba, A. Sobrino-Figueroa, O. Leoera. World journal of microbiology and biotechnology, 29 (2013) 805-814.
2. M.I. Litter, in: Environmental photochemistry part II, Springer, 2005, pp. 325-366.
3. N. Kuznetsova, sensitization of singlet oxygen formation in aqueous media, in: T. Nyokong and V. Ahsen (Eds), photosensitisers in medicine, environment and security, Springer London 2012, 267-306.

The Synthesis of Symmetric Chalcone Co, Cu, Mn and Ni Phthalocyanine Complexes and their Electrochemical Properties

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This work explores the synthesis and characterisation of four symmetrical chalcone phthalocyanine complexes Fig. 1. Literature shows that the physicochemical and electronic properties of metallated phthalocyanines (MPc) can be altered and or improved by changing the substituents and or changing the central metal [1]. This work explores the latter through the use of four different transitional metals, cobalt, copper, manganese, and nickel.

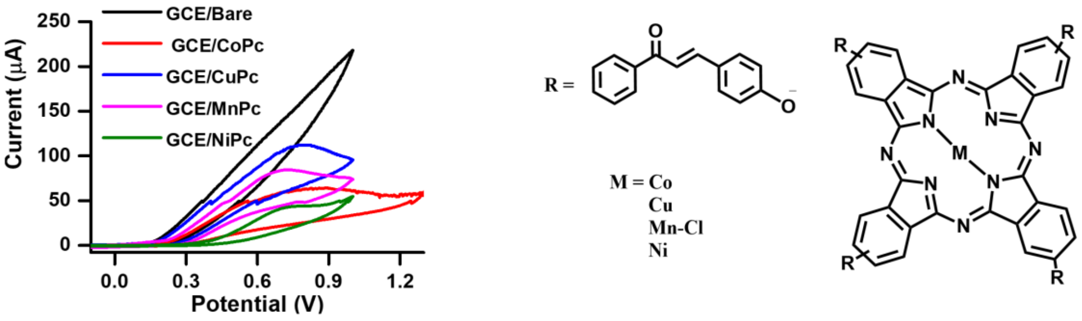

Figure 1: Cyclic voltammograms of the MPc modified electrodes towards the detection of nitrite. The structure of the MPc is shown on the side.

Phthalocyanine complexes have been extensively used as electrocatalysts in electrochemical sensing [2]. This work explores this fact by analysing the effect of the change in central metal when studying the physiochemical, electrochemical of the four MPcs, Fig. 1. Nitrite was used as the analyte of choice. All four MPcs showed good nitrite detection properties which are comparable with similar literature studies. The LoDs obtained range from 0.085 μM to 1.77 μM and the sensitivity rates were as high as 58.8 μA/mM. Cobalt showed the best results while nitrite performed the worst of the four.

REFERENCES

1. L Maurice, P. Annig, in: K. Karl M, S. Kevin M, R. Guilard (Eds.), *The Porphyrin Handbook* (2003) 118–154, Academic Press, California.
2. T. Nyokong, S. Khene, in: Electrochemistry of N4 macrocyclic metal complexes, J.H. Zagal, F. Bedioui (eds), *Springer, Cham,* **2** (2006) 225-276.

Biocompatible cobalt(II) phthalocyanine encapsulated with chitin biopolymer *via* amide bond and decorated with flower-like zinc oxide multipods for electrochemical sensing

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A simple, facile and efficient encapsulation of cobalt (II) phthalocyanine (CoPc) dye [1] with chitin (CH) biopolymer via amide bond [2], followed by decoration with flower-shaped zinc oxide multipods (ZnOMPs) is presented. In support of ZnOMPs [3], the CoPc-CH provides a stable platform and influence catalytic property due to the synergetic interactions. The characterization of the synthesized complexes, composites and composite-nanomaterial were done with different spectroscopic techniques. In addition, the potential electrochemical property of the composite nanomaterial was used to detect guanine (G) nucleobase [4]. The cyclic voltammetry were optimized and recorded in 0.1 M NaOH (pH=13.0) solution. The phthalocyanine encapsulated with chitin polymer decorated with ZnOMPs nanomaterial (CoIIPc-CH@ZnOMPs) composite showed greatly enhanced peak current at a potential +0.45 V compared with other catalyst. The cyclic voltammogram of nanocomposite (Fig. 1) shows quantitative range 1-90 and 90-490 μM with limit of detection (LoD) 0.45 and 30 μM, respectively. The kinetic parameters were performed with chronoamperometry. The nanocomposite was applied efficiently for the guanine detection in sperm-DNA samples.

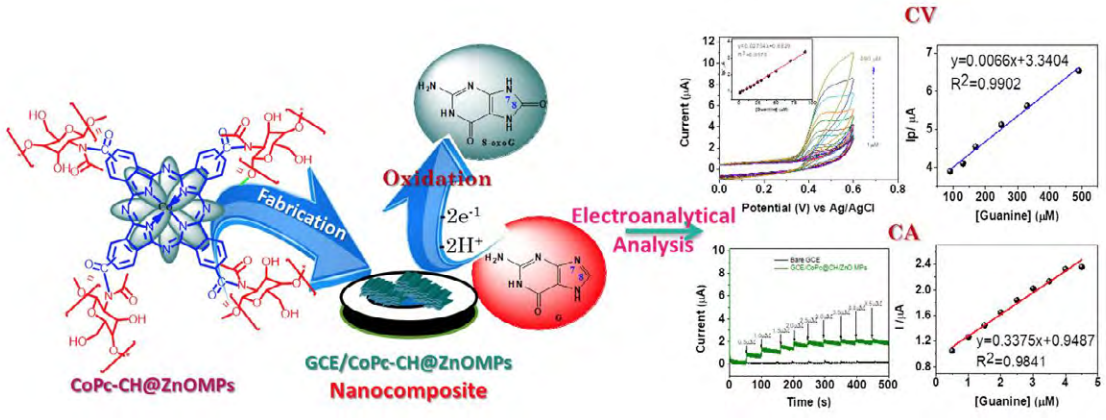

Fig.1. Process of fabrication of nanocomposite and possible electrochemical oxidation mechanism of guanine.

REFERENCES

1. Mugadza, T., & Nyokong, T. (2010). Synthesis, characterization and the electrocatalytic behaviour of nickel (II) tetraamino-phthalocyanine chemically linked to single walled carbon nanotubes. Electrochimica Acta. 55 (20), 6049-6057.
2. Rinaudo, M. (2006). Chitin and chitosan: properties and applications. Prog. Polym. Sci., 31, 603-632.
3. Tandra, G; Soumitra, K., Subhajit, B., Gautam, M., & Subhadra, C. (2007). Multipod ZnO nanoforms: low temperature synthesis and characterization. Journal of Nanoscience and Nanotechnology, 7(2), 689–695.
4. Kalaiyarasi, J., Pandian, K., Santheraleka, R., & Subash, C. B. G. (2020). Graphitic carbon nitride/graphene nanoflakes hybrid system for electrochemical sensing of DNA bases in meat samples. Scientific Reports, 10, 12860.

Photo-Sonodynamic Combination Activity of Morpholino-Phthalocyanines Conjugated to Graphene Quantum Dots Against MCF-7 Breast Cancer Cell Line

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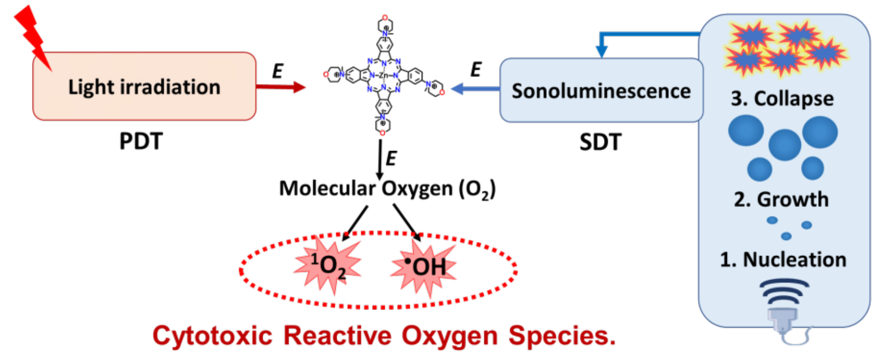
This work evaluates the effect of nitrogen (NGQDs) and nitrogen-sulfur doped (NSGQDs) graphene quantum dots on the cancer cytotoxicity of cationic morpholine-substituted zinc (II) phthalocyanine-mediated photo-sonodynamic monotherapies (PDT and SDT) and combination therapy (PSDT). The GQDs enhanced the activity of the Pcs for the PDT, SDT and PSDT treatments. This was seen with a decreasing survival-percentage of the cells post-treatments compared to prior treatments. For, SDT and PSDT, solid nanoparticles improve sensitizer activation through enhanced acoustic cavitation [1,2], Fig. 1. Furthermore, ultrasound irradiations have been shown to generate singlet oxygen ($^1O_2$) and hydroxyl radicals ($^{\bullet}$OH) reactive oxygen species (ROS), unlike PDT alone which only involves $^1O_2$ [2,3], Fig. 1. In this work, both the ROS were present for the Pcs alone and the conjugates upon ultrasound exposure. The ROS involved in the treatments were evaluated using electron paramagnetic spectroscopy. For PDT, only the $^1O_2$ was detected for all the sensitizers. Where both the $^1O_2$ and $^{\bullet}$OH radicals were evident after SDT and PSDT treatments. An increase in the $^1O_2$ generation was observed for the conjugates compared to the GQDs and the Pc alone. However, the $^{\bullet}$OH radicals were reduced in the conjugates compared to the GQDs and the Pc alone. The NGQDs generally showed better ROS generation efficacy compared to the NSGQD, alone and in the conjugates.



PDT: Photodynamic Therapy, **SDT:** Sonodynamic Therapy, ***E*:** Energy, **$^1O_2$:** Singlet Oxygen, **$^{\bullet}$OH:** Hydroxyl radicals

Fig. 1. Mechanism of Action in phthalocyanine-mediated photo-sonodynamic combination therapy.

REFERENCES

1. Xu H, Zhang X, Han R, Yang P, Ma H, Song Y, Lu Z, Yin W, Wu X, Wang H. RSC Adv 2016;6:50697.
2. Matos JC, Laurenti M, Vighetto V, Pereira LCJ, Waerenborgh JC, Gonçalves C, Cauda V. Appl Sci 2020;10:8479.
3. Nene LC, Nyokong T. J Inorg Biochem2021 ;217:111397.
4. Rosenthal I, Sostaric J, Riesz P. Sonodynamic therapy- Ultrason Sonochem 2004;11:349-363.

A comprehensive study on the electrocatalysis of nitrite using cobalt and manganese phthalocyanines

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A Chemical modification of electrodes has been shown to produce better electrochemical results in comparison to bare electrodes [1]. The most notable of these observations has been a decrease in the oxidation potential and an increase in the catalytic current [1]. With the bulk of these advancements in electrocatalysis being steered by unsubstituted and tetra-substituted Pcs [2, 3], a significant area of research pertaining to asymmetric Pcs (A_3B or AB_3) has remained unexplored. Asymmetric Pcs have been reported as being more favourable as they result in an improvement in the photo-physicochemical properties and offer better control in terms of conjugation to other materials or anchoring to surfaces [4]. In this work, symmetric (**Figure 1**) and asymmetric Pcs bearing cobalt and manganese as the central metals are presented. Acetamidophenol was used as the primary substituent. In the case of the asymmetric complexes, one of the four substituents was replaced by an alkyne-bearing substituent. The purpose of the study was to evaluate the effects of symmetry as well as the central metal in response to the electro-oxidation of nitrite. Further assessments related to the pH and the method of electrode modification (adsorption versus covalent anchoring through click chemistry) were made.

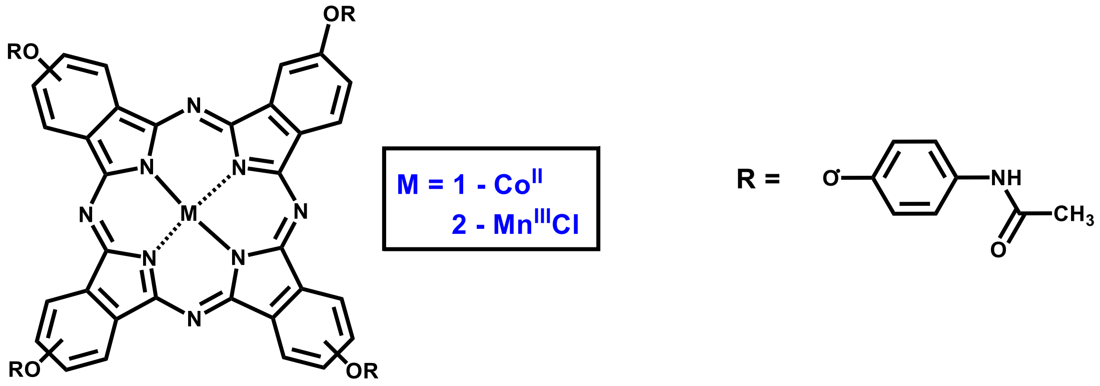

Figure 1: Molecular structures of the symmetric complexes synthesized.

REFERENCES

1. Y. Cui, C. Yang, W. Zeng, M. Oyama, W. Pu, J. Zhang, Anal. Sci. 23 (**2007**) 1421–1425.
2. S. Centane, O. J. Achadu, T. Nyokong, Electroanalysis 29 (**2017**) 2470–2482.
3. H. Xu, J. Xiao, B. Liu, S. Griveau, F. Bedioui, Biosens. Bioelectron. 66 (**2015**) 438–444.
4. G. G. Matlou, N. Kobayashi, M. Kimura, T. Nyokong, New J. Chem. 41 (**2017**) 12309–12318.

Prodrug-modified Phthalocyanine for Photodynamic Therapy

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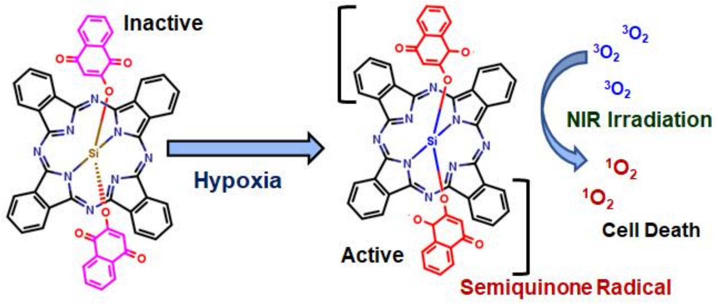
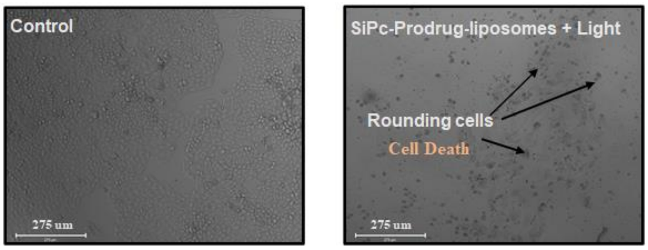
Photodynamic therapy (PDT) holds promise as an alternative treatment modality for cancer and has been shown to be effective in numerous tumour cell models [1]. This can be mainly attributed to (amongst others), its local light controllable activation as well as tolerance to repeated doses [2]. Hypoxic microenvironments within most tumours have profound therapeutic implications for PDT. Hypoxic tissues are often drug-resistant and, as such, are a major challenge in the clinical translation of PDT [3]. In this work, we sort to exploit PDT-induced hypoxia-activation and hence designed a liposome-encapsulated quinone-substituted silicon phthalocyanine (SiPc-Prodrug). Our results show efficient singlet oxygen production as well as retained PDT effect even under hypoxia and hence shows promise for clinical translation.





REFERENCES

1. Chen J, Fan T, Xie Z, Zeng Q, Xue P, Zheng T, Chen Y, Luo X and Zhang H. *Biomaterials* 2020; **237**: 119827.
2. Agostinis P, Berg K, Cengel KA, Foster TH, Girotti AW, Gollnick SO, Hahn SM, Hamblin MR, Juzeniene A, Kessel D, Korbelik M, Moan J, Mroz P, Nowis D, Piette J, Wilson BC and Golab J. *CA. Cancer J. Clin.* 2011; **61**: 250-281.
3. Casas A, Di Venosa G, Hasan T and Batlle A. *Curr. Med. Chem.* 2011; **18**: 2486-2515.

Ru *vs* Si, Pc *vs* Nc, small *vs* bulky axial substituents: design, synthesis and effect of these structural variations on photoproperties

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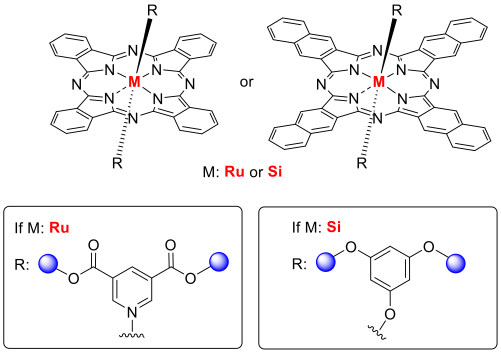
Phthalocyanines (Pcs) have unique features as advanced photosensitisers [1]. As NIR-shifted maximum absorption is desired in photodynamic therapy, naphthalocyanines (Ncs) are also promising photosensitising cores. As heavy atoms are known to increase the intersystem crossing and improve the singlet oxygen generation (SOG) capacity, a series of Pcs and Ncs has been prepared with either Si or Ru at the center of the macrocycle. Either small linear or large bulky branched moieties on the axial substituents have been used to control the aggregation. Their synthesis, photophysical and photochemical studies will be discussed.



The Scientific and Technological Research Council of Turkey (TUBITAK) and the French Embassy in Turkey are gratefully acknowledged for the bilateral Partenariat Hubert Curien between Turkey and France (project Bosphorus 120N684/ 4665SH).

REFERENCES

1. P.-C. Lo, M. S. Rodríguez-Morgade, R. K. Pandey, D. K. P. Ng, T. Torres and F. Dumoulin, *Chem. Soc. Rev.*, **2020**, *49*, 1041-1056

Fast removal of Multidrug-resistant bacterial Biofilms: Antimicrobial photodynamic therapy combined to Chemotherapy

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Biofilm-associated pathogens are particularly resistant to antibiotic treatment and microbial biofilms are the main cause of up to 80% of all human bacterial infections. Antimicrobial photodynamic chemotherapy (APDT) has been proposed as an effective alternative to treat biofilms-related diseases such as dental biofilms and chronic wound infections [1]. APDT uses non-toxic photosensitizers such as Porphyrins (Ps) which is excited by visible light to generate reactive oxygen species (ROS) that inactivate pathogens [2]. New asymmetrical Ps containing a *p*-hydroxyphenyl moiety and *p*-acetylphenyl moieties along with their functionalized silver-detonation nanodiamonds nanohybrids were investigated and they exhibited antibacterial and anti-biofilm activities on the multi-drug resistant *S. aureus* strain due to synergetic effect. Additionally, there was a stronger antibiofilm activity observed in optimal conditions following addition of low doses of Ciprofloxacin (used to treat bacterial infections) to APDT treatment.

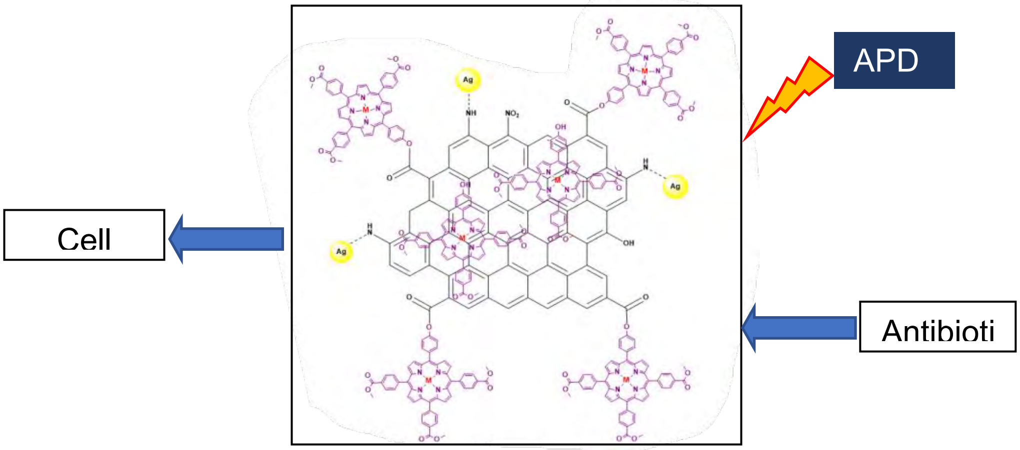

Fig. 1. Porphyrins derived silver-detonation nanodiamonds nanohybrids.

The dual therapy may be a promising candidate in combating drug resistance.

REFERENCES

1. Hu X, Huang Y-Y, Wang Y, Wang X and Hamblin MR (2018) Antimicrobial Photodynamic Therapy to Control Clinically Relevant Biofilm Infections. Front. Microbiol. 9:1299. doi: 10.3389/fmicb.2018.01299.
2. Openda YI, Ngoy BP and Nyokong T (2021) Photodynamic Antimicrobial Action of Asymmetrical Porphyrins Functionalized Silver-Detonation Nanodiamonds Nanoplatforms for the Suppression of Staphylococcus aureus Planktonic Cells and Biofilms. Front. Chem. 9:628316. doi: 10.3389/fchem.2021.628316.

Electrosynthesis and Electrochemistry of Nickel Octahalogenated Porphodimethenes: Evidence for a Metallated Porphyrinogen Dianion

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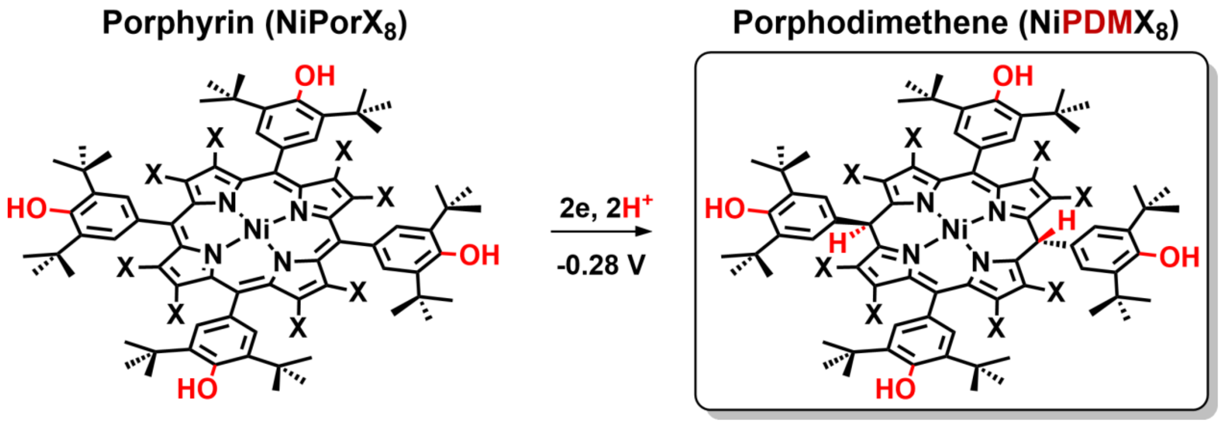
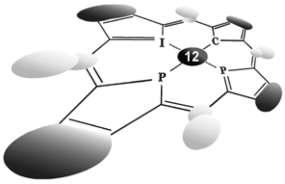
As a continuation of our earlier study on electrochemistry of perhalogenated hydroxyphenyl porphyrins,[1] two octahalogenated nickel(II) hydroxyphenylporphodimethenes, represented as $NiPDMCl_8$ and $NiPDMBr_8$ where PDM is the dianion of 5,10,15,20-(3,5-di-tert-butyl-4-hydroxyphenyl)-5H,15H-porphodimethene, were electrosynthesized from the corresponding octahalogenated porphyrins ($NiPorX_8$) *via* a two-fold reductive proton coupled electron transfer (PCET) as shown in the figure. The isolated porphodimethenes exhibit two reversible one-electron reductions and an irreversible two-electron oxidation in CH_2Cl_2 and spectroscopic properties of the reduced and oxidized products are reported. Deprotonation of the hydroxyphenyl groups on $NiPDMX_8$ occurs in DMF, resulting in a rearranged π-system of the porphodimethenes and a proposed Ni(II) porphyrinogen dianion ($NiPGNX_8$).



REFERENCES

1. Cong, L.; Chahal, M. K.; Osterloh, R.; Sankar, M.; Kadish, K. M., Synthesis, Electrochemistry, and Reversible Interconversion among Perhalogenated Hydroxyphenyl Ni(II) Porphyrins, Porphodimethenes, and Porpho-5,15-bis-paraquinone Methide. *Inorg. Chem.* **2019,** *58*, 14361-14376.



Optimization of YfeX for Applications in Biocatalysis using Site-Directed Mutagenesis

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Biocatalysts can impart stereoselectivity that is highly desirable in industrial processes, especially for the synthesis of pharmaceuticals and fine chemicals. However, industrial catalysis is dominated by the use of chemical catalysts that often lack high levels of stereoselectivity.[1-3] For reactions that deal with multiple stereocenters such as carbene insertion reactions, using biocatalysts would be highly efficient, but the lack of biocatalysts in industry is due to their instability in organic solvents.[4-6] In the work presented here, we explore the use of a novel protein scaffold, YfeX, along with rationally designed YfeX variants, to make these reactions more efficient and compatible with industrial conditions for pharmaceutical and fine chemical synthesis. The product yields, stereochemistry of the products and the catalytic mechanism were analyzed using gas chromatography-mass spectroscopy (GCMS), supercritical fluid chromatography (SFC), UV-Visible spectroscopy, and quantum mechanical molecular mechanics (QM/MM) calculations. We compare wild-type (WT) YfeX and variants to other heme-biocatalysts and artificial metalloenzymes. WT YfeX and variants show high levels of reactivity and stability in aqueous environments and in the presence of organic co-solvents. Correspondingly, YfeX shows great potential to be an alternative to traditional industrial catalysts; in addition, further optimization by site-directed mutagenesis proves valuable for fine tuning the stereoselective generation of pharmaceuticals and fine chemicals in organic cosolvents.

REFERENCES

1. Shanab, K.; Neudorfer, C.; Schirmer, E.; Spreitzer, H., Green solvents in organic synthesis: an overview. *Curr. Org. Chem.* **2013,** *17* (11), 1179-1187.
2. Sinou, D., Metal catalysis in water. *Modern Solvents in Organic Synthesis* **1999**, 41-59.
3. Horvath, I. T.; Anastas, P. T., Innovations and green chemistry. *Chem. rev.* **2007,** *107* (6), 2169-2173.
4. Lim, X., The new breed of cutting-edge catalysts. *Nature News* **2016,** *537* (7619), 156.
5. JaneáWang, Z., P450-catalyzed asymmetric cyclopropanation of electron-deficient olefins under aerobic conditions. *Catal. Sci. Technol.* **2014,** *4* (10), 3640-3643.
6. Wang, Z. J.; Peck, N. E.; Renata, H.; Arnold, F. H., Cytochrome P450-catalyzed insertion of carbenoids into N–H bonds. *Chem. sci.* **2014,** *5* (2), 598-601.

Nitrite Binding and Activation by Heme-Globins as Revealed by Resonance Raman Spectroscopy

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Nitrite that is present at micromolar levels in tissues and nanomolar levels in blood can be reduced to the bioactive nitric oxide molecule during hypoxia and mediate physiological signaling. Nitrite reacts with heme globins leading to several heme-Fe adducts and the catalyzed reaction pathways play a vital role for hemoglobin- and myoglobin-dependent nitrite activation. In this work, we present the resonance Raman characterization of the hemoglobin heme-nitrito and heme-nitrito/nitrovinyl species and compare their properties to those of the previously described myoglobin-nitrite adducts [1-2]. Differences in the spin state of the hemoglobin- versus myoglobin-nitrite adducts along with the observation of spin transitions will be discussed. The effect of temperature in the properties of heme-nitrito and heme-nitrito/nitrovinyl species will also be presented.

REFERENCES

1. Lambrou, A., Ioannou, A., Pinakoulaki, E. (2016) Spin Crossover in Nitrito-Myoglobin as Revealed by Resonance Raman Spectroscopy. *Chem. Eur. J.* 22, 12176-12180.
2. Ioannou, A., Lambrou, A., Daskalakis, V., Pinakoulaki, E. (2017) Coupling of Helix E-F Motion with the O-Nitrito and 2-Nitrovinyl Coordination in Myoglobin. *Biophys. Chem*. 221, 10–16.

Phosphorus Corrole-BSA Nanoaggregates for Theranostic Applications

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Porphyrinoids internalization is a key factor for the exploitation of these molecules as dyes or photosensitizers. Although phosphorus-corrole (PCor) is an ideal candidate for different applications in medicine due to its excellent photophysical properties [1], low water solubility of many aryl-corroles may limit their use, because molecules aggregation occurring in water decreases luminescence and makes more difficult cells internalization.

To overcome this drawback several strategies can be pursuit: for instance the functionalization with charged groups increases water solubility even if slightly lowers photophysical properties. Otherwise, small proteins can be used as shuttle to promote corrole uptake [2].

PCor/BSA nano-aggregates were prepared and the cytotoxicity toward two cancerous and non-cancerous cell lines (A549 and MRC-5, respectively) was evaluated. Severe viability decrease was observed in the case of cancer cells after 24 h. Internalization and localization studies highlight that PCor /BSA nano-aggregates enter into cells by energy-dependent mechanism and that the chromophore accumulates differently in the two cell lines.

Cellular viability, uptake and intracellular localization of lipophilic P-tritolylcorrole and of the hydrophilic sulfonated derivative were investigated. Finally we explored a different approach for nanoaggregate preparation based on bioconjugation of PCor to BSA and properties of this covalent adduct were evaluated.

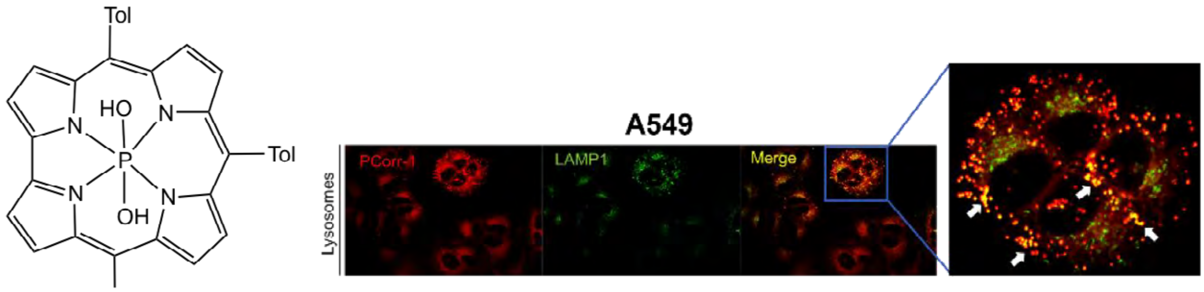

Figure 1. Left: Structure of P-tritolylcorrole. Right: intracellular localization in A549 cells after 24 h exposure.

REFERENCES

1. S. Ghidinelli, S. Abate, G. Mazzeo, R. Paolesse, G. Pomarico, G. Longhi. *ACS Omega* **2021**, *6*, 26659-26671.
2. M. Soll, T. K. Goswami, Q.-C. Chen, I. Saltsman, R. D. Teo, M. Shahgholi, P. Lim, A. J. Di Bilio, S. Cohen, J. Termini, H. B. Gray, Z. Gross. *Sci. Rep.* **2019**, 9, 1-11.

Vitamin B_{12} enables photogeneration of alkyl radicals from strained molecules

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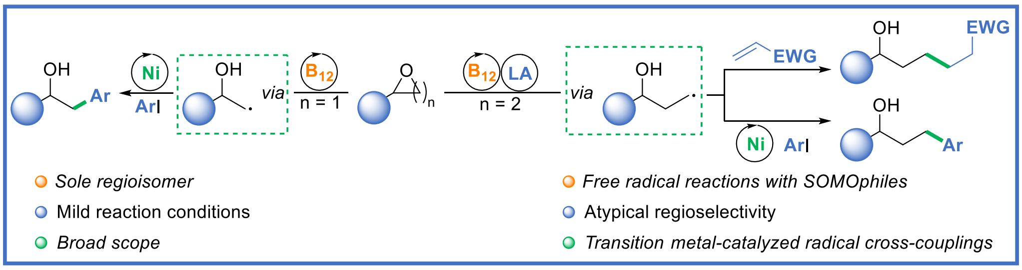
Strained molecules are of great interest in medicinal, material, and physical chemistry because of their unique reactivity. Over the past decade, strain-release-driven transformations have emerged as a powerful tool to access otherwise challenging molecular scaffolds, such as functionalized propellanes, cyclobutanes, or azetidines. In this context, our group proposed a new approach for strain-release-driven transformations that relies on the polarity reversal of the strained bicyclo[1.1.0]butanes (BCB) and bicyclo[2.1.0]pentanes (BCP) [1]. This method allows the generation of a radical localized at C3 (BCB) or C4 (BCP) atoms, which can react with electrophiles, while they are normally susceptible to nucleophilic addition. Based on the developed methodology, we wanted to obtain regioselective reactions of small heterocycles such as epoxides. Ring-opening of epoxides allows for the synthesis of linear or branched alcohols that belong to the group of classical transformations in organic synthesis. To date, research on epoxides has mostly focused on the generation of alkyl radicals from aliphatic epoxides and leads to linear alcohols with good regioselectivity. For aryl epoxides, the dominant approach involves the generation of benzyl radicals and the formation of branched products. However, the ring-opening of aryl epoxides from the less sterically hindered side remains unexplored. For the first time, we have developed a highly regioselective, Co/Ni catalyzed ring-opening reaction of epoxides with aryl halides [2]. The crucial ring opening by the Co(I) complex occurs from the less steric hindered side, leading to linear products. Furthermore, the methodology could be expanded to the 4-membered congener, oxetanes [3].

We showed that vitamin B_{12} catalysis gives access to alkyl radicals from strained molecules. Importantly, the regioselectivity in both the epoxide and oxetane ring openings is complementary to the known methodologies.



REFERENCES

1. Ociepa, M.; Wierzba, A. J.; Turkowska, J.; Gryko, D. Polarity-Reversal Strategy for the Functionalization of Electrophilic Strained Molecules via Light-Driven Cobalt Catalysis. *J. Am. Chem. Soc.* **2020**, *142* (11), 5355–5361. https://doi.org/10.1021/jacs.0c00245.
2. Potrząsaj, A.; Musiejuk, M.; Chaładaj, W.; Giedyk, M.; Gryko, D. Cobalt Catalyst Determines Regioselectivity in Ring Opening of Epoxides with Aryl Halides. *J. Am. Chem. Soc.* **2021**, *143* (25), 9368–9376. https://doi.org/10.1021/jacs.1c00659.
3. Potrząsaj, A.; Ociepa, M.; Chaładaj, W.; Gryko, D.; *unpublished results*

Water-soluble nickel phthalocyanines as sublayers in MSDI heterojunctions for ammonia sensing

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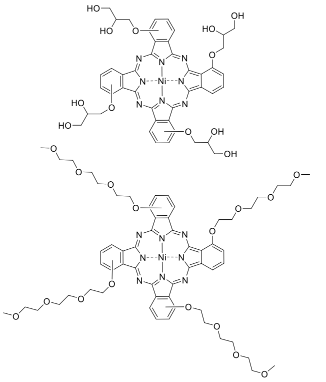
Ammonia production is one of the biggest industrial processes and is responsible for 1.5% of greenhouse gases globally [1]. Therefore, its amount in air must be controlled and measured. Fast and sensitive sensors able to detect ammonia under the 50 ppm threshold are needed in many places such as fertilizer production [2]. Ammonia sensors are divided into two parts: organic and inorganic sensors. Organic sensors have some advantages such as high sensitivity at low temperature, easy production and low cost. Among organic semiconductors, metal phthalocyanines (MPcs) are promising because of their thermodynamic and chemical stability, functionality and intramolecular-extramolecular π-π interactions via the central metal atom. MPcs demonstrate high solubility in many organic and aqueous environments due to their tunable properties [3]. Thin films of MPcs can be prepared both under high vacuum and by solvent dropping method. MPc bilayer heterostructures are other innovative approaches for the ammonia gas sensors and have been investigated by the Bouvet group. This heterostructure consists of a rather weak conducting molecular material as a sublayer covered by high-conductive molecular materials. It is referred to Molecular Semiconductor – Doped Insulator heterojunction (MSDI) [4]. In this study, water-soluble nickel phthalocyanines bearing glycerol and triethyleneglycol substituents were prepared and used in MSDI sublayers with the solvent dropping technique. LuPc2 was covered as a top layer under high vacuum. The ammonia sensing properties of these MSDI devices were investigated in different humidity conditions and the particular concentrations of ammonia at room temperature.



These works have been performed in the framework of the bilateral project PHC-Bosphorus 117Z623/ 39745WG for which the Scientific and Technological Research Council of Turkey (TUBITAK) and the French Embassy in Turkey are gratefully acknowledged.

REFERENCES

1. Ravi, M.; Makepeace, J. W., *Chem. Sci.* **2022**. https://doi.org/10.1039/D1SC04734E.
2. Zhihua, L.; Xucheng, Z.; Jiyong, S.; Xiaobo, Z.; Xiaowei, H.; Tahir, H. E.; Holmes, M., *Sens. Actuators B Chem.* **2016,** *226*, 553-562.
3. Tang, X.; Liu, Q.; Wei, C.; Lv, X.; Jin, Z.; Chen, Y.; Jiang, J., *J. Rare Earths,* **2021,** *39*, 113-120.
4. Şahin, Z.; Meunier-Prest, R.; Dumoulin, F.; Kumar, A.; Isci, Ü.; Bouvet, M., *Sens. Actuators B Chem.* **2021,** *332*, 129505.

Bio-inspired Non-heme Metal-tetrathiolate Cluster of Iron-porphyrin

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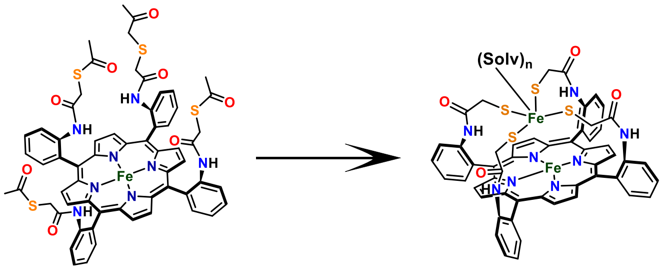
The iron-deprived porphyrin macrocycles of the heme cofactors are the derivatives of deuteroporphyrin IX (Fig 1a) which can be prepared from the readily available hemin, i.e., protoporhyrin IX iron(III) chloride (Fig 1b). Preparation of such variously substituted deuteroporphyrins IX is useful to study the effects of the differences in structure found among natural porphyrins and relative reactivities of positions on the porphyrin ring. Several preparative methods are reported demonstrating separation of substituted deuteroporphyrin IX by splitting off the central iron from the corresponding heme derivative in an organic acid upon addition of a reducing agent (ferrous iron salt, $SnCl_2$, Hg metal, diazomethane).[1-2] Similarly, the synthetic iron(III) porphyrin complexes can be also demetalated in a strong acidic medium (but not a non-complexing acid) upon chemical or electrochemical reduction of ferric iron to ferrous iron.[3] We have established a methodology for the demetalation of a synthetic ferric porphyrin complex in acid medium without adding any external reducing agent. Here, we employed an acetylthioacetate functionalized iron(III)-α_4- tetraaminophenyl porphyrin (α_4-TAPP) complex. It offers an intramolecularly catalyzed exclusion of the central iron atom from the π macrocycle of the porphyrin upon conversion of its acetylthioacetate arms into acetylthiolates. Additionally, the excluded iron further binds to the acetylthiolates resulting in a non-heme iron tetrathiolate moiety attached to a free-base porphyrin ligand. The deprotection of the thioacetate moiety of a thioacetate functionalised α_4-porphyrin to thiolate is also the key to synthesise a non-heme metal-tetrathiolate cluster attached to a Fe porphyrin.



acetylthioacetate functionalized iron(III)-α_4-tetraaminophenyl porphyrin

non-heme metal-tetrathiolate cluster attached to a Fe porphyrin

REFERENCES

1. Grinstein, M., Studies of protoporphyrin; a simple and improved method for the preparation of pure protoporphyrin from hemoglobin. *The Journal of biological chemistry* **1947,** *167* (2), 515-9.
2. Caughey, W. S.; Alben, J. O.; Fujimoto, W. Y.; York, J. L., Substituted Deuteroporphyrins. I. Reactions at the Periphery of the Porphyrin Ring1. *The Journal of Organic Chemistry* **1966,** *31* (8), 2631-2640.
3. Espenson, J. H.; Christensen, R. J., Kinetics and mechanism of the demetalation of iron(III) porphyrins catalyzed by iron(II). *Inorganic Chemistry* **1977,** *16* (10), 2561-2564.

From CO to formaldehyde and methanol with a cobalt phthalocyanine electrocatalyst

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Electrochemical reduction of CO_2 can help mitigating carbon emissions upon conversion to valuable molecules (CO, hydrocarbons, and alcohols) by using renewable energy. While molecular catalysts show high performance in the reduction of CO_2 to CO, it is difficult to generate products beyond two-electron processes. Here, we demonstrate that cobalt phthalocyanine (CoPc) immobilized at carbon nanotubes can reduce CO_2 or CO to methanol with considerable activity and selectivity. A maximum methanol Faradaic efficiency of 56.7% was obtained at −0.88 V vs. RHE in a near-neutral electrolyte. We definitely proved that formaldehyde is a key intermediate in the CO-to-methanol conversion and identified the path for its formation. This strategy enabled us to form methanol through the electroreduction of CO, expanding the scope of products available from CO_2 reduction.

Structural features of phosphorus(V) complexes with phthalocyanine

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Phosphorus(V) porphyrinoid complexes remain exotic and rarely studied compounds despite their unique absorption in the near-IR region [1] and perspectives for biological applications due to their cationic nature. Phosphorus is the smallest atom which can occupy the centre of tetrapyrrole causing specific structural features. The most prominent feature is the ruffling of macrocycle core which can influence solubility, absorption and electrochemical properties. There are several reasons for distortion mentioned in literature: small ionic radius of phosphorus, nature and position of porphyrinoid substituents, nature of axial ligands on P(V), however no attention was earlier paid to the counteranion nature in cationic Pc complexes.

In this work for the first time we systematically studied a series of cationic P(V) phthalocyanines $[PcP(OMe)_2]^+$ with different counterions: Cl^-, I^-, CF_3COO^-, TsO^-, BPh_4^-, $CF_3SO_3^-$, $HCOO^-$. All compounds were characterised by set of methods and we succeeded to grow single crystals for each complex. Single crystal XRD (SCXRD) allowed us to determine macrocycle distortion and analyze structural features for the phosphorus(V) complex with different counteranions. The degree of Pc core ruffling depends on the anion and increases in the following row: $I^- < CF_3COO^- < HCOO^- \approx CF_3SO_3^- < TsO^- < Cl^- \ll BPh_4^-$. The bond lengths of Pc core were analyzed by the harmonic oscillator model of aromaticity (HOMA). HOMA indices are close for all structures and none of them loses its aromaticity during distortion. On the other hand, the crystal packing and distortion degree essentially affect the properties of material. Thus, the diffuse reflectance spectra changes depending on anion.

Moreover earlier in our group the reversible nucleophilic addition to a phthalocyanine core was observed for complex $[PcP(OMe)_2][Cl]$. The reaction with KOH leads to a nonaromatic adduct bearing an OH group at one of the α-pyrrolic carbon atoms [2]. SCXRD confirmed that after addition of an OH^- the Pc-like skeleton becomes highly distorted because of the presence of one sp^3 carbon (Figure 1). The breakage of aromaticity was verified by substantial decrease of macrocycle HOMA coefficient. The acidic treatment of this adduct restored aromaticity and recovered the starting cationic complex. Such reversible switching of macrocycle aromaticity and distortion results in crucial changes of absorption, emission and NMR spectra. Thus, the discovered phenomenon allows us to create novel Pc-molecules with switchable properties.

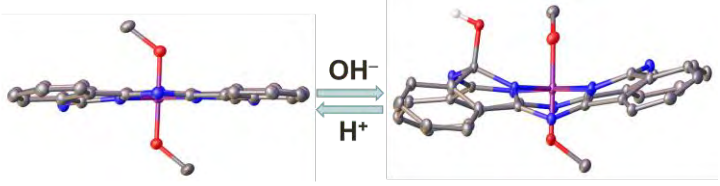

Figure 1. Side views of $[PcP(OMe)_2]^+$ and $PcP(OMe)_2OH$ according to SCXRD

This work was supported by the Russian Science Foundation (grant 22-23-01078).

REFERENCES

1. N. Kobayashi, T. Furuyama et al. *JACS* **2011** 133, 19642;
2. F.M. Kolomeychuk, E.A. Safonova et al. *JACS* **2021** 143, 14053.

Metal complexes of triply fused porphyrins: Impact of extended conjugation, metals and functional groups on electrocatalytic small molecule activation

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Electrocatalytic hydrogen evolution reaction (HER), a sustainable route for the production of hydrogen has attracted considerable attention as a new paradigm for energy storage, delivery and transport [1]. Due to the high cost and low abundance associated with noble metal catalysts, development of molecular catalyst consisting earth-abundant metal elements has been given priority for realising low-carbon economy. Metal complexes of porphyrin macrocycle in this context has been explored extensively as a catalyst for HER due to high catalytic activity, appreciable stability, and easy tunability of the ligand backbone.

In the recent past, several functional analogues based on the active site of naturally occurring metalloenzymes hydrogeneases was shown to exhibit higher efficiency than respective mononuclear analogues [2]. However, high overpotentials, requirement of strong acids and low turnover number prohibited their large-scale applications. Surprisingly, dinuclear analogues of metalloporphyrin i.e. fused porphyrins have largely remained unexplored for electrocatalytic hydrogen evolution reaction. Recently, a report from Moore and co-workers highlighted enhanced catalytic activity of the doubly fused dinuclear Cu(II)-porphyrin towards HER in comparison to the respective monomeric analogue [3]. It was followed by a report from the group of Apfel and coworkers demonstrating higher faradaic efficiency and 2-fold increase in HER activity of a bimetallic Ni(II) macrocycle over its monomeric analogue [4].

We have investigated for the very first time, catalytic efficiency of the bimetallic triply-fused Cu(II)-porphyrin (**Cu-1**) towards electrochemical HER and compared its activity with the respective monomeric counterpart (**Cu-2**). Dinuclear analogue was observed to exhibit significantly enhanced catalytic efficiency with a rate constant of ~10^7, which is among the highest reported in literature along with significant reduction in the over potential (~320 mV) as compared to respective monomer. Consistent with the higher catalytic activity of the triply fused metalloporphyrins, two different sets of Ni(II) functionalised triply fused porphyrins (**Ni-1** and **Ni-2**) containing a large solubilizing and moderate functional groups along the long axis with 4-carboxymethylphenyl functionality along the short axis were synthesised and characterised to address the low soluility associated with these type of frameworks .Comparative analysis of the HER activity of these complexes revealed that **Ni**-2 with lareg alkoxy groups at the peripheral position catalyses proton reduction at lower overpotential and higher activity in comparison to analogous **Ni-1** with moderate functional groups, as confirmed from the higher i_{cat}/i_p and turnover frequency values. Mechanistic elucidation of the reaction pathway using disclosed involvement of the doubly reduced species to drive the heterolytic protonolysis leading to the generation of H_2.

REFERENCES

1. Lee, C. H.; Dogutan, D. K.; Nocera, D. G. J. Am. *Chem. Soc.* **2011**, 133 (23),8775−8777.
2. Lubitz, W.; Ogata, H.; Rüdiger, O.; Reijerse, E. *Chem Rev* **2014**, 114, 4081–4148.
3. Khusnutdinova, D.;Wadsworth, B. L.; Flores, M.; Beiler, A. M.;Reyes Cruz, E. A.; Zenkov, Y.; Moore, G. F. *ACS Catal.* **2018**, 8, 9888−9898.
4. Jökel, J.; Schwer, F.; Delius, M. von; Apfel, U.-P. *Chem. Commun.* **2020**, 56, 14179–14182.

Novel dihydro-1*H*-diazepinoporphyrazines as potential photosensitizers and p*H*-sensitive fluorophores

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Porphyrazines containing 1,4-diazepine fragments with two acceptor imino groups [1] and their tetrahydro derivatives with donor amino groups [2] are described in the literature. In this work, novel near-IR-absorbing symmetric and low-symmetry porphyrazines with 6,7-dihydro-1*H*-1,4-diazepine rings, combining acceptor imino and donor amino groups, were prepared. The dinitrile precursors (6,7-dihydro-1*H*-1,4-dicarbonitriles) which were obtained by condensation of diaminomaleonitrile with acetone or cyclohexanone, according to the method [3]. Molecular structure of 2,3-dicyano-5,7,7-trimethyl-6,7-dihydro-1H-1,4-diazepine was determined by single crystal X-ray diffraction analysis. The obtained structural data confirm the conclusions made on the basis of spectral study and quantum-chemical modelling and evidence that –N= and –NH– groups in 6,7-dihydro-1H-1,4-diazepine ring can be considered as pyridine- and pyrrole-type nitrogens, and the electronic lone pair of the latter is involved in formation of quasi-aromatic conjugated heterocyclic system [4].

Trimethyl and cyclohexyl derivatives of dihydro-1*H*-diazepine-2,3-dicarbonitriles were cyclotetramerized in the presence of magnesium butoxide affording the Mg(II) complexes, while reaction with lithium butoxide leads directly to the corresponding metal free macrocycles. Also, mixed sterically controlled cyclization of phthalonitrile and dihydro-1*H*-1,4-diazepine-2,3-dicarbonitrile in the presence of lithium butoxide gave a low symmetry A_3B type metal free porphyrazine.

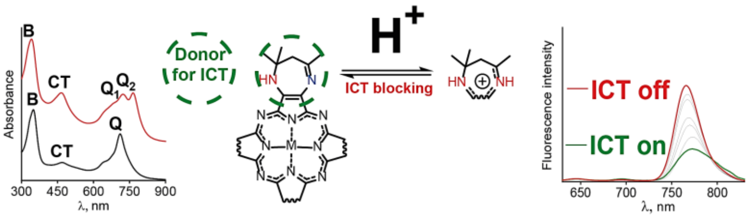

Figure 1.

The formation of novel macrocyclic compounds was confirmed by IR, MALDI-TOF, ^{1}H NMR and their properties were characterized using UV-Vis-spectroscopy and cyclic voltamperometry. The NH-groups in the diazepine fragments participating in intramolecular charge transfer (ICT) strongly quench the fluorescence (**Figure 1**). Spectrophotometric titration, ^{1}H NMR measurements and quantum chemical molecular modeling indicate that protonation of the diazepine rings which occurs on the pyridine nitrogen atoms switches off the ICT effect and increases the fluorescence quantum yields by 2-4 times [5]. The observed effect of fluorescence switching allows us to consider the obtained diazepinoporphyrazines as perspective pH-sensitive fluorescence materials.

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REFERENCES

1. Donzello M.P., Ercolani C., Stuzhin P.A., *Eur. J. Inorg. Chem*., 1999, (**11**), 2075-2084.
2. Baum S.M., et al., *J. Org. Chem*., 2003, **68**(5), 1665–1670.
3. R.W. Begland, et al., *J. Org. Chem*., 1974, **39**(16), 2341–2350.
4. Skvortsov I.A., Fazlyeva A.M., Somov N.V., Stuzhin P.A. *Macroheterocycles*., 2021, **14**(3), 198-200.
5. Skvortsov I.A., Fazlyeva A.M., Khodov I.A., Stuzhin P.A., *New J. Chem*., 2020, **44**(42), 18362–18371.

Managanese(III) tetraphenylporphyrins with *N*-haloamide axial ligands: Precursors to nitrenes *via* photolysis

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Manganese complexes supported by macrocyclic tetrapyrrole ligands represent an important platform for nitrene transfer catalysis and have been applied to both C–H amination and olefin aziridination catalysis [1-2]. The reactivity of the transient high-valent Mn nitrenoids that mediate these processes renders characterization of these species challenging. Here we report the synthesis and nitrene transfer photochemistry of a family of Mn(III) tetraphenylporphyrin (TPP) complexes with an *N*-haloamide ($[X\text{-}N\text{-}Ts]^-$, X = Cl, Br, I; Ts (tosyl) = *p*-$H_3CC_6H_4SO_2$) axial ligand. These $S = 2$ Mn(TPP) *N*-haloamide complexes are characterized by ^1H NMR, UV-vis, IR, and high-frequency and -field EPR (HFEPR) spectroscopies, as well as single-crystal X-ray diffraction. Although Mn(tetrapyrrole)X (tetrapyrrole = porphyrin [3], corrole [4-5], and corrolazine [6] ; X = halide[3] and other axial ligands such as $OPPh_3$[4], as well as free of axial coordination[5]) have been studied extensively by HFEPR, the present work is the first with a nitrogen-donor ligand of any type, in this case a haloamide. HFEPR demonstrates that the Mn(III) centre is unremarkable in terms of its electronic structure as reflected in the $S = 2$ spin Hamiltonian parameters of the X = Cl, Br, and I series. Nevertheless, photolysis of these Mn(TPP)(XNTs) complexes results in the formal transfer of a nitrene equivalent to both C–H bonds, such as the a-C–H bonds of tetrahydrofuran, and olefinic substrates, such as styrene, to afford aminated and aziridinated products, respectively. Low-temperature spectroscopy (including X-band EPR) and analysis of kinetic isotope effects for C–H amination indicate halogen-dependent photoreactivity: Photolysis of *N*-chloroamides proceeds via initial cleavage of the Mn–N bond to generate Mn(II) and amidyl radical intermediates; in contrast, photolysis of *N*-iodoamides proceeds via N–I cleavage to generate a Mn(IV) nitrenoid (i.e., $\{MnNR\}^7$ species). These results establish N-haloamide ligands as viable precursors in the photosynthesis of metal nitrenes and highlight the power of ligand design to provide access to reactive intermediates in group-transfer catalysis**.**

REFERENCES

1. Y. Park, Y. Kim, S. Chang, *Chem. Rev*. **2017**, *117*, 9247–9301.
2. C.-M. Che, V. K.-Y. Lo, C.-Y. Zhou, J.-S. Huang, *Chem. Soc. Rev.* **2011**, *40*, 1950–1975.
3. A. N. Bone, S. E. Stavretis, J. Krzystek, Z. Liu, Q. Chen, Z. Gai, X. Wang, C. A. Steren, X. B. Powers, A. A. Podlesnyak, X.-T. Chen, J. Telser, H. Zhou, Z.-L. Xue, *Polyhedron* **2020**, *184*, 114488.
4. J. Bendix, H. B. Gray, G. Golubkov, Z. Gross, *Chem. Commun*. **2000**, 1957–1958.
5. J. Krzystek, A. Schnegg, A. Aliabadi, K. Holldack, S. A. Stoian, A. Ozarowski, S. D. Hicks, M. M. Abu-Omar, K. E. Thomas, A. Ghosh, K. P. Caulfield, Z. J. Tonzetich, J. Telser, *Inorg. Chem.* **2020**, *59*, 1075–1090.
6. D. E. Lansky, B. Mandimutsira, B. Ramdhanie, M. Clausén, J. Penner-Hahn, S. A. Zvyagin, J. Telser, J. Krzystek, R. Zhan, Z. Ou, K. M. Kadish, L. Zakharov, A. L. Rheingold, D. P. Goldberg, *Inorg. Chem*. **2005**, *44*, 4485–4498.

Hemicucurbituril complexes with Porphyrins – chirality induction and sensing

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Metalloporphyrins are well–known for their vivid colours, which may change upon a guest binding; therefore, serve as molecular sensors [1]. An appealing application of chemosensors is recognition of chiral compounds due to typically large differences in biological activity of enantiomers. However, it is demanding and expensive to synthesize chiral porphyrins [2], which could fulfill such recognition function themselves.

In our approach we utilize chiral macrocyles cyclohexanohemicucurbit[*n*]urils (**cycHC[*n*]**s, *n* = 6, 8) [3] to induce chirality in simple inexpensive planar zinc(II) porphyrins through supramolecular interactions (Fig. 1A) [4]. Specifically, zinc is coordinated to oxygen of urea moiety. Hence, **cycHC[*n*]** may bind simultaneously other compounds at unoccupied monomeric units or inside its cavity. Our target is to explore if such ternary complexes can effectively sense chirality of third component (analyte).

In addition, binding of **cycHC[*n*]** with bis(zinc octaethylporphyrin) (**bis–ZnOEP**) (Fig. 1B) — known for its ability to recognize enantiomers of various chiral molecules [5] — was examined to compare the chirality induction efficiency with single porphyrins and to discover if **bis–ZnOEP** can recognize differences in size and chirality of **cycHC[*n*]** [6].

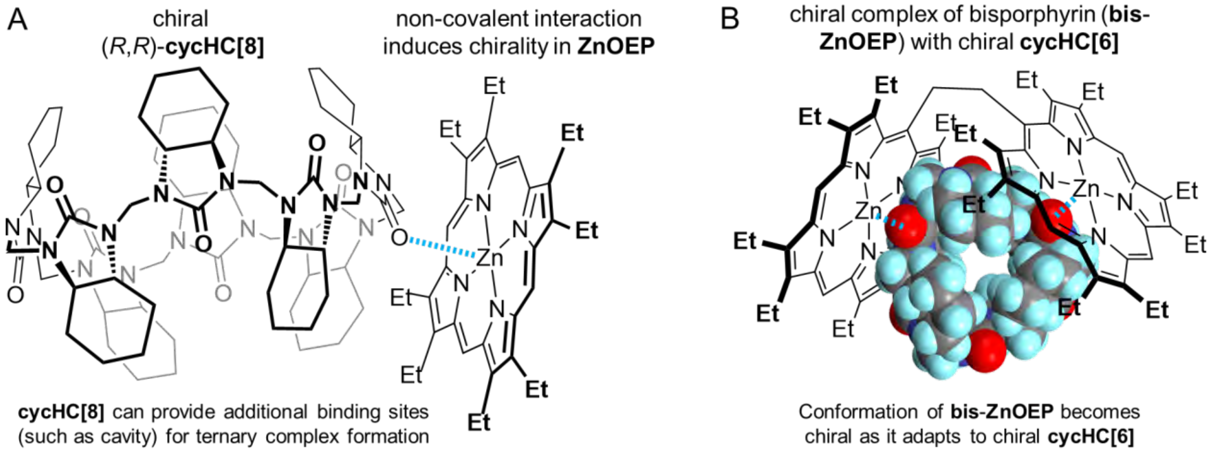

Figure 1: (A) originally planar **ZnOEP** forms complex with **cycHC[8]**, which leads to chirality induction at porphyrin. (B) **bis–ZnOEP** binds **cycHC[6]** and accommodates chiral tweezer–like conformation.

REFERENCES

1. Norvaiša K., Kielmann M. and Senge M.O. *ChemBioChem* **2020**; 21: 1793-1807.
2. Senge M.O., Sergeeva N.N. and Hale K.J. *Chem. Soc. Rev.* **2021**; 50: 4730-4789
3. Aav R. *et al. Org. Lett.* **2013**; 15: 3786-3789; Prigorchenko E. *et al. Chem. Commun.* **2015**; 51: 10921-10924
4. Ustrnul L. *et al. Chem. Commun.* **2019**; 55: 14434-14437
5. Borovkov V.V., Hembury G.A. and Inoue Y. *Acc. Chem. Res.* **2004**; 37: 449-459
6. Šakarašvili M. *et al. Molecules* **2022**; 27: 937

Structure of the Cu$_B$-NO in the binuclear center of heme-copper oxidoreductases

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The formation of the hyponitrite species from two NO molecules is the key intermediate in the reduction of NO to N_2O in denitrification. In bacterial respiration the reduction of NO_2^-/NO to N_2O by terminal oxidoreductases supports the hypothesis of a common evolutionary origin of bacterial denitrification and aerobic respiration. Activation of NO in denitrification and bacterial respiration provides the means to identify conserved structural features, which can be assumed to be involved in basic functions common to both classes. The most commonly encountered metals in the biological reduction of NO_2^- to NO and subsequently to N_2O are iron and copper in mononuclear, binuclear, and dinuclear centers. The oxidoreductases contain Cu$_A$, one low-spin, six coordinated heme b, and a binuclear center that consists of Cu$_B$ and a high-spin heme a$_3$ in which the catalytic reactions take place (Figure 1) [1]. A full elucidation of the structures and the electronic configurations of various intermediates are of profound importance for understanding the mechanism by which the enzymes form and cleave NO-containing bonds [1-4]. Resonance Raman studies of the NO_2^-/NO structures formed in the binuclear heme Fe-Cu$_B$ center will be presented.

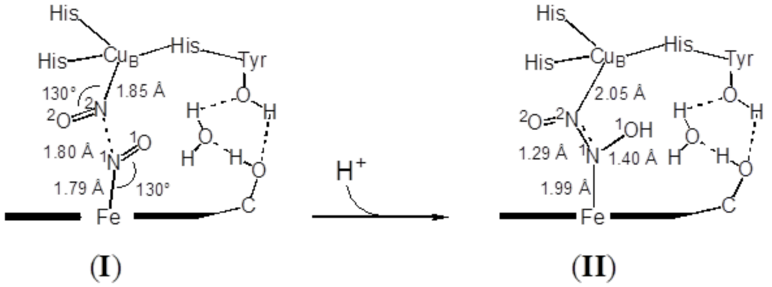

Figure 1. Structures of reaction intermediates in the binuclear center of heme-copper oxidoreductases.

REFERENCES

1. C. Koutsoupakis, T. Soulimane, C. Varotsis, *Acc. Chem. Res.,* 52 (5), 1380-139, **2019.**
2. A. Loullis, M.R. Noor, T. Soulimane, E. Pinakoulaki, *Chem. Commun.,* 51 (2), 286-289, **2015**.
3. C. Varotsis, T. Ohta, T. Kitagawa, T. Soulimane, and E. Pinakoulaki, *Angew. Chem. Int.* 46, 2210-2214, **2007**.
4. T. Ohta, T. Kitagawa, C. Varotsis, *Inorg. Chem.* 45, 3187-3190, **2006**.

Photodynamic inactivation of pathogenic microorganisms on fish fillet

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The increase in the consumption of raw fish, often carrying multi-drug resistant microbial strains, has emerged as a new global health threat being responsible for serious foodborne diseases for the consumer [1,2]. To prevent these infections, new strategies to decontaminate fishery products must be developed. Therefore, in this study we aimed to investigate the photodynamic inactivation (PDI) of *Escherichia coli* and *Vibrio parahaemolyticus* in fish fillets considering the high pathogenicity of these bacteria and their often transmission through contaminated fish to humans. The efficiency of the developed protocol was also evaluated in the photoinactivation of microorganisms naturally present on fish fillets. The treatments were performed *in vitro* and *ex-vivo* (fish fillet) in the presence of two photosensitizers (PSs), 5,10,15,20-tetrakis(1-methylpyridinium-4-yl)porphyrin tetra-iodide (**Tetra-Py(+)-Me**) and Methylene Blue (**MB**) under irradiation with white light (100 mW.cm^{-2}). *In vitro*, both PSs at a concentration of 0.5 µM were efficient to reduce *E. coli* and *V. parahaemolyticus* viability until the detection limit of the method (~8 log of CFU.mL^{-1}) after 30-45 min of PDI treatment. In fish fillet, **Tetra-Py(+)-Me** and **MB** (50 µM) were also able to promote the photoinactivation of *E. coli* in *ca.* 99% after 60 min of PDI treatment, although for *V. parahaemolyticus* a more pronounced inactivation was achieved with **MB** (> 99.9%). Furthermore, the PDI treatments were even more efficient in the photoinactivation of the fish natural microorganisms with reductions of 99.998% and 99.9997% with **Tetra-Py(+)-Me** and **MB**, respectively. These results reveal that the developed protocol was not only efficient to inactivate *E. coli* and *V. parahaemolyticus* in contaminated fish fillet but also to photoinactivate the fish natural microorganisms that can compromise the fish quality and consumer safety. In summary, the results suggest that PDI can be a promising approach to decontaminate fish fillets and provide safe food to the consumer.

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REFERENCES

1. Novoslavskij, A., Terentjeva, M., Eizenberga, I.; Valciņa, O.; Bartkevičs, V.; Bērziņš, A. Major foodborne pathogens in fish and fish products: a review. *Ann Microbiol.* **2016**, 66, 1–15.
2. Miguéis, S.; Santos, C.; Saraiva, C; Esteves, A. Evaluation of ready to eat sashimi in northern Portugal restaurants. *Food Control.* **2015**, 47, 32–36.

A New Research for Different Linkage Bridged Cobalt(II) Phthalocyanine Analog Compounds

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Phthalocyanines, which were used as dyes and pigments when they were first discovered, later on have taken place in many technological applications, such as solar cells, gas sensors, liquid crystals, etc [1].
Phthalocyanine chemistry has been an endless researching area for researchers due to its variety by changing central metal atom and peripheral / nonperipheral substituents. There are also varieties of phthalocyanines such as asymmetric, sub, super, sandwich, clamshell, ball type Pcs. Recently phthalocyanines contain nanocarbon and nanoparticle, have been attracted researchers due to their wide applications for energy [2].

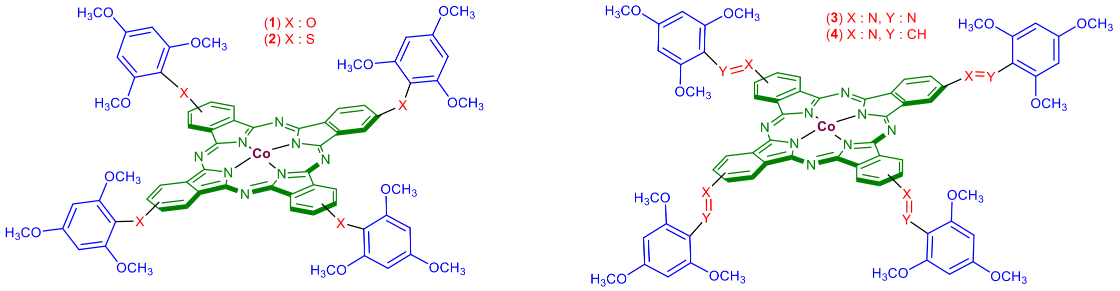

Figure 1. Molecular Structure of beta substituted cobalt(II) Phthalocyanine Analogs

One way to provide this diversity is to use different linkage bridges other than the most preferred oxygen bridged derivatives. Therefore, four different species were selected in order to investigate the effects of the linkage bridge difference on the phthalocyanine properties in this study. The original starting materials 4-(2,4,6-trimethoxyphenoxy)phthalonitrile**(1)**, 4-((2,4,6-trimethoxyphenyl)thio)phthalonitrile**(2)**, (E)-4-((2,4,6-trimethoxyphenyl)diazenyl)phthalonitrile**(3)**, (E)-4-((2,4,6-trimethoxybenzylidene)amino)phthalo-nitrile**(4)** and their oxo, thio, azo and imine bridged metal free Pcs were synthesized. The original compounds were purified by column chromatography or crystallization methods and their structures were characterized using spectroscopic methods (UV, FT-IR, ^{1}H-NMR and ^{13}C-NMR, MALDI-TOF-MS).

REFERENCES

1. Salan, Ü., Kobayashi, N., Bekaroğlu, Ö., Tetrahedron Letters, 2009, 50, 6775–6778.
2. Ragoussi, M., Katsukis, G., Roth, A., Malig, J., de la Torre, G., Guldi, D. M., Torres, T., J. Am. Chem. Soc. 2014, 136, 4593−4598.

Synthesis and characterization of oxo, thio, azo and imino bridged beta substituted metal-free Phthalocyanine Analogs

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Metal-free phthalocyanine (H_2Pc) was obtained by accident for the first time in 1907 as a by-product during the preparation of 2-cyanobenzamide [1]. H_2Pcs are not only synthesized for directly using for some applications, but also used for the synthesis of metallo Pcs because this method might be more practical. Most of the time, it is difficult to obtain H_2Pcs due to lack of metallic template effect [2].

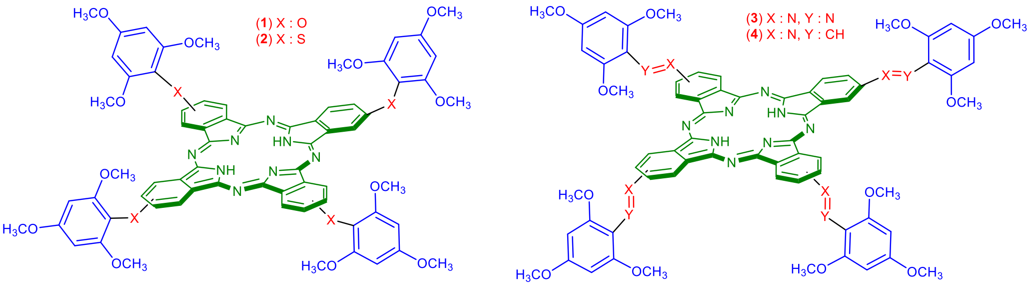

Figure 1. Molecular Structure of beta substituted metal-free Phthalocyanine Analogs

The aim of this study is to synthesize original starting compounds with different linkage bridges and their phthalocyanines derivatives and to investigate differences in synthesis and characterization properties. Thus, 4-(2,4,6-trimethoxyphenoxy)phthalonitrile, 4-((2,4,6-trimethoxyphenyl)thio)phthalonitrile (E)-4-((2,4,6-trimethoxyphenyl)diazenyl)phthalonitrile, (E)-4-((2,4,6-trimethoxybenzylidene)amino)phthalonitri-le and their oxo, thio, azo and imine bridged metal free Pcs were synthesized. The original compounds were purified by column chromatography or crystallization methods and their structures were characterized using spectroscopic methods (UV, FT-IR, ^{1}H-NMR and ^{13}C-NMR, MALDI-TOF-MS).

REFERENCES

1. Hanack, M., Heckmann, H., Polley, R., Meth. Org. Chem. (houben-Weyl), 1998, E9d, 717-846.
2. Cetinkaya, M., Piskin, M., Altun, S., Odabas, Z., Durmuş, M., Journal of Photochemistry and Photobiology A: Chemistry, 2017, 335, 17-25.

Stepwise Oxidative C-C Coupling and/or C-N Fusion of Zn(II) *meso*-Pyridin-2-ylthio-Porphyrins

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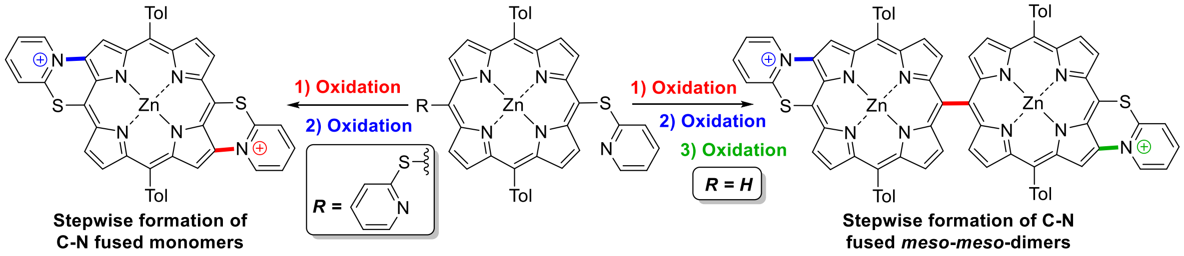
Extending the π-conjugation of aromatic molecules, in particular porphyrinoids, *via* C-C or C-N coupling(s) with peripheral aromatic fragment(s) has been the focus of numerous researches over the last two decades [1]. Indeed, C-C/C-N fusion of one are several hydrocarbon(s) or aromatic heterocycle(s) onto the porphyrin periphery forces the porphyrin core and the substituent to be coplanar, that enhances the electronic communication between both fragments. π-extended porphyrins display important changes in their optical and electrochemical properties such as 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 zinc(II) *meso*-(pyridin-2-ylthio)porphyrins will be presented affording the C-N fused (bis)pyridinium derivatives in a stepwise manner. When one *meso* position remains free, the first oxidative reaction consists in the *meso*,*meso* C-C dimerization. The resulting pyridinium derivatives exhibits important changes in their physico-chemical properties (NMR, UV-vis., CV) as compared to their initial unfused precursors.



REFERENCES

1. Grzybowski, M.; Skonieczny, K.; Butenschön, H.; Gryko, D. T. *Angew. Chem.*, *Int. Ed.* 2013, **52** (38), 9900–9930, doi.org/10.1002/anie.201210238.
2. (a) Matsuo, Y.; Sato, Y.; Niinomi, T.; Soga, I.; Tanaka, H.; Nakamura, E. *J. Am. Chem. Soc*. 2009, 131 (44), 16048–16050. doi: org/10.1021/ja9048702; (b) Zimmerman, J. D.; Diev, V. V.; Hanson, K.; Lunt, R. R.; Yu, E. K.; Thompson, M. E.; Forrest, S. R. *Adv. Mater*. 2010, **22** (25), 2780–2783. doi.org/10.1002/adma.200904341; (c) Jurow, M.; Schuckman, A. E.; Batteas, J. D.; Drain, C. M. *Coord. Chem. Rev.* 2010, 254 (19), 2297–2310, doi.org/10.1016/j.ccr.2010.05.014; (d) Satrialdi; Munechika, R.; Biju, V.; Takano, Y.; Harashima, H.; Yamada, Y. *Chem. Commun.* 2020, **56** (7), 1145–1148, doi.org/10.1039/C9CC08563G.
3. Berthelot, M.; Akhssas, F.; Dimé, A. K. D.; Bousfiha, A.; Echaubard, J.; Souissi, G.; Cattey, H.; Lucas, D.; Fleurat-Lessard, P.; Devillers, C. H., 2022, *submitted*.

Metal Ion Detection by Macrocycles with Sensitive Axial Ligands

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Phthalocyanines and their analogues have interesting and highly applicative photophysical properties in areas such as photodynamic therapy, fluorescence sensing, dyes manufacturing, and the development of logic gates.[1] Switching of their photophysical properties, needed for fluorescent probes, switches and sensors of metal cations, is usually achieved by photo-induced electron transfer (PET).[2]

The aim of this work was to prepare florescence sensors for metal cations by the introduction of sensitive azacrown ether ligand into the axial positions of various macrocycles (Fig. 1 below), which is only rarely reported. Advantageously peripheral positions on macrocycles may be used for improving water solubility, *e.g.* by the introduction of sulfonated groups.

The synthetic pathway included the synthesis of the macrocycles with suitable central atoms after which the metal ion sensitive ligands were attached to the axial positions. Finally, switching properties were studied by titration with various metal cations by observing UV-vis absorption and fluorescence emission, which enabled the calculation of appropriate binding constants. Selectivity and sensitivity of prepared series towards various metal cations was compared within the series.

Acknowledgement: The work was supported by Czech Science Foundation (project No. 21-14919J).

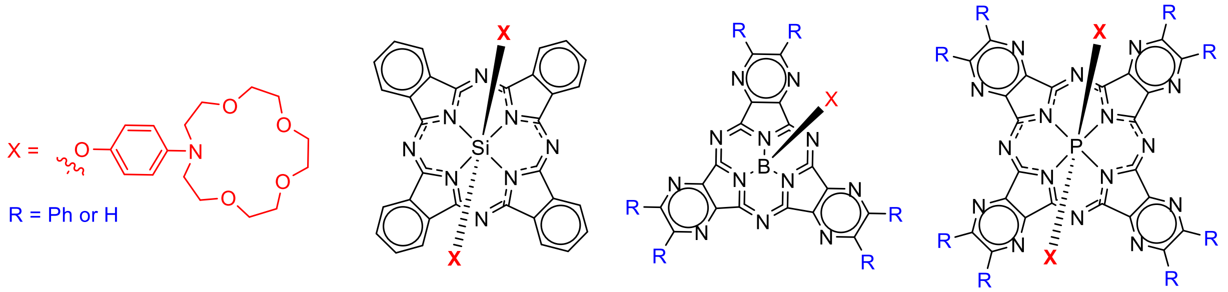

Figure 1: Phthalocyanine, Subporphyrazine, and Tetrapyrazinoporphyrazine macrocycles respectively, attached with a metal cation sensitive axial ligand.

REFERENCES

1. Claessens CG, Hahn U, Torres T, Chem. Rec., 2008, 8 (2), p. 75-97.
2. Novakova V, Donzello MP, Ercolani C, Zimcik P, Stuzhin PA, *Coord. Chem. Rev.*, 2018, 361, p 1-73.

Synthesis of a Tellurium Containing Porphyrinoids

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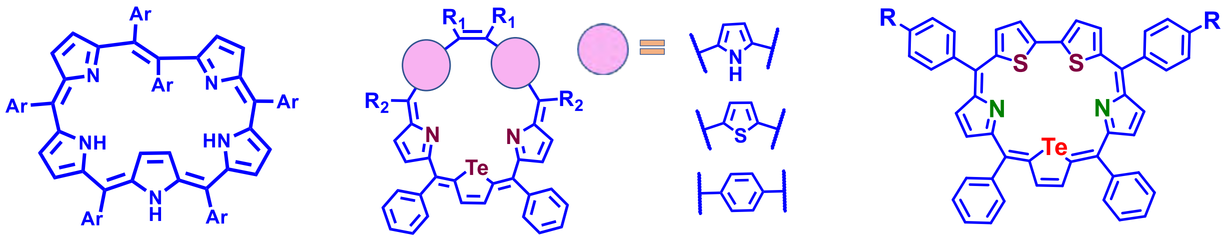
Porphyrinoids are polypyrrolic macrocycles with varied core sizes and aromaticity, which have found applications in various fields. Telluraporphyrinoids [1] are a class of tellurium containing heteroporphyrinoids which exhibit distinct and interesting properties owing to the large size of tellurium atom. Though the synthesis of core modified pentaphyrins (2.1.1.1.1) and sapphyrins [2] have been reported in recent years, telluorophene containing homopentaphyrins and sapphyrins have not been synthesized due to the unavailability of suitable precursors. In this poster, we report synthesis of different tellurophene containing core-modified pentaphyrin(2.1.1.1.1)s [3] and sapphyrins under ambient reaction conditions in decent yields (chart). Our studies showed that telluorophene containing core-modified homopentaphyrins are non-aromatic whereas telluorophene containing dithiasapphyrins are aromatic in nature. Furthermore, the tellurophene containing dithiasapphyrins showed ring flipping upon protonation. The synthesis, structure, spectral and electrochemical properties of these tellurium containing expanded porphyrinoids will be presented in the poster.



Chart

REFERENCES

1. Alka, A.; Shetti, V. S.; Ravikanth, M. Telluraporphyrinoids: An Interesting Class of Core-Modified Porphyrinoids. *Dalt. Trans.* **2019**, *48*, 4444–4459.
2. Chatterjee, T.; Srinivasan, A.; Ravikanth, M.; Chandrashekar, T. K. Smaragdyrins and Sapphyrins Analogues. *Chem. Rev.* **2017**, *117*, 3329–3376.
3. Ali, M. A.; Laxman, K.; Ravikanth, M. *manuscript submitted.*

Diverse Zn porphyrin structures effect the photocatalytic H_2 production

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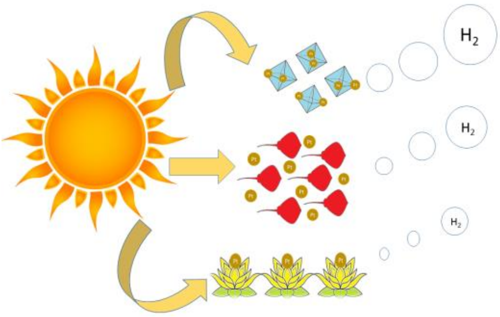
Hydrogen is regarded a promising molecular fuel for clean energy production, capable of replacing fossil fuels and contributing to the resolution of global energy and environmental problems. Therefore, the efficient production of H_2 is of great significance, with the most promising strategy being the photocatalytic splitting of water.[1] In this study, different supramolecular architectures, such as “flowers”, octagonal and “manta ray” shaped structures, were obtained using the “good-bad” solvent self-assembly protocol. More specifically, the bad solvent was retained (CH_3OH) and the good solvent was altered, leading to different assemblies after 48 hours. These different structures were observed and studied by Scanning Electron Microscopy, UV-Vis and IR spectroscopy, as well as XRD. The prepared structures were found to be effective solid photosensitizers for H_2 production, in the presence of 5% w/w Pt-nanoparticles as the catalyst and ascorbic acid as the sacrificial electron donor. Moreover, depending on the structure of the chromophore that was formed, the amount of H_2 production varied. The maximum H_2 evolution was obtained with the octagonal structures.



Acknowledgments : The Special Research Account of the University of Crete is gratefully acknowledged for the financial support of this research.

REFERENCES

1. K. Ladomenou, M. Natali, E. Iengo, G. Charalampidis, F. Scandola, A. G. Coutsolelos, *Coord. Chem. Rev.*, **2015**, *304*, 38-54.

Synthesis and Characterization of Bis-Functional Electron-Donor and Electron-Acceptor Porphyrins for Application in Dye-Sensitized Solar Cells

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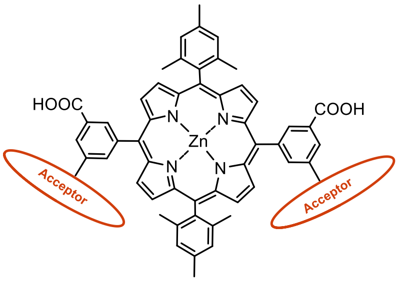
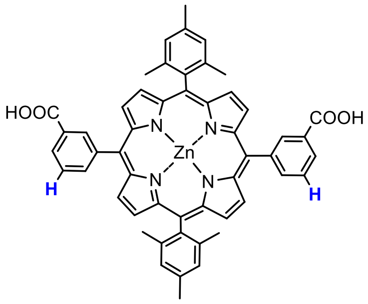
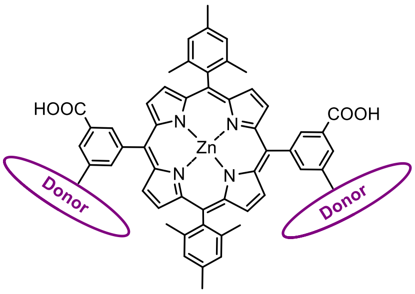
Porphyrins have been extensively used in Dye Sensitized Solar Cells (DSSCs),[1] due to their characteristic and intense absorption in the visible region, which results from their extended conjugated system. In this work, novel meso Zinc (II) porphyrins bearing an electron-withdrawing and an electron-donating group at the same phenyl rings have been synthesized. The porphyrin-based sensitizers can be adsorbed onto TiO_2 semiconductor electrode through carboxylic acid anchoring groups. The nature of the different substituents influences significantly the optical, electrochemical and photovoltaic properties of these sensitizers, as shown via UV-Vis, emission and electrochemical studies. Furthermore, the corresponding analogues lacking the electron-donor and electron-acceptor functional groups have been also synthesized and utilized as reference chromophores in the photovoltaic studies.







Acknowledgments: The Special Research Account of the University of Crete is gratefully acknowledged for the financial support of this research.

REFERENCES

1. Panda M. K., Ladomenou K., Coutsolelos A. G., *Coordination Chemistry Reviews*, **2012**, *256*, 2601-2627.

Understanding the failure to generalize the reversed 'breaking and mending' strategy towards pyrrole modified porphyrins containing large heterocycles

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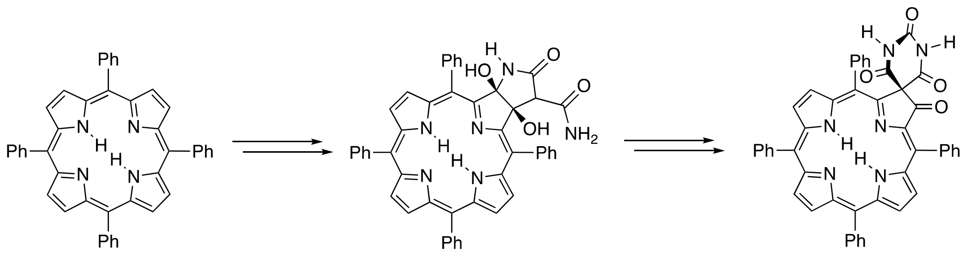
Pyrrole modified porphyrins (PMPs) are porphyrin analogues in which at least one of the pyrrolic rings of the tetrapyrrolic macrocycle was formally replaced by a non-pyrrolic ring have found applications in chemosensing, biomedicine, catalysis, near IR emitters, as well as enhanced the understanding of interplay of factors influencing the optical properties of the porphyrin macrocyle [1]. The two main strategies employed to access PMPs are either total synthesis or stepwise conversion of porphyrins; the latter we formalized as a the 'breaking and mending approach' [1b]. While this approach has proven to be versatile in the generation of PMPs containing four-, five-, and six-membered non-pyrrolic heterocycles, it failed to generate larger heterocycles. Larger ring-based PMPs collapsed to form thermodynamically more stable five membered non-pyrrolic heterocycles.

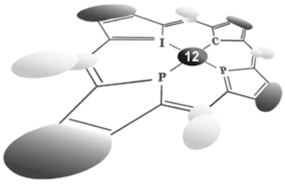
We recently showed that by using a reversal of our breaking and mending strategy, we were able to afford in select cases an eight-membered ring-based PMP [2]. Here, we will report on our efforts in using this annulation → oxidative cleavage strategy towards 9- and 10-membered ring PMPs. Access to large ring PMPs have remained inaccessible due to a host of side reactions. Nonetheless, our investigation allowed us to isolate a number of novel macrocycles that allowed us to learn more about the mechanism of the reactions that failed to generate the target PMPs (Scheme 1).



Scheme 1

REFERENCES

1. (a) Brückner, C.; Akhigbe, J.; Samankumara, L., In *Handbook of Porphyrin Science*, Kadish, K. M.; Smith, K. M.; Guilard, R., Eds. World Scientific: Singapore, 2014; Vol. 31, pp 1–276. (b) Brückner, C. *Acc. Chem. Res.* **2016**, 49, 1080–1092. (c) Ning, Y.; Jin, G.-Q.; Zhang, J.-L., *Acc. Chem. Res.* **2019,** *52*, 2620–2633.
2. (a) Luciano, M.; Tardie, W.; Brückner, C. *Chem. Commun.* **2016**, 52, 10133–10136. (b) Luciano, M.; Atoyebi, A. O.; Tardie, W.; Zeller, M.; Brückner, C. *J. Org. Chem.* **2020**, 85, 15273–15286. (c) Luciano, M. P. PhD Thesis, University of Connecticut: Storrs, CT, **2017**.



Engineering Fused Ni(II) Porphyrin polymer: Effect of Substituent on Electro-chemical and Opto-electronic Properties

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Porphyrins belong to a widespread class of compounds playing a key role in natural catalytic phenomena such as photosynthesis and respiration.[1] Their properties can be easily tuned from the attachment of substituents to one or several of the eight *β*- and four *meso*- positions of the porphin ring and/or from the introduction of a cation inside the porphyrin core.[2] In recent times, the cooperative effect promoted by conjugated covalent links between porphyrins was demonstrated for catalytic applications.[3] Particularly, directly fused metalloporphyrin conjugated polymers display interesting opto-electronic and electrocatalytic properties.[3,4] In general, despite of 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-meltability.[5] In this context, Oxidative Chemical Vapor Deposition (*o*CVD) has afforded a promising solution to prepare and engineer multiply fused porphyrin conjugated polymers directly on the desired surface, overcoming the limitation related to solution-based approaches.[5]

Herein, we show the *o*CVD technique to prepare different di-*meso*-substituted Ni(II) porphyrin conjugated polymers containing phenyl groups with variety of substituents. The substituted groups on phenyl rings are shortlisted based on their electron donating, withdrawing and steric properties. High resolution mass spectroscopy displays the formation of doubly and triply fused porphyrin oligomers. Direct linkage between metalloporphyrins results in the increased conjugation between metalloporphyrin's leading to the absorption in NIR region. All the polymerized material exhibits improved conductivity and electrocatalytic properties in comparison to monomers. Computational calculations also display interesting delocalization of frontier molecular orbitals on the polymerized metalloporphyrinoids. This study paves the way toward the engineering and future implementation of porphyrin-based systems comprising of donor-acceptor properties for clean and efficient solar fuel production.

REFERENCES

1. Zhang W, Lai W, Cao R. *Chem. Rev.* **2017**, *117*, 3717.
2. Mori H, Tanaka T, Osuka A. *J. Mater. Chem. C.* **2013***, 1, 2500.*
3. Huerta-Flores AM, Bengasi G, Baba K, Boscher ND. *ACS Appl. Energy Mater.* **2020**, *3 (10),* 9848–9855.
4. Tsuda A, Osuka A. *Science* **2001***, 293,* 79.
5. Bengasi G, Baba K, Frache G, Desport J, Gratia P, Heinze K, Boscher ND. *Angew.Chem.* **2019***, 131,* 2125.

IR and Raman spectroscopy study of nanostructured LS films of vitamin B12 derivative

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Stable nanoparticles of a hydrophobic derivative of vitamin B12 – aquacyanocobyrinic acid heptabutyl ester (AC) in the layers at air-water interface and Langmuir-Schaefer (LS) films were formed. Regions of existence and characteristics of the structure and properties of nanostructured layers were determined with the method of quantitative analysis of compression isotherms of floating layers [1].

To reveal the nature of responsible intermolecular interactions in LS film IR and Raman spectra of the film were compared with those of the film deposited by drop coating technique from the AC monomer solution. Main differences are observed in the range from 2850 to 3050 cm-1. The bands in this range are mainly attributed to the stretching vibrations of C-H bonds of the side substituents in the corrin macrocycle, which are most sensitive to intermolecular interactions. The bands in the IR spectrum of LS film are shifted to a lower frequency region. This may suggest the formation of hydrogen bonds between neighboring supermolecular entities (SMEs) and/or hydrophobic interaction between side hydrophobic substituents of neighboring molecules. The same tendency is also observed in the Raman spectra.

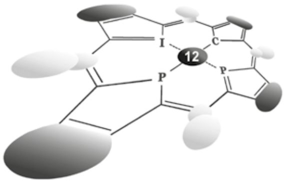
Changes in the spectral region corresponding to macroheterocycle deformations (specifically, C-C-N or C-N-C bending are also observed in the Raman spectrum of the LS film. The increase in relative intensities of the Raman bands in the range from 450 to 650 cm-1 is clearly noticeable. This is in accordance with strong intermolecular interactions in nanoparticles in the film, as revealed by UV-Vis spectral studies.

Furthermore, additional interactions via hydrogen bonds between axial ligands (CN···H2O) of cobalt centers in neighboring nanoparticles are confirmed. The shift of the band associated with O-H stretching vibrations and an increase in its intensity may be an indication of these hydrogen bonds. A wide band is observed in the IR spectrum of the drop coated film with a maximum located around 3430 cm-1, while in the spectrum of LS film the band shifts to the region of lower frequencies (~3330 cm-1), and its intensity increases noticeably.

The work was financially supported by the grant of the RSF (20-12-00175, film formation and study), ISUCT, and Ministry of Science and Higher Education of the RF (FZZW-2020-0008, synthesis of the compound).

REFERENCES

1. L.A. Maiorova et al. *ACS Langmuir* 2018, 34, 9322-93293; Vu T.T. et al. *Macroheterocycles* 2016, 9(1), 73-79; Valkova LA. et al. *Bull. Russ. Acad. Sci.: Phys.* 1997, 61, 631; Maiorova LA. et al. *Prot.Met.Phys.Chem.* 2015, 51, 85-92; Kharitonova N.V. et al. *JPP* 2018, 22(6), 509-520.



Interaction of potential PDT chlorin e_6 type sensitizers with micellar and polymer carriers in aqueous media

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Photodynamic therapy (PDT) is considered to be an alternative to conventional methods of tumor cells or pathogenic microflora inactivation and can be used as an effective addition to chemotherapy. PDT strategy is based on selective accumulation of pigments – photosensitizers (PS) in malignant or microbial cells to kill them when exposed to visible light in the presence of oxygen [1, 2]. One of the most important problems in clinical PDT when using macroheterocyclic PSs such as porphyrins and chlorins is their aggregation in aqueous solutions at therapeutic concentrations [1, 3-6]. Aggregation of PS reduces the efficiency of reactive oxygen species (ROS) generation, drug bioavailability, its circulation time in the bloodstream ae tropism [1]. These problems are solved by using a wide range of carriers for both passive and active delivery of drugs to abnormal cells, including polymer and micellar surfactants, liposomes, nanoparticles, vector carriers, etc. [1]. Non-ionic micellar surfactants like Tween 80 and biocompatible polymer carriers as PVP, PEG or P123 are known to be effective and widely used passive delivery vehicles. Here we present the results on the interaction of chlorin e_6 type PSs with micellar and polymer carriers including the binding constants PS/surfactants calculated, size of nanocontainers estimated and the depth of PS penetration into the micelle evaluated depending on the substitution pattern of the macrocycle. Results are discussed in a poster.

This work was s*upported by the Russian Science Foundation (project N 21-13-00398).*

REFERENCES

1. L. Yakavets, M. Millard, V. Zorin, H.P. Lassalle, L. Bezdetnaya, *J. Contr. Release*, **2019**, *304*, 268-287.
2. A.V. Kustov, D.B. Berezin, O.I. Koifman, *In: Functional materials based on tetrapyrrol macroheterocycli*c *compounds.* O.I. Koifman ed., Moscow, URSS, **2019***, 49 p.* (in Russian)
3. D.B. Berezin, A.V. Kustov, M. A. Krest'yaninov, O.V. Shukhto et al., *J. Mol. Liq.,* **2019**, *283*, 532-536.
4. D.B. Berezin, V.V. Makarov, S.A. Znoyko, V.E. Mayzlish, A.V. Kustov, *Mend. Commun.,* **2020**, *30(5),* 621-623.
5. A.V. Kustov, M.A. Krestyaninov, S.O. Kruchin, O.V. Shukhto, T.V. Kustova, D.V. Belykh, I.S. Khudyaeva, M.O. Koifman, P.B. Razgovorov, D.B. Berezin, *Mend. Commun.,* **2021**, *31(1)*, 65-67.
6. O.V. Shukhto, I.S. Khudyaeva, D.V., Belykh, D.B. Berezin, *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Kh*im. *Tekhnol.]),* **2021**, *64(11)*, 86-96.

H-bonding stabilized molecular complexes of phenyl-substituted corroles and other porphyrinoids with electron donor solvents

Dmitry B. Berezin[a], **Anastasiya E. Likhonina**[b] , **Dmitry R. Karimov**[a],
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A comprehensive study of different classes of phenyl-substituted aromatic macroheterocycles (MHC) including N-substituted, isomeric, contracted and inverted porphyrin analogues (H_nPn) was carried out using a combination of spectral (UV-Vis, Fl, ^{1}H NMR) and thermal (calorimetry, thermogravimetry), electrochemical (electrical conductivity) and quantum-chemical methods (DFT, NBO) [1-6]. It was shown that inverted porphyrinoids and *meso*-substituted corroles only have a pronounced chemical reactivity of NH bonds, which is appeared in the ability of these compounds to interact with a weak electron donors B to form acid-basic molecular complexes ($H_nPn \cdot B$) with incomplete proton transfer [1, 2, 6].

The tendency of porphyrinoids to molecular complexation with electron donors is controlled by the combination of several factors, as an MHC ability to form solvent-dependent tautomeric forms, an increase of polarization of the molecular π-system and decrease in its aromaticity [5, 6].

It was demonstrated for the first time that the inner-cyclic NH-proton of MHC forms an intermolecular hydrogen bond with the electron-donor center of B molecule within molecular complex resulting in incomplete acid-base interaction. NH-active forms of corrole and an inverted analog of porphyrin are formed in polar electron-donor media, for example, in N,N-dimethylformamide solutions. Molecular complexes formed under these conditions, similarly to 1:1 electrolytes, demonstrate concentration dependences of the enthalpy of solution ($\Delta_{sol}H$), as well as a shift and broadening of signals of proton NH in the ^{1}H NMR spectrum, however, they do not show a change in the value of specific electrical conductivity of the solution in comparison with a pure solvent. These data indicate the formation of H-bound forms, rather than anionic particles in solutions of these porphyrinoids.

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REFERENCES

1. D.B. Berezin, B.D. Berezin / In: *Chemical processes with participation of biological and related compounds.* Eds. T.N. Lomova, G.E. Zaikov. Brill: Leiden, **2008**, 169-217.
2. D.B. Berezin, D.R. Karimov, M*acroheterocycles*, **2009**, *2(1)*, 42-51.
3. D.B. Berezin, M.A. Krest'yaninov, *Struct. Chem.,* **2014**, *55(5)*, 868-876.
4. D.B. Berezin, D.R. Karimov, V.P. Barannikov, A.S. Semeykin, *Russ. J. Phys. Chem. A*, **2011**, *85(12)*, 2171-2176.
5. D.B. Berezin, A.E. Talanova, M.A. Krest'yaninov, I.N. Serov, A.S. Semeykin, *Russ. J. Phys. Chem*., **2016**, *90(10)*, 1948-1955.
6. A.E. Likhonina, M.B. Berezin, M.A. Krest'yaninov, D.B. Berezin, *ChemChemTech* [*Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*], **2021**, *64(10)*, 29-39.

Regioselective Amination of Porphyrins *via* Ring-Opening of Electrogenerated Pyridinium Precursors

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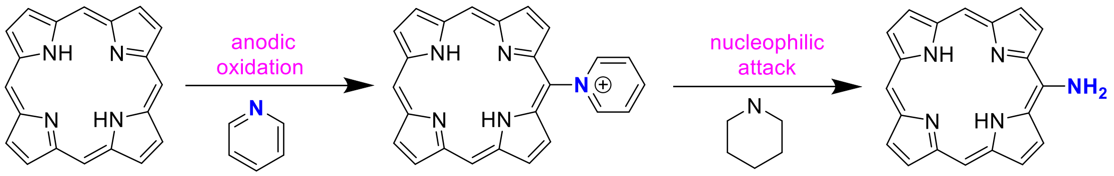
For many decades, porphyrins have attracted considerable attention due to their implication in natural processes (photosynthesis, O_2 transport in blood…) and their recent applications in various research fields such as photovoltaic solar cells, non-linear optical materials, photodynamic therapy and molecular electronics. To finely tune and improve the performance of porphyrin-based materials, peripheral functionalization of the porphyrin ring with judicious (hetero) atoms or molecular fragment(s) is essential. In particular, the introduction of a nitrogen atom directly bonded to the *meso* or *β* position of the porphyrin induces intense alterations of the electronic, optical, and electrochemical properties.

Numerous methods exist to introduce an amine function on porphyrin (reduction of a nitro function [1], Buchwald-Hartwig coupling with palladium [2] or attack of an azide anion on a brominated porphyrin [3]). However, they remain not always selective and require pre-functionalization of the porphyrin core.

This poster will present our recent electrochemical/chemical two-step one-pot amination of porphyrins based on 1) the regioselective anodic nucleophilic substitution of the porphyrin with pyridinium, 2) the chemical ring-opening of the pyridinium-porphyrin *via* nucleophilic attack of piperidine (Scheme 1). [4]



Scheme 1. Electrochemical /Chemical two-step one-pot amination of porphyrins.[4]

REFERENCES

1. J. E. Baldwin*, M. J. Crossley and J. DeBernardis, *Tetrahedron*, **1982**, 38, 685–692.
2. L. J. Esdaile, M.O. Senge and D.P. Arnold*, *Chem. Commun.*, **2006**, 4192-4194.
3. K.-I. Yamashita*, K.Kataoka, S. Takeuchi and K.-I. Sugiura*, *J.Org. Chem.*, **2016**, 81, 11176-11184.
4. Asmae Bousfiha, Abdou K. D. Dimé, Amelle Mankou-Makaya, Julie Echaubard, Mathieu Berthelot, Hélène Cattey, Julien Roger, Charles H. Devillers*, *Chem. Commun*. **2020**, 56, 884-887

Selective synthesis of GNRs towards directly linked porphyrin-GNR conjugates

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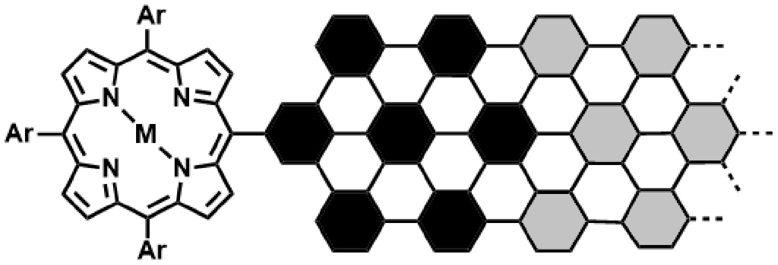
Polycyclic aromatic hydrocarbons, such as hexa-*peri*-hexabenzocoronenes (HBCs) can be synthesized as model compounds for graphene. Since HBCs and porphyrins show exceptional photophysical properties, a coupling of both moieties generates interesting photo/redox – active systems, in which energy transfer processes from HBC to porphyrin were observed.[1] Because HBC-porphyrin conjugates show interesting electronic communication between both chromophoric units, the next logical step was to extend the size of the aromatic framework, whereby a dependency of the energy transfer direction and the size of the GNR was discovered.[2] However, most synthetic approaches towards GNRs rely on polymerization reactions, which lack of control on the size, shape and edge structure.[3] Herein, we present the selective synthesis of a well-defined GNR and the subsequent coupling towards a porphyrin-GNR conjugate to further elucidate the photophysical characteristics of such compounds.



REFERENCES

1. Lungerich D, Hitzenberger J F, Hampel F, Drewello T, Jux N. *Chem. Eur. J.* 2018; **24**: 15818–15824.
2. a) Perkins W, Fischer FR. *Chem. Eur. J.* 2017; **23**: 17687–17691. b) Umeyama T, Hanaoka T, Yamada H, Namura Y, Mizuno S, Ohara T, Baek J, Park J, Takaano Y, Stranius K, Tkachenko NV, Imahori H. *Chem. Sci.* 2019; **10**: 6642–6650.
3. Chen L, Hernandez Y, Feng X, Müllen K. *Angew. Chem. Int. Ed.* 2012; **51**: 7640–7654.

β-Functionalized π-Extended Porphyrins: Facile Synthesis, Spectral, Electrochemical Redox Properties, and their Utilization as Efficient Two-Photon Absorbers

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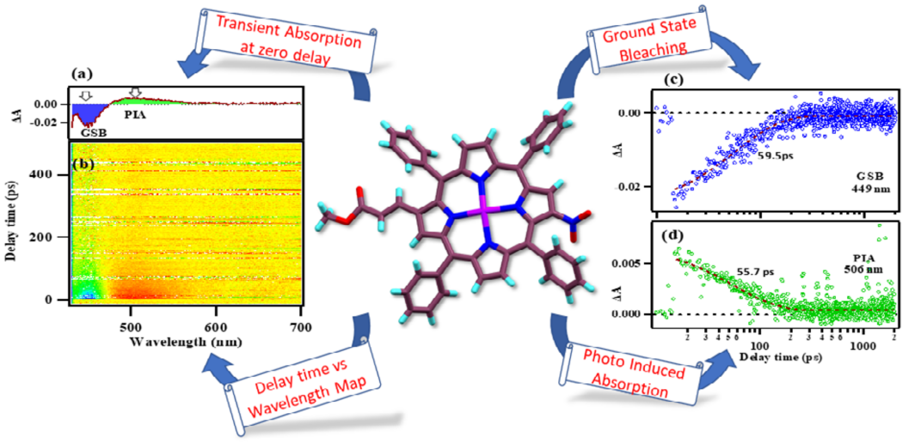
β-Functionalized porphyrins with mixed substituents pattern are of growing interest due to their utilization in the field of nonlinear optics, anion sensing, gas storage, photodynamic therapy (PDT) and solar cells (DSSC). Modulating the degree of π-conjugation and introducing suitable donor-acceptor substituents at β-positions result red-shifted electronic spectral features, low HOMO-LUMO gap and high ground state dipole moment which are essentials for enhanced nonlinear optical behaviour.[1] Benzoporphyrin derivatives are currently under investigation as photosensitizers for PDT application.[2] Herein, we report one pot facile synthesis of β-disubstituted porphyrins with two different substituents at the antipodal positions to each other and β-nitro-mono-benzoporphyrins, and their characterization by various spectroscopic techniques *viz*. UV-vis, fluorescence and NMR and MALDI-TOF mass spectrometry and SC-XRD. Further, the investigation of second order and third order nonlinear optical properties has been carried out. The synthesized disubstituted porphyrins and benzoporphyrins exhibited significantly red-shifted electronic spectral features as compared to their precursor porphyrins. Further, these porphyrins exhibited a large anodic shift in reduction and cathodic shift in oxidation potentials due to the extended π-conjugation and the electron-withdrawing β-substituents. All the synthesized porphyrinoids exert prominent two-photon absorption coefficient and third order nonlinear index. The detailed NLO investigation suggests that our porphyrins stand superior compared to recent literature reports as promising NLO materials.



REFERENCES

1. (a) Senge, M. O. *et al. Eur. J. Org. Chem.* **2011**, 5797. (b) Dar, T. A. *et al. Green Chem.* **2019**, *21*, 1757. (c) Kumar, R. *et al. ACS Appl. Energy Mater.* **2018**, *1*, 2793. (d) Rohal, R. K. *et al. Inorg. Chem.* **2022**, *61*, 1297.
2. (a) Zeng, J. Y. *et al. ACS Nano* **2018**, *12*, 4630. (b) Grover, N. *et al. Inorg. Chem.* **2019**, *58*, 2514.

Synthesis, Spectral and Electrochemical Studies of Triply Fused Porphyrins and Their Utilization in Anion Sensing

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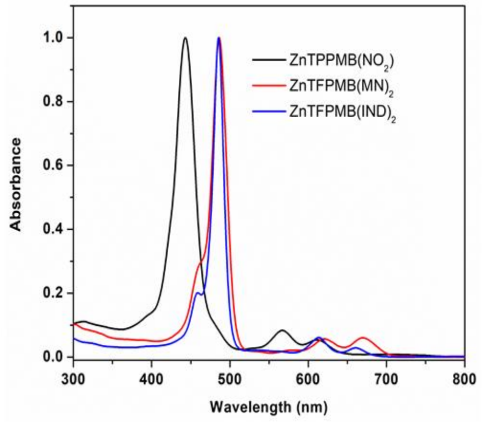
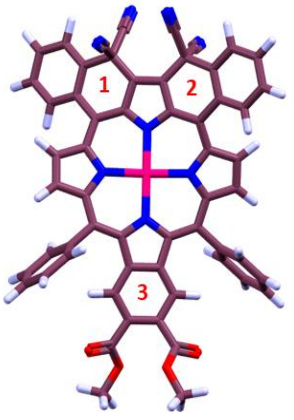
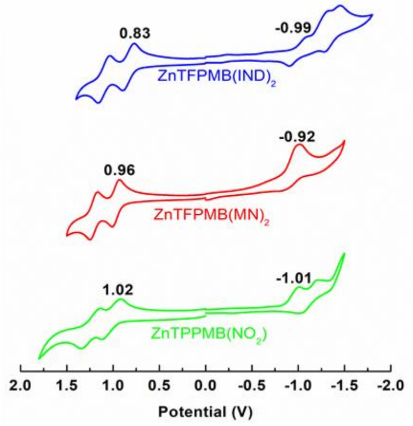
Porphyrins with extended π-conjugation is considered as an exciting subject of research due to their potential application in sensing, nonlinear optics and solar cells. π-Extension employing intramolecular fusion has attracted much attention because of its unique photophysical and tunable spectro-electrochemical properties, making them good candidates for an immense variety of applications, including photovoltaics and photoacoustic imaging, two-photon absorbers and toxic ion sensors [1]. The fusion at the *meso* and *β*-pyrrolic positions (i.e., *meso-β* fusion) and at two adjacent *β*-pyrrolic positions (i.e., *β-β'* fusion) both have shown to afford porphyrinoids with enhanced chemical stability, near-infrared optical absorption and reduced HOMO-LUMO gap, indicated to be a better photosensitizer for photodynamic therapy and optoelectronic devices [2]. Herein, we present a facile synthesis, spectral and electrochemical properties of triply fused porphyrins and their Zn(II) complexes. Further, the complete characterization of all the porphyrins was carried out by various spectroscopic techniques including UV-vis, fluorescence, NMR, single crystal XRD, spectro-electrochemical studies, and MALDI-TOF mass spectrometry. The synthesized Trifused porphyrins exhibited significantly red-shifted electronic spectral features as compared to their precursor porphyrins. These porphyrins showed a significant anodic shift in reduction and cathodic shift in oxidation potentials from their parent molecule due to the extended π-conjugation. Further, we will explore the Trifused Zn(II) complexes as a promising toxic ion sensor.







REFERENCES

1. (a) Kumar, S. *et al*. *Dalton Trans*. **2021**, *50*, 17086. (b) Banala, S. *et al. Chem. Sci.* **2017**, *8*, 6176. (c) Tanaka, T. *et al*. *Chem. Soc. Rev*. **2015**, *44*, 943. (d) Kumar, R. *et al. ACS Appl. Energy Mater.* **2018**, *1*, 2793.
2. (a) Chaudhri, N. *et al*. *Inorg. Chem.* **2018**, *57*, 6658. (b) Grover, N. *et al. Inorg. Chem.* **2019**, *58*, 2514. (c) Inokuma, Y. *et al. Chem. Commun*., **2005**, 3782.

Synthesis and Properties of Subphenanthrenocyanines

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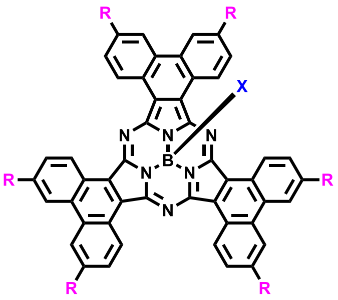
Subphthalocyanines (SubPcs) constitute a class of curved, aromatic macrocycles, consisting of three isoindole subunits connected through their 1,3-positions by aza-bridges.[1] These compounds belong to the group of tripyrrolic porphyrinoids, a large family of heteroannulenes that also comprises subporphyrazines (SubPzs),[2] subporphyrins (SubPs)[3] and benzosubporphyrins (BzSubPs)[4] as the four cornerstones.[5] Some common features within this family are their cone-shaped, aromatic structure, arising from a 14 π-electron circuit, and their ability to coordinate exclusively boron(III). Indeed, these macrocycles exist only as boron (III) complexes. The smaller aromatic circuit of SubPcs related to that of phthalocyanines (Pcs) (18 *vs* 14 electrons π), produces blue shifted absorption bands with respect to the corresponding tetrapyrrolic systems. In the present work we explore the preparation of novel subporphyrinoid derivatives with extended conjugation, which are non-existent in the literature, and we have named Subphenanthrenocyanines. These compounds consist of three dibenzoisoindole units linked through their 1 and 3 positions by aza bridges and coordinating a boron atom within their central cavity. The optical and electrochemical properties of these new macrocycles with larger bowl-depths have been studied.



REFERENCES

1. Claessens, C.G.; González-Rodríguez, D.; Rodríguez-Morgade, M.S.; Medina, A.; Torres, T. Subphthalocyanines, Subporphyrazines, and Subporphyrins: Singular Nonplanar Aromatic Systems. *Chem. Rev.* **2014**, *114*, 2192-2277.
2. Guilleme, J.; González-Rodríguez, D.; Torres, T. Triflate-Subphthalocyanines: Versatile, Reactive Intermediates for Axial Functionalization at the Boron Atom. *Angew. Chem.* **2011**, *123*, 3568 –3571
3. Higashino, T.; Rodríguez-Morgade, M.S.; Osuka, A.; Torres, T. Peripheral Arylation of Subporphyrazines. *Chem. Eur. J.* **2013**, *19*, 10353-10359.
4. Kobayashi, N. in The Porphyrin Handbook, (Eds.: Kadish, K. M.; Smith, K. M.; Guillard, R.), *Academic Press, San Diego*, CA, **2003**, *15*, 161-262
5. C. G. Claessens, D. González-Rodríguez, M. S. Rodríguez-Morgade, A. Medina, and T. Torres, *Chem. Rev.*, **2014**, 114, 2192.

Olive leaves-derived carbon dots for efficient photocatalytic H_2 production and CO_2 reduction

Georgios Charalambidis[a], Kalliopi Ladomenou[b], Georgios Landrou[a], Emmanouil Nikoloudakis[a], Aspasia Stoumpidi[a] and Athanassios G. Coutsolelos[a]

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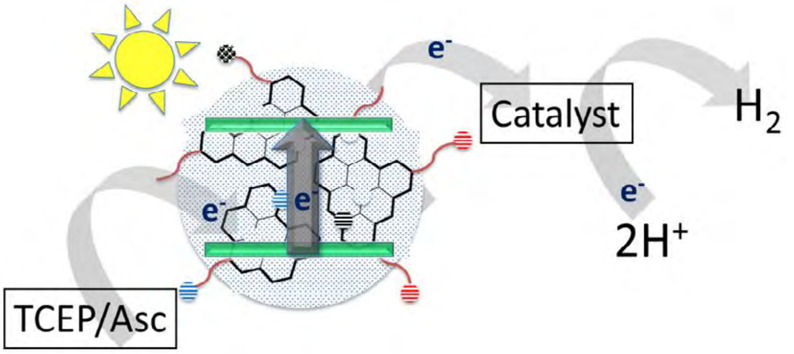
The decrease of total available reserves of fossil fuels along with the environmental problems caused by increased CO_2 emissions, have turned the interest of the research community towards developing catalytic systems which convert solar energy into exploitable fuels.[1] The zero-emission energy carrier, H_2 is an ideal alternative to carbon-based fuels especially when it is generated photocatalytically from water. Additionally, the photocatalytic conversion of CO_2 into chemical fuels can reduce the CO_2 emissions and have a positive environmental and economic impact. Therefore, the preparation of efficient catalytic systems that exploit solar irradiation for H_2 production and CO_2 reduction can contribute to an ultimate green sustainable development of our planet, solving energy and environmental issues.
In this report carbon dots (CDot) and N-doped carbon dots (NCDot) have been synthesized as light harvesters to direct photocatalysis of protons to H_2 with the use of molecular cobalt catalysts. The photocatalytic studies demonstrated that this system produces 17.1 mmol of H_2 (TON_{CAT} = 859) after 52 h of irradiation.[2] Moreover, in an effort to produce CDot with lower cost olive leaves were used as starting material and after pyrolysis resulted in the formation of novel CDot. The newly synthesized CDot were utilized as chromophores in the photocatalytic CO_2 reduction using Fe porphyins and Co complexes as molecular catalysts.



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REFERENCES

1. K. Ladomenou, M. Natali, E. Iengo, G. Charalampidis, F. Scandola, A. G. Coutsolelos, *Coord. Chem. Rev.*, **2015**, *304*, 38-54.
2. K. Ladomenou, G. Landrou, G. Charalambidis, E. Nikoloudakis, A. G. Coutsolelos, *Sustainable Energy Fuels*, **2021**, *5*, 449–458.

Porphyrin based dye-sensitized photocatalytic systems for efficient photocatalytic H_2 production

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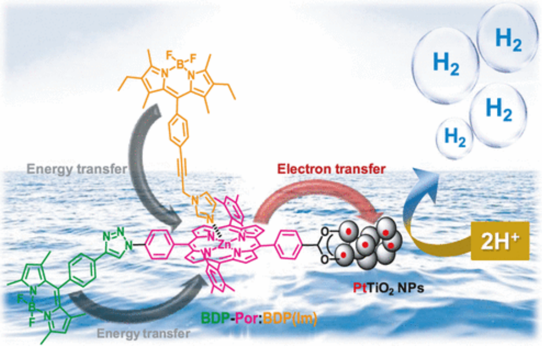
Photocatalytic hydrogen (H_2) production from water is an auspicious approach since an abundant precursor can be converted into a useful fuel. In this context, numerous photocatalytic systems have been developed over the years that are able to convert solar energy into H_2.[1]

In this study, we report the utilization of BODIPY-(Zn)Porphyrin hybrids in photocatalytic H_2 production from water. These entities were applied as photosensitizers upon their chemisorption onto the surface of platinum-doped titanium dioxide nanoparticles (Pt-TiO_2), which acted as photocatalysts. To evaluate the impact of the different connectivity between the chromophores, we employed two diverse BODIPY-(Zn)Porphyrin entities, in which the BODIPY moiety is either covalently attached (BDP-Por) or axially coordinated (BDP(Im)-Por) with the (Zn)Porphyrin. The covalently connected dyad presented higher catalytic activity compared to the axial coordinated BDP(Im)-Por. In BDP-Por dyad, an additional BDP(Im) moiety was introduced and the formed hybrid outperformed the aforementioned systems, due to the enhanced light harvesting ability. Overall, we developed highly efficient dye-sensitized photocatalytic systems (DSPs) based on noble-metal-free photosensitizers reaching 18 600 TONs.[2]



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REFERENCES

1. K. C. Christoforidis, P. Fornasiero, *ChemCatChem*, **2017**, *9*, 1523-1544.
2. V. Nikolaou, G. Charalambidis, G. Landrou, E. Nikoloudakis, A. Planchat, R. Tsalameni, K. Junghans, A. Kahnt, F. Odobel, A. G. Coutsolelos, *ACS Appl. Energy Mater*, **2021**, *4*, 10042–10049.

Fast, facile, base-free microwave-assisted metalation of bacteriochlorophylls and corresponding high yield synthesis of TOOKAD

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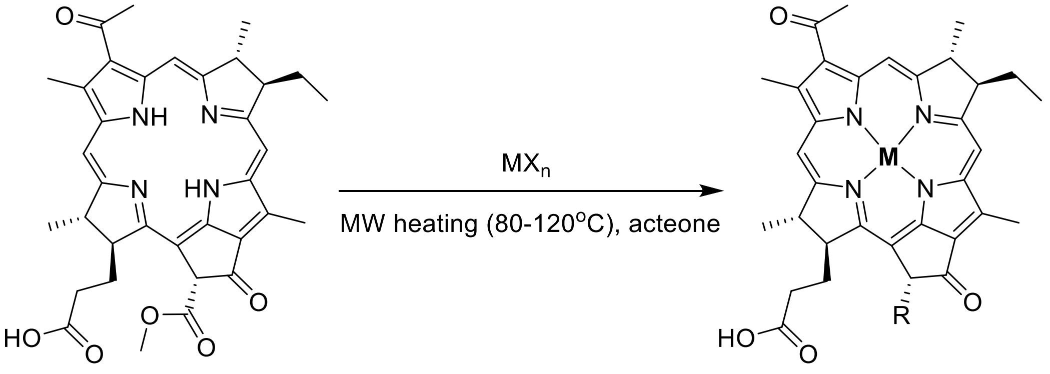

- ✓ **Direct and efficient metalation**
- ✓ **Base-free**
- ✓ **Fast and simple**

R= H, CO_2CH_3, (=O)

M= Pd, Cu, Zn, Cd, Sn, InOH, Mn, Co

Naturally-derived metallo-bacteriochlorophylls have attracted much attention since their clinical approval for cancer photodynamic therapy. Their therapeutic properties are rooted in the metal complexation of bacteriochlorophylls, which endows them with optical properties favourable for biophotonic and biomedical applications, including near-infrared light-activated reactive oxygen species generation at therapeutic levels. Despite these advantages, the utility of these chromophores has been limited by synthetic challenges associated with bacteriochlorophyll metallation; specifically, a slow reaction rate and necessity of complex purification procedures remain barriers towards metalated bacteriochlorophyll synthesis. Here, these limitations are overcome through the development of a new fast, facile, efficient, base-free microwave heating metallation method for the synthesis of a series of metallo (Pd, Cu, Zn, Cd, Sn, In, Mn, Co) bacteriopyropheophorbides. The preparation and structural and optical spectral characterization of these complexes are presented. This microwave-enabled synthetic method is then applied to generate the clinical photosensitizer agent Pd-bacteriopheophorbide (TOOKAD) effectively and efficiently, followed by validation of its metallation-enhanced ROS generation.

Influence of counteranions on electrochemical properties of water – soluble porphyrins

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Due to their unique chemistry, porphyrins are used in number of ways: oxygen transportation [1], solar cells [2] (light conversion), ligands, photodynamic inactivation of bacteria (PDI) [3], photodynamic therapy (PDT) [4]. One part of our research is dedicated to the synthesis and characterization of water–soluble porphyrins. Synthesis of the first water-soluble porphyrins such as tetraanionic tetra-4-sulfonatophenylporphyrin (TPPS) [5] and tetracationic tetra-4-N-methylpyridinium porphyrin (TMPyP) [6] were reported in the early 1970s. Several years after their discovery, these compounds quickly become promising candidates for biological and medical applications due to their high stability and ability to generate reactive oxygen species. The biological activity of these porphyrinoids depends on their solubility, degree of aggregation and redox behavior, properties which are influenced by several factors such as counter anion, type of central metal ion and number of positively charged substituents.

In the present paper, we present trisubstituted porphyrin derivatives $[(TriMPyP)M]^{3+}X^{-}_{3}$ (where M = 2H or Zn^{II} and $X^- = Cl^-$, Br^-, I^- or $tosyl^-$) containing three N-methyl-4-pyridyl groups. These macrocycles were synthesized and characterized electrochemically and spectroscopically. Their physicochemical properties were compared, under the same solution conditions, to several free base and metal tetracationic porphyrins $[(TMPyP)M]^{4+}X^{-}_{4}$ (where M = 2H or Zn^{II} and $X^- = Cl^-$, Br^-, I^- or $tosyl^-$). The type of anions and symmetry of the macrocycle were found to strongly influence the properties and redox behavior of these cationic porphyrins.

REFERENCES

1. E. Tsuchida, H. Nishide, M. Ohyanagi, *J. Macromol. Sci.-Chem. A*, 1988, **25**, 1327-1338.
2. T. Hasobe, *J. Physical Chem. Lett.,* 2013, **4**, 1771-1780.
3. B. Habermeyer, T. Chilingaryan, R. Guilard, Bacterial Efficiency of Porphyrin Systems, *J. Porphyrins* Phthalocyanines, 2021, **25**, 359-381.
4. R. Schneider, F. Schmitt, C. Frochot, Y. Fort, N. Lourette, F. Guillemin, J.F. Muller, M. B. Heyobe, *J. Bio. and Med. Chem.*, 2005, **13**, 2799-2808.
5. E.B. Fleischer, J.M. Palmer, T.S. Srivastava, Chatterjee, A. *J. Am. Chem. Soc.* 1971, **93**, 3163.
6. P. Hambright, E.B. Fleischer, *J. Inorg. Chem.* 1970, **9**, 1757.

Porphyrinoid Derivatives with Application in Light Harvesting Photovoltaic Systems

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Metal halide perovskite solar cells (PSCs) and organic solar cells (OSCs) are among the best performing solution-processable photovoltaic devices with certified power conversion efficiencies (PCEs) over 25.5% and 19.0%, respectively. [1] However, they still suffer from some instability issues originating from the inferior interface quality and poor nanomorphology of the absorber layer. In this work, we introduce a series of judiciously functionalized boron-dipyrromethene BODIPY molecules as ultra-thin interlayers at the absorber/electron transport layer interface. Our study indicates that BODIPY compounds with a high molecular dipole moment can enhance the device performance mainly due to better interface energy level alignment. They also induce passivation of defect traps and improvement in the charge transport properties of the absorber layer coated on top of them. Among the various compounds used, amino-functionalized BODIPY, owing to the synergetic effect of the above-mentioned factors, enabled the highest power conversion efficiency in organic (15.69%) as well as in perovskite solar cells (20.12%). Amino-functionalized BODIPY also demonstrated an enhanced stability under continuous illumination (in nitrogen) without and with heating (at 65 °C) for 1000 h. These results pave the way for the implementation of molecules with tailor-made functionalities in high efficiency and stabile solution-based photovoltaic devices of the future.

Acknowledgments
The Special Research Account of the University of Crete is gratefully acknowledged for the financial support of this research.

REFERENCES

1. Y. Cui, Y. Xu, H. Yao, P. Bi, L. Hong, J. Zhang, Y. Zu, T. Zhang, J. Qin, J. Ren, Z. Chen, C. He, X. Hao, Z. Wei, J. Hou, *Advanced Mater.*, **2021**, *33*, 2102420.

Photocatalytic Hydrogen Evolving Systems Based on Self-assembled Porphyrin-Dipeptide Hybrids

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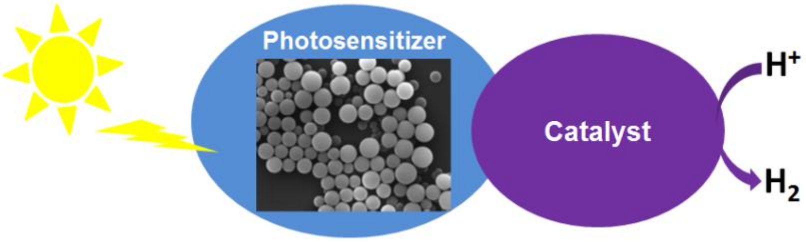
In order to establish a sustainable and green future for our planet, we need to diminish the use of fossil fuels and rely on inexhaustible, clean and abundant energy sources. Thus, it is imperative to develop devices that effectively exploit solar energy into energy-rich and storable compounds that can be used as fuels. Motivated by natural photosynthesis, plenty of scientific reports deal with the photocatalytic conversion of sunlight into H_2.

In this work, diphenylalanine dipeptide was covalently attached to porphyrin macrocycles in order to conveyed self-assembling properties to the resulting hybrid. We demonstrated that the metal in the porphyrin core and the solvent mixture direct the self-assembly behaviour of the hybrid molecules leading to various supramolecular architectures such as fibrils and nanospheres. For the development of the H_2 evolving systems, two different approaches were applied. In the first one, porphyrin nanostructures acted as the photosensitizers and Pt nanoparticles (NPs) played the role of the catalyst.[1] While in the second approach Pt NPs were replaced by a molecular cobaloxime catalyst.[2]



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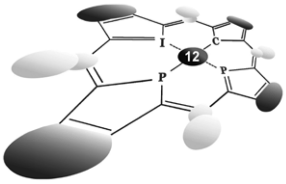
REFERENCES

1. V. Nikolaou, G. Charalambidis, A. G. Coutsolelos, *Chem. Commun.*, **2021**, 57, 4045-4058.
2. E. Nikoloudakis, M. Pigiaki, M. N. Polychronaki, A. Margaritopoulou, G. Charalambidis, E. Serpetzoglou, A. Mitraki, P.A. Loukakos, A. G. Coutsolelos, *ACS Sustainable Chem. Eng.*, **2021**, *9*, 7781-7791.



Synthesis of neutral, low molecular weight, *meso*-tetra(dioxanyl)porphyrins of considerable solubility in aqueous solutions

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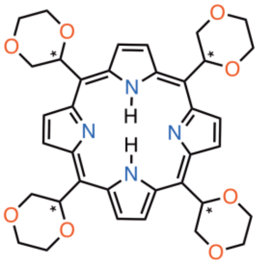
Aqueous solubility of porphyrins is frequently desired for their utilization in biological applications such as anti-microbial agents [1], cancer photodynamic therapeutics [2], as well as in technical applications, such as (photo)catalysis [3] or chemo sensing [4,5]. While surfactants or their incorporation into liposomes can introduce water soluble properties into porphyrins [5], porphyrins with inherent aqueous solubility is often more convenient and thus preferred.



Herein we describe the synthesis of the low-molecular weight, neutral *meso*-tetra(dioxanyl)porphyrin [6]. This work focuses on the expansion of the accessibility of chiral porphyrins and neutral porphyrins with solubility in aqueous solutions. The key intermediate dioxan-2-carbaldehyde is achievable in three steps as in either racemic or in stereo-pure forms from commercially available starting materials. The title *meso*-tetradioxanylporphyrin is synthesized using 4×1 or 2+2-type syntheses in modest yields from the stereo-pure aldehydes. The racemic aldehyde results in an inseparable mixture of many porphyrin diastereomers. The enantiopure porphyrin isomers, both as their free base or as zinc complexes, display substantial solubility properties in both organic and aqueous solvents, though free water-solubility was not accomplished.

REFERENCES

1. Hanakova, A.; Bogdanova, K.; Tomankova, K.; Pizova, K.; Malohlava, J.; Binder, S.; Bajgar, R.; Langova, K.; Kolar, M.; Mosinger, J.; *et al. Microbiol. Res.* **2014**, *169*, 163–170.
2. Ethirajan, M.; Chen, Y.; Joshi, P.; Pandey, R. K. *Chem. Soc. Rev.* **2011**, *40*, 340–362.
3. Rybicka-Jasinska, K.; Shan, W.; Zawada, K.; Kadish, K. M.; Gryko, D. *J. Am. Chem. Soc.* **2016**, *138*, 15451–15458.
4. Spencer, J. A.; Ferraro, F.; Roussakis, E.; Klein, A.; Wu, J.; Runnels, J. M.; Zaher, W.; Mortensen, L. J.; Alt, C.; Turcotte, R.; et al. *Nature* **2014**, *508*, 269–273.
5. Luciano, M.; Brückner, C., *Molecules* **2017**, *22*, 980.
6. Huynh, E.; Lovell, J. F.; Helfield, B. L.; Jeon, M.; Kim, C.; Goertz, D. E.; Wilson, B. C.; Zheng, G. *J. Am. Chem. Soc.* **2012**, *134*, 16464–16467.
7. Jiang, X.-L.; Damunupola, D.; Brückner, C. *J. Porphyrins Phthalocyanines* **2021**, *25*, 734–740.

Azaphthalocyanines as dark quenchers in triple labeled oligodeoxynucleotide probes

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Long oligodeoxynucleotide (ODN) probes are used for the detection of viral genetic information. The advantage of long ODN probes lies in the possibility of recognizing viruses even though they have several point mutations. ODN probes for Taq-man assays are usually consist of ODN strand with one fluorophore and one quencher. However, several studies indicate that the presence of one fluorophore and two quenchers is beneficial for quenching efficiency.[1] In our study, we compare the presence of one or two quenchers to quenching efficiency. Two different structures of quenchers were chosen for comparison – the first one, commercially available BlackBerry® Quencher 650, and the second one was azaphthalocyanine (AzaPc) quencher.[2] AzaPcs have versatile usage thanks to their interaction with light. In this study, we focused on their ability quench fluorescence of other compound – in presence of heterodimer or after hybridization via Förster resonance energy transfer (thanks to their panchromatic absorption). At first two AzaPc quenchers were synthetised and subsequently connected to the ODN strand, which had to be purified. After that, we tested different positions of quencher - e.g., two quenchers (intrastrand and 3′-end), only intrastrand quencher, or only quencher at 3′-end. After analysis of quenching efficiency in random coil and after hybridization (**Figure 1**), we observed results that were in contrast with observation other groups because presence of the second has not a significant role in quenching efficiency.

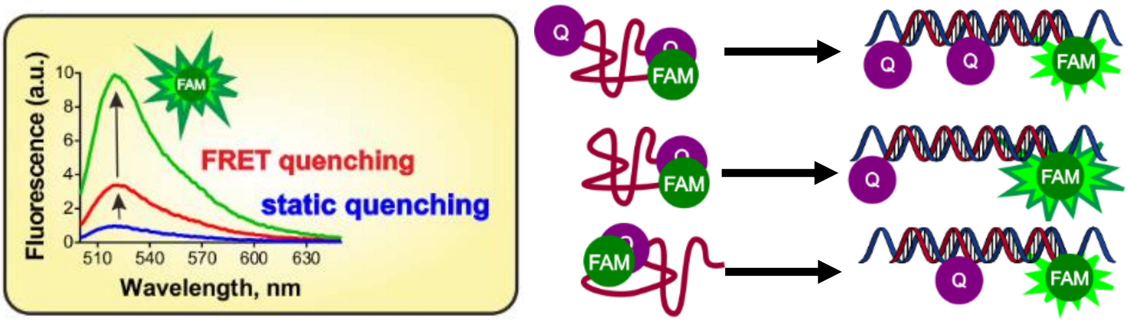

Figure 1. General changes in fluorescence during hybridization study.

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REFERENCES

1. Wilson, P. M.; Labonte, M. J.; Russell, J., et al., Nucleic Acids Res., 39 (17), 2011, E112-U19.
2. Demuth, J.; Miletin, M.; Kucera, R., *et al.,* Org. Chem. Front., 7 (3), 2020, 445-456.

Synthesis of Porphyrinoid-PDMS polymers for analysis of Light-Matter coupling in optical cavities

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The chemical stability and the optical properties of porphyrinoids have made them very favourable candidates for application-oriented as well as fundamental research [1-2]. It has been reported that the properties of molecules can be altered by coupling them with light in optical cavities [3]. We aim to analyze this light-matter coupling phenomena with porphyrinoid molecules by constructing optical cavities in which the target molecule will be distributed in a concentrated and homogeneous manner. To achieve this aim, we needed to incorporate our target molecule into a polydimethylsiloxane (PDMS) based polymer matrix in a covalent fashion [3-4]. 5,10,15,20-tetrastyrylporphyrin was synthesized and the PDMS based hybrid polymer was fabricated by adapting a scheme using Karstedt's catalyst [4]. Control experiments using 5,10,15,20-tetraphenylporphyrin-PDMS hybrid polymer was carried out to check and confirm the covalent insertion of the monomer into the polymer. The absorption spectrum of the polymer was measured and found to be similar to that of the poprhyrin molecule in solution. The obtained spectrum was compared with the absorption spectrum of a second PDMS control polymer devoid of the porphyrin to confirm that the absorption properties were not resulting from the presence of any other constituents of the polymer medium. The emission spectrum of the polymer was measured and found to be similar to that of the monomer in solution. Fluorescence decay of the polymer was found to be monoexponential and the decay time was found to be similar to that of similar reported porphyrins. The IR spectrum of the polymer was measured and the peak corresponding to the N-H stretching vibration was found to be present, similar to that of the porphyrin IR spectrum. These findings suggest that this hybrid polymer can be used as a good candidate to fabricate optical nanocavities and microcavities to study the light-matter coupling phenomenon in such porphyrinoid molecules.

REFERENCES

1. G. Anguera; D. Sánchez-García *Chem. Rev.* **2017**, *117*, 2481-2516
2. D. Sánchez-García; J. L. Sessler *Chem. Soc. Rev.* **2008**, *37*, 215-232
3. M. Hertzog; M. Wang; J. Mony; K. Börjesson *Chem. Soc. Rev.* **2019**, *48,* 937-961
4. T. Ono; H. Shinjo; D. Koga; Y. Hisaeda *Eur. J. Org. Chem.* **2019**, *46*, 7578-7583

Synthesis and Encapsulation Properties of Porphyrin Cages Assembled from N-heterocyclic Carbene-Metal Bonds

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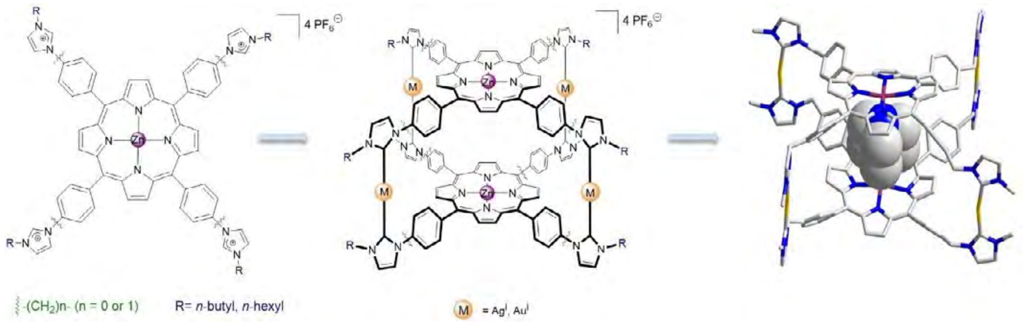
N-heterocyclic carbenes (NHCs) and porphyrins have become ubiquitous ligands in the fields of organometallic chemistry and catalysis.[1] Over the last decade, NHCs have also emerged as promising ligands for the synthesis of metallosupramolecular architectures featuring M−CNHC bonds.[2] For this purpose, 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.[3,4] Silver(I) was used as assembling 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 lability of Ag(I)−CNHC bonds offers the possibility to generate new structures by transmetalation reactions forming more stable bonds like Au(I)−CNHC 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).



REFERENCES

1. S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612-3676.
2. N. Sinha, F. E. Hahn, *Acc. Chem. Res.* **2017**, *50*, 2167-2184.
3. C. Rose, A. Lebrun, S. Clément, S. Richeter, *Chem. Commun.* **2018**, *54*, 9603-9605.
4. L. Poyac, C. Rose, M. Wahiduzzaman, A. Lebrun, G. Cazals, C. H. Devillers, P. Yot, S. Clément, S. Richeter, *Inorg. Chem.* **2021**, *60*, 19009-19021

5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin as Photoactive Scaffold for Peptide Cyclisation

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Polyfluoroaromatics readily react with thiols via nucleophilic aromatic substitution (S_NAr) and provide excellent templates on to which cysteine-containing peptides can be assembled through side-chain macrocyclisation. [1] The reactivity of hexafluorobenzene towards cysteine was initially investigated [2] and the study was subsequently extended to polyfluorinated porphyrins, with the aim of exploring the tetrapyrrole ring as photoactive scaffold for peptide coupling and cyclisation. Particularly, if compared to linear analogues, macro- and multicyclic peptides exhibit greater chemical and conformational stability, potentially resulting in improved interactions with targets and improved biological activity. In addition, the inclusion of a porphyrin scaffold within the cyclic architecture allows multiple functionalisations, metal coordination and light responsive applications. Here we will present a novel technique for 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin coupling with fully-deprotected di-cysteine peptides, in solution and under peptide-compatible conditions, to afford the corresponding macrocyclic products. A variety of peptide sequences with different inter-thiol distances was employed to demonstrate the generality, chemo-selectivity, and wide applicability of this method. The combination of these results with those from a similar methodology applied to 5,15-bis(pentafluorophenyl)porphyrin gave us important insights regarding the geometrical constraints of the macrocyclisation as well as the minimal number of amino acids required to reach the *para* positions of *trans* and *cis* meso phenyl groups. The remaining *para* positions are also available for further functionalisation and, with appropriate cysteine-rich amino acid sequences, peptide multicyclisation is also possible. As proof of concept, the Skin Penetrating and Cell Entering (SPACE) peptide [3] was tested for cytotoxicity and cellular uptake on squamous cell carcinoma cells (SCCIC8) after cysteine crosslinking with 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin. This water-soluble conjugate retained cell penetration properties without influencing cell viability, while the presence of the porphyrin core imparts fluorescence. In conclusion, this robust and accessible synthetic tool allows the conjugation of two biologically active compounds, joining and concurrently improving their individual properties. Despite the many examples of porphyrin-peptide conjugates, polyfluorinated porphyrins and thiol-fluoride S_NAr have scarcely been used for this purpose and little is known of porphyrins strapped with peptide chains. Moreover, the possibility to 'dial-in' the peptide sequence and exploit the photoactive tetrapyrrolic scaffold opens the way to a wide range of applications in biological systems, especially as molecular probes, drugs and sensors.

REFERENCES

1. A.M. Spokoyny, Y. Zou, J.J. Ling, H. Yu, Y.S. Lin, B.L. Pentelute, A perfluoroaryl-cysteine SNAr chemistry approach to unprotected peptide stapling, *J. Am. Chem. Soc*. 135 (**2013**) 5946–5949. doi:10.1021/ja400119t.
2. P. Dognini, P.M. Killoran, G.S. Hanson, L. Halsall, T. Chaudhry, Z. Islam, F. Giuntini, C.R. Coxon, Using 19F NMR and two-level factorial design to explore thiol-fluoride substitution in hexafluorobenzene and its application in peptide stapling and cyclisation, *Pept. Sci*. 113 (**2021**) e24182. doi:10.1002/pep2.24182.
3. T. Hsu, S. Mitragotri, Delivery of siRNA and other macromolecules into skin and cells using a peptide enhancer, Proc. Natl. Acad. Sci. U. S. A. 108 (**2011**) 15816–15821. doi:10.1073/pnas.1016152108.

Axial Functionalization of Ruthenium Phthalocyanines for their Bioconjugation to nanocarriers for Cancer Photodynamic Therapy (PDT)

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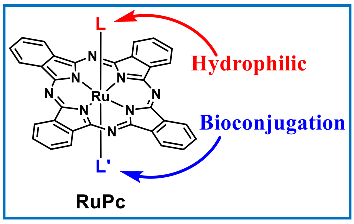
Photodynamic therapy (PDT) allows the selective, non-invasive and localized destruction of tumor cells, with reduced side effects. This therapy combines light, molecular oxygen and a photosensitizer (PS) to produce reactive species, such as singlet oxygen ($^1O_2$) and free radicals, which lead to oxidative stress and cell death. [1]

Phthalocyanines[2] (Pcs) are aromatic porphyrinoids consisting of four isoindole units, linked together through their 1,3 positions by *aza*-bridges. Unlike porphyrins, the absorption spectra of phthalocyanines are dominated by a very intense Q band in the red region of the visible spectrum, usually centered at 620-700 nm, which is responsible for its blue-green color.[3] The latter makes Pcs promising as photosensitizers for PDT, as their Q-absorption allows the penetration of the irradiated light into deep tissue layers. In addition, Pcs show high efficiency to generate singlet oxygen and low toxicity in the dark.[4]



The aim of this project is the synthesis of Ru(II) Pc complexes and the study of their photophysical and photochemical properties for their application in PDT. For this purpose, the Pc derivatives have been functionalized at the two axial positions with two different ligands L and L'. The L-type ligands contain hydrophilic entities that increase Pcs biocompatibility, while L'-type ligands contain maleimide or alkyne units, for the bioconjugation of the PSs to nanocarriers using "click" chemistry.[5] The RuPcs containing a maleimide unit will be conjugated in a second stage to the peptides exendin-4 and octreotide through thiol-maleimide coupling. Likewise, RuPcs endowed with alkynes will be subjected to Huisgen 1,3-dipolar cycloaddition reactions with elastin-like polypeptides (ELP) for multimodal therapy of ovarian cancer.

REFERENCES

1. J. M. Dąbrowski, B. Pucelik, A. Regiel-Futyra, M. Brindell, O. Mazuryk, A. Kyzioł, G. Stochel, W. Macyk, L. G. Arnaut. *Coord. Chem. Rev.* **2016**, 325, 67.
2. K. M. Kadish, K. M. Smith and R. Guilard. Handbook of Porphyrin Science, World Scientific, Singapore, **2016**.
3. N. Kobayashi. Synthesis and Spectroscopic Properties of Phthalocyanine Analogues, in The Porphyrin Handbook, Ed. K. M. Kadish, K.M. Smith and R. Guilard, Academic Press, San Diego CA, **2003**, vol. 15, pp. 161–262.
4. P.-C. Lo, M. S. Rodríguez-Morgade, R. K. Pandey, D. K. P. Ng, T. Torres, F. Dumoulin, Chem. Soc. Rev. **2020**, 49, 1041.
5. V. Almeida-Marrero, E. van de Winckel, E. Anaya-Plaza, T. Torres, A. de la Escosura. *Chem. Soc. Rev.* **2018**, 47, 7369.

Novel Octa-Phenoxy Substituted Pyrazinoporphyrazines: Synthesis and Photochemical Properties

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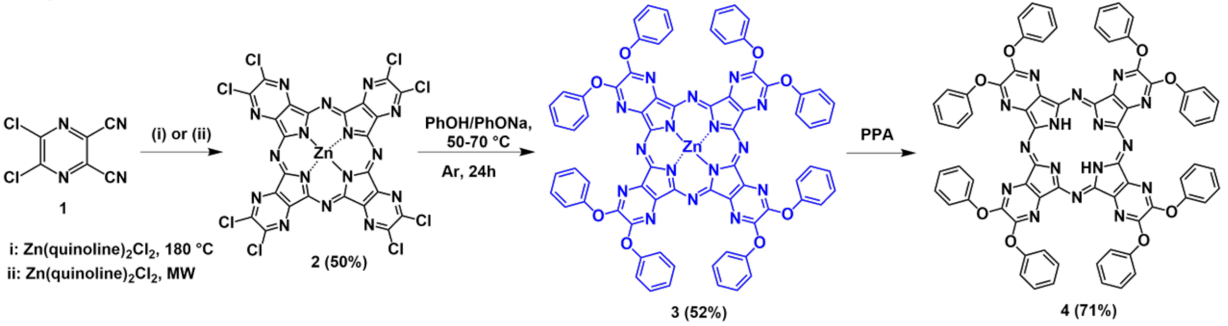
A new approach to the synthesis of octa-phenoxy-substituted pyrazinoporphyrazines through the stage of nucleophilic substitution in pyrazinoporphyrazine macrocycle is presented. This approach allows avoiding the template synthesis of the target compound from the phenoxy-substituted dinitrile, during which oligomerization and phenol release occur.



Several scientific groups [1,2] reported the unsuccessful attempts to preparation of octa-phenoxy substituted pyrazinoporphyrazines. It was found, that phenoxy groups are too labile in template synthesis, as well as, lithium phenolates are not useful for mediating of phthalocyanine formation. In addition, phenolate anions are superior leaving groups. To solve this problem, we used *post*-synthetic strategy to modification of pyrazinoporphyrazine macrocycle through the nucleophilic substitution of eight chlorine atoms in octa-chloro-pyrazinoporphyrazine. Initial octa-chloro-pyrazinoporphyrazine was obtained in a melt of initial nitrile and quinoline complex of zinc. Microwave and thermal activation were chosen for macrocyclization procedure. A successful demetallation of zinc complex **3** was realised in a medium of polyphosphoric acid.

Target products were analyzed by ^{1}H NMR, UV-vis, IR spectroscopy and MALDI-TOF mass spectrometry. Target complex demonstrates short but intense triplet signals in triplet absorption spectrum. The lifetime of the triplet state was 1.0 ms. The singlet oxygen quantum yield for sample **3**, measuring using singlet oxygen phosphorescence, was 0.38. This value is similar to corresponding one obtaining for phenyl-substituted analogs.

REFERENCES

1. Morkved, E. H., Ossletten, H., & Kjosen, H. (1999). Preparation of octa (alkoxy) azaphthalocyanines. Acta Chemica Scandinavica, 53(12), 1117-1121.
2. Makhseed, S., Ibrahim, F., Bezzu, C. G., & McKeown, N. B. (2007). The synthesis of metal-free octaazaphthalocyanine derivatives containing bulky phenoxy substituents to prevent self-association. Tetrahedron Letters, 48(41), 7358-7361

Synthesis and Optical Properties of Substituted Carbazolocyanine Ligand

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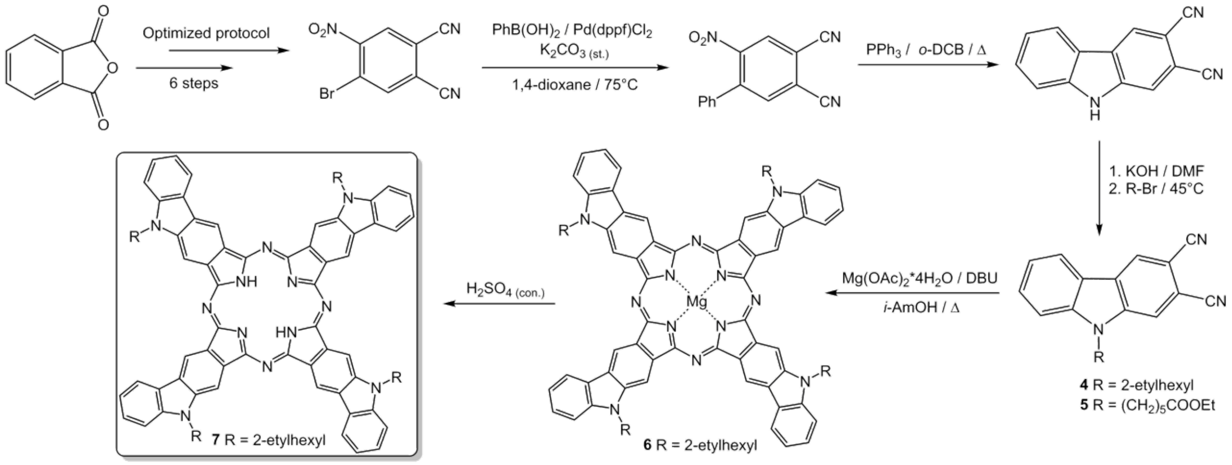
Carbazolocyanines – tetracarbazolo-annelated porphyrazine analogs possess significant research interest due to the strong electron-releasing effect of carbazole moiety combined with overall extension of π-electron conjugation system. However, the synthesis of carbazolocyanines has been reported only once, considering zinc complexes [1].

In present study we report synthetic approach towards carbazolocyanine ligand, the important building block curtail for the further metallation reactions.

Firstly, two N-substituted carbazole dinitriles were synthesised, according to well-known approach (Suzuki cross-coupling with subsequent Cadogan-Sundberg ring-closure) [1]. Then on the basis of N-(2-ethylhexyl) substituted carbazole 4 novel magnesium carbazolocyanine 6 was obtained by template condensation reaction. Finally, target carbazolocyanine ligand was prepared by demetallation of the corresponding magnesium complex in the concentrated sulfuric acid.

In addition, the synthetic protocol towards important intermediate – 4-bromo-5-nitrophthalonitrile has been significantly modified comparing to literature data [2]. Hence the six-step approach starting from phthalic anhydride resulted in 16% overall yield.

The optical and photophysical properties of novel complexes **6** and **7** were studied.



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REFERENCES

1. *Asian J. Org.Chem.* 2017, 6, 544.
2. *Russ. J. Gen. Chem.* 1998, 68, 813.

Heme in the History of Life: Unexpected Heme Metabolism in Methanogenic Archaea

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Porphyrins and related macrocycles are ancient compounds, found in fossilized form in oil and shale. Though abiotic synthesis of these compounds has been described, the discovery of a complete, anaerobic biosynthetic pathway for heme in a methanogenic Archaeon [1] suggested that biological roles for heme may likewise be ancient. We conducted a wide scale informatics study of >300 methanogen genomes in order to identify the potential reach of heme synthesis and usage in both deeply branching class I and more recently diverging class II species. This work revealed an unexpected diversity of heme-associated biochemistry in these species, as well as evidence of transitions from iron-sulfur cluster dependent pathways. Recent work in our groups demonstrated that methanogens are likewise surprisingly competent metal mobilizers, even using pyrite mineral as a sole source of iron and sulfur. We hypothesized that *Methanosarcina barkeri* could survive with heme as its sole source of iron, and subsequently observed that it indeed can. These results as well as potential genetic components responsible for heme uptake are described.

REFERENCES

1. Kuhner, Haufschildt, Neumann, Storbeck, Streif, Layer 2014 The alternative route to heme in the methanogenic archaeon *Methanosarcina barkeri. Archaea* 2014:327637. https://doi.org/10.1155/2014/327637.
2. Johnson, DuBois, Boyd *et al.* 2021 Pathways of iron and sulfur acquisition, cofactor assembly, destination, and storage in diverse archaeal methanogens and alkanotrophs. *Journal of Bacteriology* Aug 9; 203(17): e0011721.

NIR-absorbing propargylated phthalocyanines: Design and synthetic strategies

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Organosilica nanoparticles made of photosensitising phthalocyanines have been recently reported [1-2]. Indeed, the maximum absorption of phthalocyanines commonly centred around 700 nm is an intrinsic advantage for photodynamic therapy [3]. It can be pushed towards NIR wavelengths with appropriate substitution pattern [4]. As organosilica nanoparticles are easily fabricated from propargylated organic precursors, the design of propargylated NIR-absorbing phthalocyanines and their synthetic strategies will be presented.

REFERENCES

1. C. Mauriello-Jimenez, M. Henry, D. Aggad, L. Raehm, C. Charnay, X. Cattoen, M. Wong Chi Man, S. Alpugan, V. Ahsen, D. K. Tarakcı, P. Maillard, M. Maynadier, M. Garcia, F.Dumoulin*, M. Gary-Bobo*, J.-L. Coll, V. Josserand* and J.-O. Durand*, *Nanoscale*, **2017**, *9*, 16622-16626
2. G. Ekineker, C. Nguyen, S. Bayir, S. Dominguez-gil, U. Isci, M. Daurat, A. Godefroy, L. Raehm, C. Charnay, E. Oliviero, V. Ahsen, M. Gary-Bobo, J.-O. Durand and F. Dumoulin, *Chem. Commun*. **2019**, *55*, 11619-11622
3. P.-C. Lo, M. S. Rodríguez-Morgade, R. K. Pandey, D. K. P. Ng, T. Torres and F. Dumoulin, *Chem. Soc. Rev.*, **2020**, *49*, 1041-1056
4. S. Z. Topal, Ü. İşci, U. Kumru, D. Atilla, A. G. Gürek, C. Hirel, M. Durmuş, J.-B. Tommasino, D. Luneau, S. Berber, F. Dumoulin* and V. Ahsen*, *Dalton Trans.* **2014**, *43*, 6897-6908

Porphyrins or phthalocyanines: how the porphyrinoidic macrocycle affects the biosensing properties of graphene

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Porphyrins and phthalocyanines are often combined with graphene to fabricate composite sensing and biosensing electrochemical materials. Such materials exhibit usually very good sensitivity to detect either pollutants such as volatile organic compounds [1-2], or various biomarkers [3-5]. For each of these two macrocyclic cores, electrochemically active metals are used. Fe, Co and Cu are hence amongst the most common metals.

However, no systematic comparison of the effect of the macrocycle itself on the properties of graphene composite has been reported.

An analogous substitution pattern allowing a good solubility of tetra phenyl porphyrin (-meta position) and phthalocyanine (-non-peripheral position) in organic solvents have been selected, and metalation by Cu and Co has been performed.

These derivatives have been combined with reduced graphene oxide to form composites where these structural and electronic properties should be modified after such association. For this purpose, we have been investigated a study of composites properties through various physicochemical methods. Thus, structural and morphological characterisations were studied through FT-IR, XPS and SEMs. Electrochemical methods such as cyclic voltammetry and electrochemical impedance spectroscopy were performed with various redox markers to underline electrical properties.

REFERENCES

1. J. Avossa, R. Paolesse, C. Di Natale, E. Zampetti, G. Bertoni, F. De Cesare, G. Scarascia-Mugnozza and A. Macagnano, *Nanomaterials*, **2019**, *9*, 280
2. R. Paolesse, S. Nardis, D. Monti, M. Stefanelli and C. Di Natale, *Chem. Rev.* **2017**, *117*, 2517
3. Y. Wang, Z. Hsine, H. Sauriat-Dorizon, R. Mlika, H. Korri-Youssoufi, *Electrochim. Acta*, **2020**, *357*, 136852
4. Y. Wang, H. Sauriat-Dorizon, H. Korri-Youssoufi, *Sens. Actuators B: Chem.*, **2017**, *251*, 40.
5. H. Xu, C. Liao, Y. Liu, B.-C. Ye and B. Liu, *Anal. Chem.* **2018**, *90*, 4438

Vitamin B_{12}-catalyzed reactions of alkyl bromides under visible light irradiation

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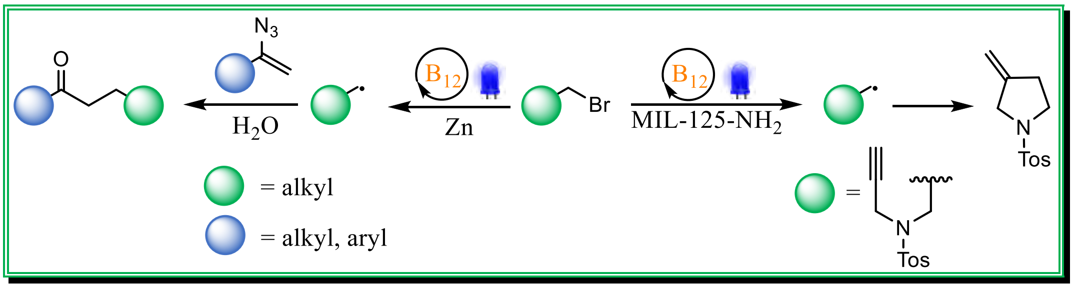
Vitamin B_{12} is a natural cobalt catalyst that plays an important role in living organisms. Its usefulness in organic chemistry has been proven in a number applications.[1] Mainly, it is used as Co-catalyst. The catalytic properties of this compound rely on the redox properties of the Co-ion. Once reduced to Co(II)-form it is radical in nature, while the Co(I) has nucleophilic character. These reactive species can be obtained using various reducing agents. In most of reactions, activated zinc powder is used as well as $NaBH_4$ or manganese, which narrows the possible scope of reagents (i.e. for aldehydes). A few attempts for the photoreduction of B_{12} has been reported, utilizing either noble metal complexes (Ir, Ru) [2, 3] or an organic dye (Rose Bengal) [4]. We propose a heterogenous photocatalytic reduction system with a titanium-based Metal Organic Framework as the active photoreductant of a cobalt centre.

Our recent contributions to the vitamin B_{12} catalysis involve, among others, light-induced transformation of vinyl azides to ketones [5] and photocatalytic cyclization of terminal alkynes to pyrrolidines. In particular, vinyl azides can form different chemical entities, like amides or ketones. [6] The latter can be synthesized in a reaction of vinyl azides with nucleophiles. Moreover, radical precursors are reported to yield ketones in such reaction, yet utilization of simple electrophiles remained unexplored. Based on our previous work with vitamin B_{12}, we know that alkyl radical species can be formed from alkyl bromides with the nucleophilic form of cobalamin under visible light irradiation. We proposed a catalytic system in which we utilize electrophiles as radical precursors and a vitamin B_{12} derivative as Co-catalyst to obtain asymmetric ketones. This method gives products in decent yields in regard to the bromide scope (30%-82%).



REFERENCES

1. Giedyk, M. ; Goliszewska, K. ; Gryko, D. *Chem. Soc. Rev*., **2015**, *44*, 3391−3404.
2. Shimakoshi, H.; Nishi, M.; Tanaka, A.; Chikama, K.; Hisaeda, Y. *Chem. Commun*., **2011**, *47*, 6548–6550.
3. Tian, H.; Shimakoshi, H.; Park, G.; Kim, S.; You, Y.; Hisaeda, Y. *Dalton Trans*., **2018**, *47*, 675–683.
4. Yerien, D. E.; Postigo, A,; Baroncini M.; Barata-Vallejo, S. *Green Chem*., **2021**, *23*, 8147–8153.
5. Dworakowski, K. R.; Pisarek, S.; Hassan, S.; Gryko, D. *Org. Lett.* **2021**, *23*, 9068−9072.
6. Fu, J.; Zanoni, G.; Anderson, E. A.; Bi, X. *Chem. Soc. Rev.* **2017**, *46*, 7208– 7228.

Design, Synthesis, and Study of Tunable Spin Information Relays in Metalated Porphyrin Systems

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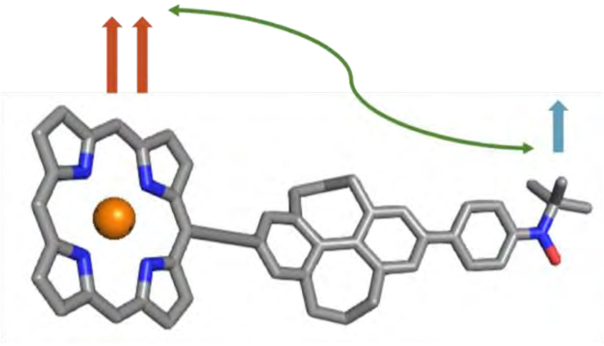
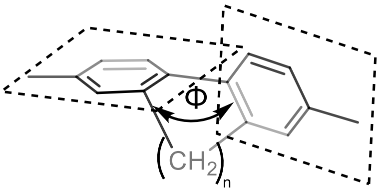
Highly versatile photogenerated multi-spin systems are promising candidates for a wide range of applications such as artificial photosynthesis, molecular spintronics, and spin catalysis.[1] While the radical acts as an efficient sensitizer that improves the intersystem crossing rate, the delicate covalent linkage between chromophore-radical systems serves as a means of controlling the excited state dynamics of the chromophore.[2] The aim of this project is to develop covalent multi-spin systems to study spin-information transfer and storage. This is performed by engineering systems that consist of at least two organic spin centers that we connect by a conjugated framework.





The bridge between the two spin centers is then systematically modified in order to trace the changes in the resulting spin communication. By choosing a bridged biphenyl [3] as the linker between the chromophore and the radical, the electronic communication throughout the synthon is expected to vary with the torsion angle Φ between the planes of the two phenyl rings, which in turn modulates the spin-spin interaction.

REFERENCES

1. S. Yamauchi, *B. Chem. Soc. Jpn,* **2004**, *77*, 1255-1268.
2. O. Nolden, N. Fleck, E. R. Lorenzo, M. R. Wasielewski, O. Schiemann, P. Gilch, S. Richert, *Chem-Eur. J,* **2021**, *27*, 2683.
3. D. Vonlanthen, J. Rotzler, M. Neuburger, M. Mayor, *Eur. J. Org. Chem,* **2010**, 120-133.

Comparative photophysical and photochemical study of Zn and Pd phthalocyanines tetra non-peripherally substituted with dimethoxyphenyl moieties

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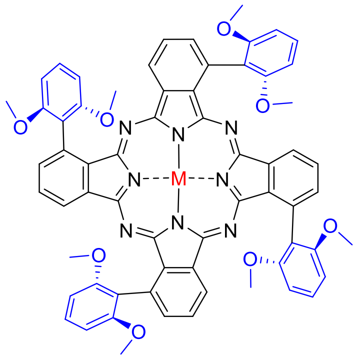
Phthalocyanines (Pc) are amongst the best photosensitisers for photodynamic therapy (PDT) because of their maximum absorption in the phototherapeutic window [1]. The photophysical properties of Pcs are strongly dependent on the nature of the coordinated central metal ion [2] and of the substitution pattern [3]. The presence of heavy atoms of a photosensitiser increases their singlet oxygen generation ability [4]. To compare the effect of Zn vs Pd metalation, the phthalocyanines shown here have been designed and their photophysical and photochemical properties will be presented.



M = Zn or Pd

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REFERENCES

1. P.-C. Lo, M. S. Rodríguez-Morgade, R. K. Pandey, D. K. P. Ng, T. Torres and F. Dumoulin, *Chem. Soc. Rev.*, **2020**, *49*, 1041-1056
2. Yunus Zorlu, Fabienne Dumoulin, Mahmut Durmus and Vefa Ahsen, *Tetrahedron* **2010**, *66*, 3248-3258.
3. Sevinc Z. Topal, Ümit İşci, Ufuk Kumru, Devrim Atilla, Ayşe G. Gürek, Catherine Hirel, Mahmut Durmuş, Jean-Bernard Tommasino, Dominique Luneau, Savas Berber, Fabienne Dumoulin* and Vefa Ahsen*, *Dalton Trans*. **2014**, *43*, 6897-6908
4. Derya Topkaya, Shie Yin Ng, Yann Bretonnière, Dominique Lafont, Lip Yong Chung, Hong Boon Lee, Fabienne Dumoulin, *Photodiagn. Photodyn. Ther.*, 2016, 16, 12-14

Dimeric annulated fused photosensitising phthalocyanines for photodynamic therapy

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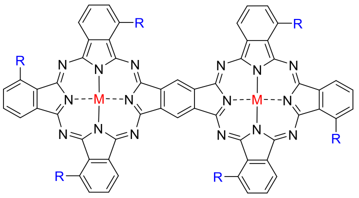
The maximum absorption of phthalocyanines centred around 700 nm gives them a very sought advantage over other photosensitisers [1], as it allows to illuminate them with wavelengths of the phototherapeutic window (limiting the excitation of endogeneous chromophores), and to have a deeper tissue penetration of the light.

Dimeric annulated fused phthalocyanines exhibit NIR-shifted absorption that is particularly interesting [2], and can be further enhanced with non-peripheral substitution. This is why the phthalocyanine derivatives shown below have been designed.



The Scientific and Technological Research Council of Turkey (TUBITAK) and the French Embassy in Turkey are gratefully acknowledged for the bilateral Partenariat Hubert Curien between Turkey and France (project Bosphorus 120N684/ 4665SH).

REFERENCES

1. P.-C. Lo, M. S. Rodríguez-Morgade, R. K. Pandey, D. K. P. Ng, T. Torres and F. Dumoulin, *Chem. Soc. Rev.*, **2020**, *49*, 1041-1056
2. M. Köç, A. G. Gürek, Fa. Dumoulin and V. Ahsen, *Turkish J. Chem.* **2012**, *36*, 493-502

Theoretical electronic spectra of metal-free tetrabenzoporphyrin and its metal complexes

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The possibility of fine tuning of the macroheterocycles properties provides a lot of applications in different fields, for example, it can be used as sensors of molecular oxygen, semiconductors, in photodynamic therapy.

The electronic spectra of metal-free tetrabenzoporphiryn (H2TBP) and its metal complexes MTBP (M = Zn, Cd) and MClTBP with the axial –Cl (M = Al, Ga, In) were calculated by DFT (PBE0 functional with the dispersion correction D3 provided by Grimme [1] using def2-TZVP basis set). The lowest excited states have been computed with the use of time-dependent density functional theory (TDDFT) calculations.

The calculated spectra are shown in Figure 1. The fact that the spectra are similar indicates the minor influence of the metal nature on the position of the Q-band. It should be noted that HOMO-LUMO gap is the lowest for metal-free H2TBP. Nevertheless a negligible bathochromic shift observed in the case of MClTBP, while a hypsochromic shift occurs for MTBP with introducing of metal since the Q-band can be assigned to both transitions from the highest occupied molecular orbital (HOMO) and HOMO-1 to the doubly-degenerated lowest unoccupied MOs (LUMOs). The shapes of these MOs are typical for macrocycles and can be described by the Gouterman model. The HOMO is predominantly representing the linear combination of atomic orbitals of the pyrrole rings, while the HOMO-1 is localized on the carbon atoms in meso-positions.

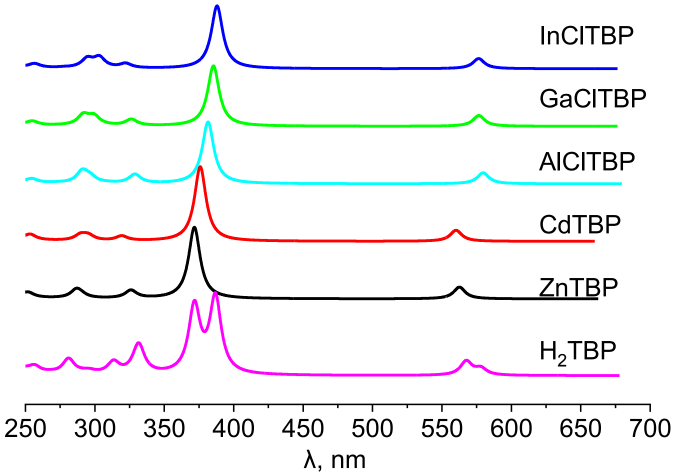

Figure 1. Calculated TDDFT electronic absorption spectra for H_2TBP, MTBP and MClTBP complexes.

This work was supported by the Russian Science Foundation grant 21-73-10126.

REFERENCES

1. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J. Chem. Phys. 2010, 132, 154104.

Vapor composition over metal-free tetrabenzoporphyrin and its complex with zinc (II)

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The studies of vapor composition over metal-free tetrabenzoporphyrin (H_2TBP, fig. 1a) and its complex with zinc (ZnTBP, fig. 1b) were carried out using the magnetic mass-spectrometer MI-1201. Solid samples were evaporated from a molybdenum Knudsen effusion cell.

(a) (b)

Figure 1. Molecular models of metal-free tetrabenzoporphyrin (a) and its complex with Zn (b)

The most intensive peak in the mass-spectrum of ZnTBP (Fig. 2) is molecular ion M^+, m/z = 572 a.u.m. The mass-spectrum also contains a doubly charged molecular ion M^{2+} and fragment ions, mainly corresponding to isoindole dimers.

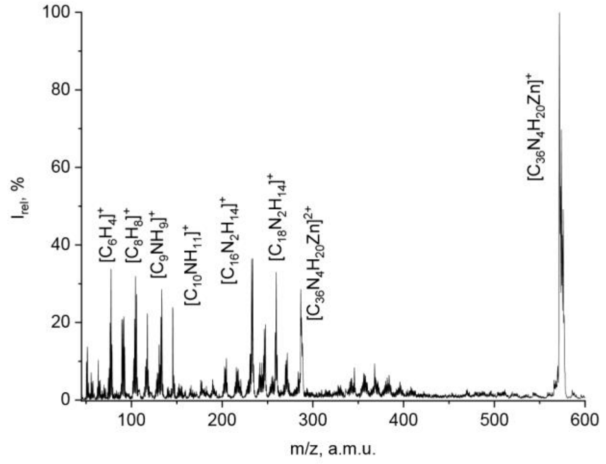

Figure 2. ZnTBP mass-spectrum, T = 730 K with ionizing voltage U_{ion} = 50 V.

It should be noted that metal-free H_2TBP decomposes when heated to 780 K. A molecular ion is present in the spectrum; however, it has a lower intensity compared to fragmentary ions or/and decomposition products and gradually disappears from the spectrum.

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Antimony Corroles

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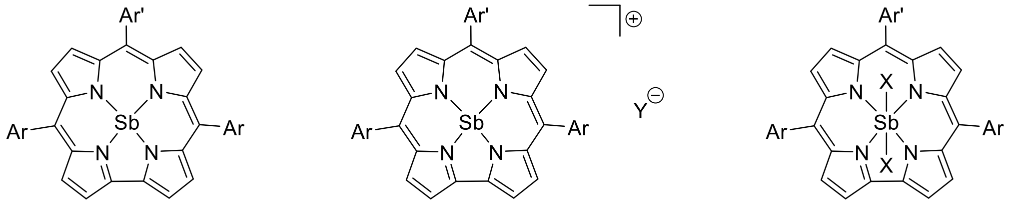
Porphyrinoid macrocycles are enjoying constant popularity, not least because of their versatile occurrence in nature, for example as leaf and blood pigments [1, 2]. Corroles, in contrast to porphyrins, are reduced by one methine unit, leading to a smaller N_4 cavity and a formal trianionic nature. This enables the ability to stabilize not only transition but also main group metals in unusually high oxidation states. Thus, in the past, a small number of antimony corroles in the oxidation states +III and +V have already successfully been synthesized, including the attachment of oxygen and halogens as axial ligands [3, 4, 5]. Furthermore, evidence has been found for the existence of an antimony (IV) species [6].



X = F, Cl, ...

Fig. 1: Overview over some of the investigated antimony corroles in the oxidation states +III (left), +IV (middle) and +V (right).

We have investigated antimony corroles from a coordination chemists' perspective and will present our recent result on the synthesis and characterization of novel antimony corroles in the oxidation states +III, +IV and +V, including the attachment of various functionalized groups, on the poster.

REFERENCES

1. I. Fleming, *Nature* **1967**, *216*, 151-152.
2. M. F. Perutz, M. G. Rossmann, A. F. N. N. Cuillis, H. Muirhead, G. Will, A. C. T. North, *Nature* **1960**, *185*, 416-422.
3. I. Luobeznova, M. Raizman, I. Goldberg, Z. Gross, *Inorg Chem* **2006**, *45*, 386-394.
4. A. Mahammed, Z. Gross, *Angew Chem Int Ed* **2015**, *54*, 12370-12373.
5. C. M. Lemon, S. J. Hwang, A. G. Maher, D. C. Powers, D. G. Nocera, *Inorg Chem* **2018**, *57*, 5333-5342.
6. K. M. Kadish, C. Erben, Z. Ou, V. A. Adamian, S. Will, E. Vogel, *Inorg Chem* **2000**, *39,* 3312-3319.

Photodynamic Therapy with bioconjugates in the treatment of Age-related Macular Degeneration

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Photodynamic Therapy (PDT) has been successfully employed in the treatment of various types of tumors [1] and, more recently, in the treatment of Age-related Macular Degeneration (AMD), a painless eye condition that affects the macular region of the retina [2]. This therapy results from the combination of three main elements: a chemical compound (photosensitizer, PS), light in the far visible-to-near infrared region, and molecular oxygen [3]. The PS excitation with a specific wavelength of light can generate cytotoxic reactive oxygen species (ROS) from intracellular oxygen [3]. The wide diversity of biological functions in these molecules demonstrates that minor changes in their base structure may lead to distinct properties. The covalent conjugation of hydrophilic groups with this type of dyes plays an important role in their biocompatibility [4]. Their conjugation with specific biomotifs, such as carbohydrates, is a widely used drug synthetic strategy to reach specific biologic targets. The higher specificity has the potential to lead to enhanced PDT efficacy and reduced toxicity of adjacent healthy cells [4]. Therefore, the main aims of this work were the bioconjugation of TPPF20 and its chlorin derivative ChlF20 with the thioglucose (Glc) and thiogalactose (Gal) moieties, and evaluation of their in vitro efficacy as potential photosensitizing agents for AMD treatment. The PSs´ photobiological properties (cellular uptake of PSs, dark toxicity, and photodynamic effect) were investigated using a human retinal pigment epithelial cell line.

Acknowledgements: This work has been supported by the FCT 2020-2023 multiannual funding to CQE (UIDB/00100/2020 and UIDP/00100/2020), CIBB (UIDB/04539/2020 and UIDP/04539/2020) and COMPETE-FEDER (POCI-01-0145-FEDER-007440); Centro 2020 Regional Operational Program: BRAINHEALTH 2020 (CENTRO-01-0145-FEDER-000008). Sandra Beirão, Sara Fernandes and Beatriz Martins acknowledge FCT for their Ph.D. scholarship SFRH/BD/140098/2018, SFRH/BD/129200/2017 and 2020.04811.BD, respectively.

REFERENCES

1. S.R.G. Fernandes, B. Sarmento, P.M.R. Pereira, J.P.C. Tomé, *Org. Biomol. Chem.* 2019, 17(10), 2579-2593.
2. K. A. D. F. Castro, F. Figueira, R. F. Mendes, J. A. S. Cavaleiro, M. G. P. M. S. Neves, M. M. Q. Simões, F. A. A. Paz, J. P. C. Tomé, S. Nakagaki *ChemCatChem* 2017, 9, 2939 – 2945.
3. C. F. Pereira, F. Figueira, R. F. Mendes, J. Rocha, J. T. Hupp, O. K. Farha, M. M. Q. Simões, J. P. C. Tomé, F. A. Almeida Paz *Inorg. Chem.* 2018, 57, 3855-3864.
4. S. Singh, A. Aggarwal, S. Thompson, J.P.C. Tomé, X. Zhu, D. Samaroo, M. Vinodu, R. Gao, C.M. Drain *Bioconjugate Chem*. 2010, 21, 2136–2146.

Light-triggered Racemization of Enantiopure Samples of Axially-chiral Subphthalocyanine-“extended” TCNQ-aniline Conjugates

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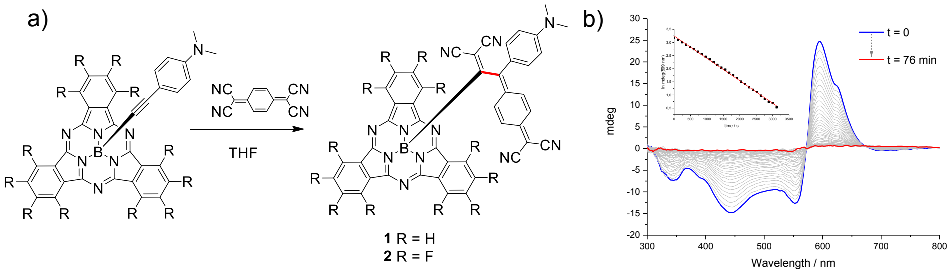
Subphthalocyanines (SubPcs) are cone-shaped aromatic macrocycles that can be functionalized at their peripheral and/or axial positions. When properly functionalized with electroactive units, SubPcs can give rise to electron donor-acceptor (D-A) systems, in which photoinduced charge separation can occur, a process quite interesting for optoelectronic applications.[1] Herein, two novel D-A SubPcs **1** and **2** have been synthesized by a cycloaddition-retroelectrocyclization reaction[2] between R_{12}SubPcs (R = H or F) axially substituted with an ethynyldimethylaniline subunit and 7,7,8,8-tetracyanoquinodimethane (TCNQ), a strong electron-withdrawing molecule (Figure 1a). The presence of a chiral axis (highlighted in red in Figure 1a) in the “extended” TCNQ axial moiety gives rise to the formation, for both conjugates **1** and **2**, of a racemic mixture composed by the S_a and R_a atropisomers which could be separated by chiral high performance liquid chromatography. Circular dichroism (CD) racemization experiments were carried out on enantiopure samples of **1** and **2** (Figure 1b), and the results analysed and compared to previously reported analogues comprising SubPcs[3] and subporphyrins[4].

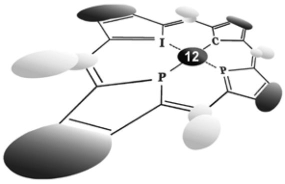


1 R = H
2 R = F

Figure 1. a) Synthetic route leading to SubPc-TCNQ-aniline **1** and **2**. b) Time-dependent CD spectra of an O_2-free and illuminated toluene solution of an atropisomer of **2** heated at 80 °C. Inset: Linear fitting of the variation of the CD absorbance monitored at 599 nm (ln mdeg) in (b) as a function of time.

REFERENCES

1. Claessens, C. G.; González-Rodríguez, D.; Rodríguez-Morgade, M. S.; Medina, A.; Torres, T. *Chem. Rev.* **2014**, *114*, 2192–2277.
2. Michinobu, T. ; Diederich, F. *Angew. Chem. Int. Ed.* **2018**, *57*, 3552-3577.
3. a) Winterfeld, K. A.; Lavarda, G.; Guilleme, J.; Sekita, M.; Guldi, D. M.; Torres, T.; Bottari, G. *J. Am. Chem. Soc.* **2017**, *139*, 5520–5529 ; b) Lavarda, G.; Bhattacharjee, N.; Brancato, G.; Torres, T.; Bottari, G. *Angew. Chem. Int. Ed.* **2020**, *59*, 21224–21229
4. Winterfeld, K. A.; Lavarda, G.; Yoshida, K.; Bayerlein, M. J.; Kise, K.; Tanaka, T.; Osuka, A.; Guldi, D. M.; Torres, T.; Bottari, G. *J. Am. Chem. Soc.* **2020**, *142*, 7920–7929



Does Oxygen Spin Density Correlate with C-H Bond Activation Reactivity of Metal Oxo Compounds?

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Metal-oxo complexes, common reactive intermediates in biological oxidation reactions, do a very important and difficult reaction: the activation of inert C-H bonds. While these are widely studied reactions, there is a debate about the role of oxygen spin density in the C-H bond activation by metal-oxos. The debate is focused on whether ground state thermodynamics play the dominant role in determining reactivity or whether the spin density on the oxygen atom can provide an intrinsic lowering of the reaction barrier.[1,2] This issue has been very hard to address due to the difficulty of thermodynamic and spin density measurements and the lack of a series of isoelectronic and isostructural compounds over which these parameters can be varied. In order to shed light on this debate, we have labelled the oxygen in a series of C-H bond activating heme protein Compound I species with oxygen-17 and used Q-band pulse Davies ENDOR to determine the oxygen-17 hyperfine values. These hyperfine values were used to obtain oxygen spin densities. The measured oxygen spin densities provide insight into the interplay between donation, spin density, charge density, basicity and C-H bond activation reactivity in metal oxo complexes.

REFERENCES

1. Saouma, C. T.; Mayer, J. M., Do spin state and spin density affect hydrogen atom transfer reactivity? *Chem Sci* **2014,** *5* (1), 21-31.
2. Dietl, N.; Schlangen, M.; Schwarz, H., Thermal Hydrogen-Atom Transfer from Methane: The Role of Radicals and Spin States in Oxo-Cluster Chemistry. *Angew Chem Int Edit* **2012,** *51* (23), 5544-5555.

Vanadyl TPyzPz as material for organic electronic, synthesis and properties.

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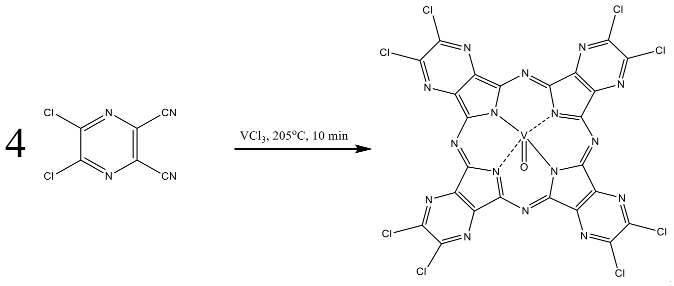
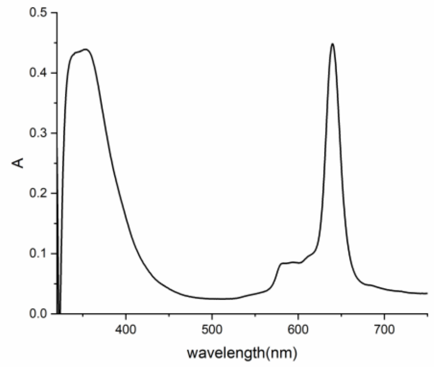
Tetrapyrrolic macroheterocycles such as phthalocyanines (Pcs) and analogues are widely studied as perspective materials for organic electronics. Among modified Pcs their heterocyclic analogues containing electron-deficient heterocycle instead of benzene rings as especially interesting as acceptor materials 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 and etc) have been illustrated [1]. Electron affinity of TPyzPA macrocycle can be enhanced by its peripheral halogenation and perchlorinated TPyzPA, [$Cl_8TPyzPAH_2$] and its complexes with aluminium subgroup metals ([$Cl_8TPyzPAM$, M = AlOH, GaOH, InOH], as well with with Fe^{II} and Sn^{IV} were reported Vanadyl phthalocyanines attracted much attention as fairly promising material for organic electronic as field-effect transistors and vanadyl porphyrazine with four 1,2,5-thiadiazole fragments exhibits a high-density carrier accumulation in the organic semiconductors through the formation of electric double layers within them [2].

In the presented work, we prepared the vanadyl complex [$Cl_8TPyzPAV{=}O$] and studied its spectral, electrochemical, and photochemical properties. Influence of peripheral halogenation of TPyzPA complexes on their electronic structure was also studied by DFT method.





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REFERENCES

1. Donzello. Tetrapyrazinoporphyrazines and their metal derivatives. Part I: Synthesis and basic structural information/ M.P. Donzello; C. Ercolani; V. Novakova; P. Zimcik; P.A. Stuzhin. *Coordination Chemistry Reviews* – 2016. - V.309. - P. 107–179.
2. Awaga. Crystal Structure, Spin Polarization, Solid-State Electrochemistry, and High n-Type Carrier Mobility of a Paramagnetic Semiconductor: Vanadyl Tetrakis(thiadiazole)porphyrazine/ Y. Miyoshi, K. Takahashi, et al. *Chemistry* 2012 51 (1), 456-462 DOI: 10.1021/ic201880g

Novel *meso*-disubstituted porphycenes: Synthesis and properties

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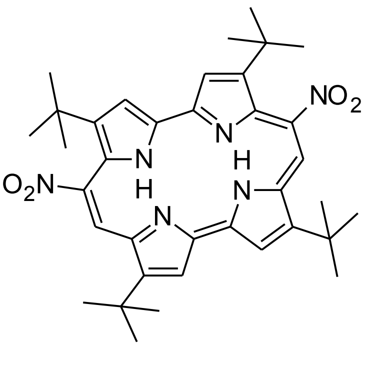
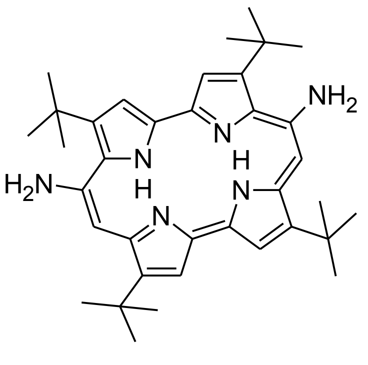
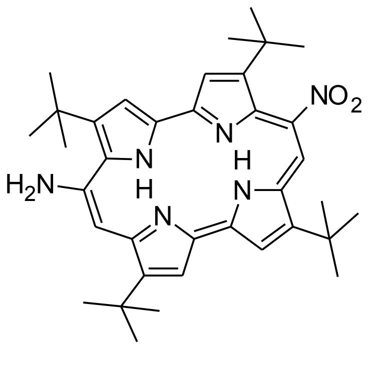
Porphycene, synthesized for the first time by Vogel *et al.*[1], has an ability to strongly absorb red light and to photosensitize formation of singlet oxygen, which makes it a good candidate for a photosensitizer in photodynamic therapy (PDT).[2] Introducing substituents on the porphycene backbone is a powerful method to control the reactivity, solubility, electronic structure, and photophysical properties. Moreover, extending the diversity of the porphycene family provides good models to examine the mechanism of intramolecular double hydrogen transfer.[3] Peripheral substituents affect the distance between the inner nitrogen atoms and, in consequence, hydrogen bond strength and symmetry. Different possible locations of two hydrogen atoms in the inner cavity result in three pairs of tautomeric forms. These tautomers are pairwise degenerate when the substituents on the *β*, *β*' or *meso* positions are identical. The degeneration of tautomers is lifted for any other type of substitution. Substitution also specifically affects spectral and photophysical properties. Continuing our ongoing project,[4-5] we have prepared a set of novel, doubly *meso*-substituted porphycenes bearing electron-withdrawing and/or electron-donating substituents. Spectroscopy, photophysics, and tautomeric properties of these compounds will be discussed.







REFERENCES

1. Vogel E, Köcher M, Schmickler H, Lex J. J. *Angew. Chem. Int. Ed. Engl.* 1986, *25*, 257.
2. Stockert J C, Cañete M, Juarranz A, Villanueva A, Horobin R W, Borrell J I, Teixidó J, Nonell S. *Curr. Med. Chem.* 2007, *14*, 997.
3. Waluk J. *Chem Rev*. 2017, *117*, 2447.
4. Listkowski A, Kharchenko A, Ciąćka P, Kijak M, Masiera N, Rybakiewicz R, Luboradzki R, Fita P, Waluk J. *ChemPlusChem*, 2020, *85*, 2197.
5. Listkowski A, Masiera N, Kijak M, Luboradzki R, Leśniewska B, Waluk J. *Chem. Eur. J.* 2021, *27*, 6324.

Saddle-Shaped Porphyrinoids for Energy Transfer

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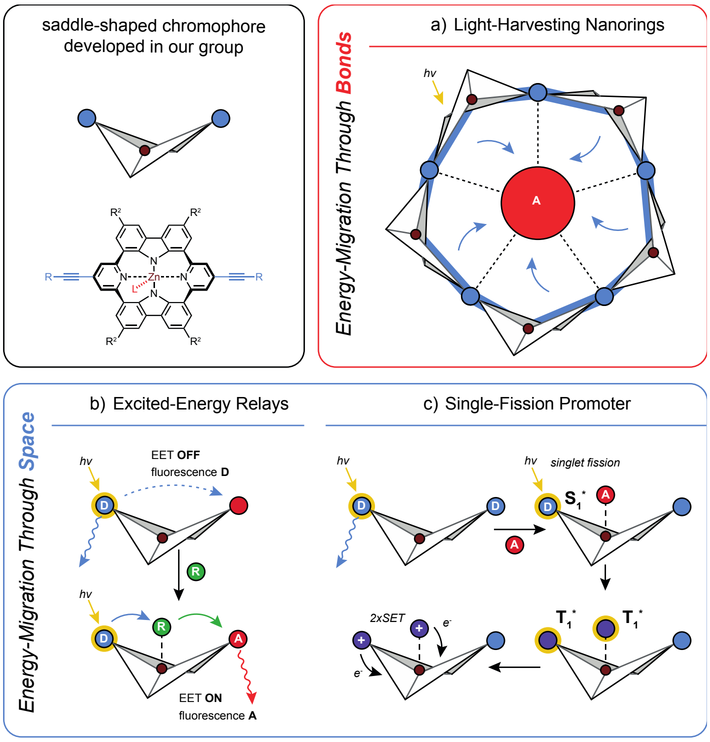
Carpyridines (CPs) are porphyrin-related metal-containing macrocycles bearing two carbazole and two pyridine units alternately connected through *ortho* aryl-aryl bonds [1-2]. This arrangement results in a saddle-shaped structure, where prefunctionalized building blocks allow the synthesis and tuning of properties of these macrocycles. Despite the decoupling of the subunits within the system, conjugation passes from linker *via* pyridine and goes through the metal, making these structures interesting for the study of energy transfer. These properties have taken us to study (a) CPs as inherently curved building blocks for Light-Harvesting Nanorings, (b) CPs as π spacers for Excited-Energy Relays and (c) CPs as Promoters for Singlet Fission chromophores, and the energy migration through bond and through space within these structures [3].



REFERENCES

1. L. Arnold, H. Norouzi-Arasi, M. Wagner, V. Enkelmann, K. Müllen, *Chem. Commun.,* 2011, 47, 970–972.
2. J. F. Woods, L. Gallego, P. Pfister, M. Maaloum, A. Vargas Jentzsch, M. Rickhaus, DOI: 10.26434/chemrxiv-2022-7f103, *submitted.*
3. *Unpublished results.*

Synthesis of Fused-Phthalocyanine-Perylenebenzimidazole Systems

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Nowadays, the synthesis of new highly extended conjugated phthalocyanine-based π-systems as molecular materials is becoming an interesting issue due to their outstanding optoelectronic properties, useful for optical data storage, as electronic components, and as light-harvesting systems [1].

Here, we report on the synthesis and characterization of new fused phthalocyanine-perylenebenzimidazole dimeric arrays on the basis of the technological importance of near infrared donor-acceptor systems. With the aim of obtaining conjugated ensembles with varied electronic features (Figure 1), we used a similar strategy previously reported by us [2], based on the condensation of diaminosubstituted phthalocyanines with perylenecarboxyanhydrides. The new conjugated ensembles have been fully caracterized by ^{1}H-NMR, UV-Vis and cyclic voltammetry. The measurements revealed molecular and supramolecular interactions between phtalocyanine and perylene moieties [3].

This research was supported by the European Regional Development Fund “A way to make Europe” and the Spanish Ministerio de Ciencia e Innovación/Agencia Estatal de Investigación (PID2019-109200GB-I00).

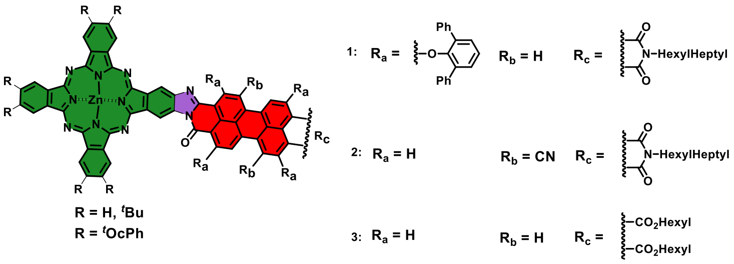

Figure 1. Different fused ZnPc-perylenebenzimidazole systems

REFERENCES

1. a) J. Follana-Berná, S. Seetharaman, L. Martín-Gomis, G. Charalambidis, A. Trapali, P. A. Karr, A. G. Coutsolelos, F. Fernández-Lázaro, F. D’Souza, Á. Sastre-Santos, *Phys. Chem. Chem. Phys.* **2018**, *20*, 7798-7807; b) S. Seetharaman, J. Follana-Berná, L. Martín-Gomis, G. Charalambidis, A. Trapali, P. A. Karr, A. G. Coutsolelos, F. Fernández-Lázaro, Á. Sastre-Santos, F. D’Souza, *ChemPhysChem* **2019**, *20*, 163-172; c) J. Follana-Berná, D. Inan, V. M. Blas-Ferrando, N. Gorczak, J. Ortiz, F. Manjón, F. Fernández-Lázaro, F. C. Grozema, Á. Sastre-Santos, *J. Phys. Chem. C* **2016**, *120*, 26508–26513.
2. V. M. Blas-Ferrando, J. Ortiz, K. Ohkubo, S. Fukuzumi, F. Fernández-Lázaro, Á. Sastre-Santos, *Chem. Sci.* **2014**, *5*, 4785–4793.
3. Manuscript in preparation.

Highly functionalized tetrabenzoporphyrins

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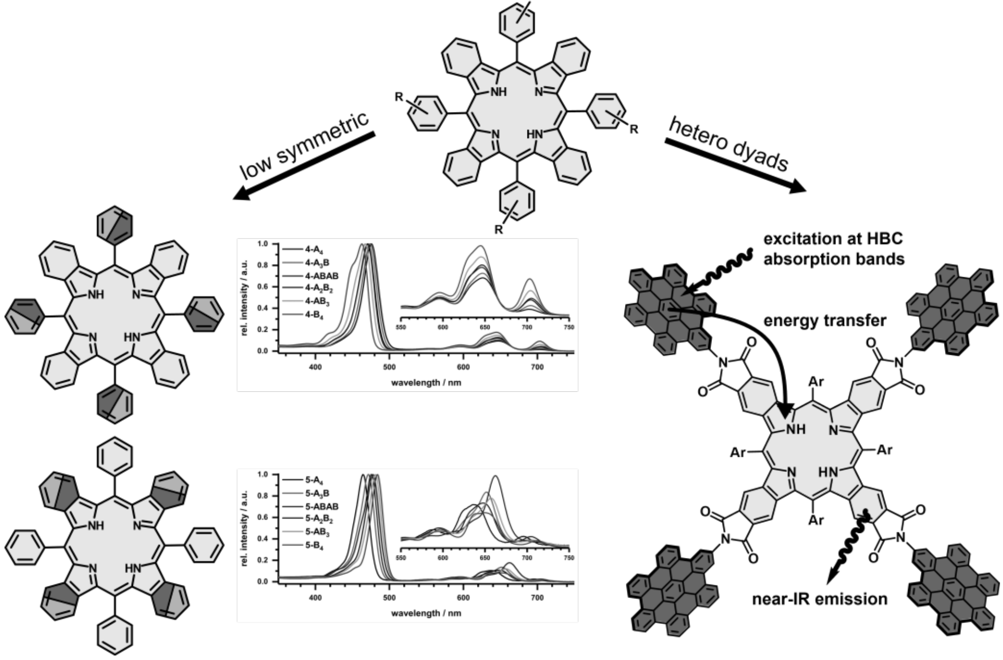
Compared to porphyrins counting as one of the most exploited nitrogen-containing macrocycles, the linear π-extended tetraaryltetrabenzoporphyrins (TATBPs) seem rather underrepresented despite their potential in various fields of materials sciences and medicinal chemistry [1,2]. Previous reports of our group established a synthetic protocol to prepare a library of A_4-symmetric TATBPs [3]. In order to shed light on even more refined systems, this work focuses on the introduction of low-symmetric derivatives [4] and the formation of donor-acceptor hetero dyads consisting of hexa-*peri*-hexabenzocoronene (HBC) substituents attached to the tetrabenzoporphyrin core [5].



REFERENCES

1. Dedic D, Dorniak A, Rinner U and Schofberger W. *Front Chem* 2021; **9**: 685619.
2. Otvagin VF, Kuzmina NS, Kudriashova ES, Nyuchev AV, Gavryushin AE and Fedorov AY. *J. Med. Chem.* 2022; **65**: 1695-1734.
3. Ruppel M, Lungerich D, Sturm S, Lippert R, Hampel F and Jux N. *Chem. Eur. J.* 2020; **26**: 3287-3296.
4. Ruppel M, Gazetas LP, Lungerich D, Hampel F and Jux N. *J. Org. Chem.* 2020; **85**: 7781-7792.
5. Ruppel M, Gazetas LP, Lungerich D and Jux N. *Eur. J. Org. Chem.* 2020; **2020**: 6352-6360.

Functional Nanostructured Molecular Architectures for Optoelectronic Applications

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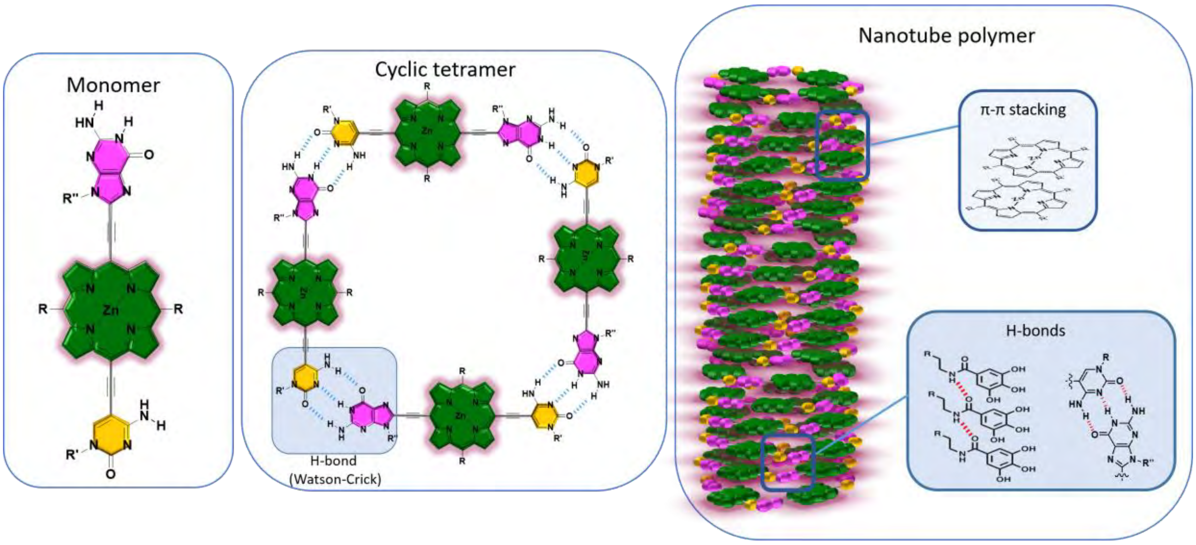
This Project focuses on establishing an unconventional and versatile strategy to prepare predesigned π-electronic function a self-assembled structures where we can control the size, shape, composition and the organization at the nanoscale by supramolecular chemistry. Cyclic tetramers are formed through a self-assembly process from 4 monomeric π-conjugated units via Watson-Crick hydrogen bonding.[1] Following the formation of cyclic tetramers, self-assembled nanotubes will be accomplished through a nucleation-growth cooperative mechanism in organic solvents, due to the combination of π-π stacking between central unit and the hydrogen bonding interactions of the nucleobases that form the monomer.[2, 3] Once the role of molecular organization is understood, the aim is to optimize the parameters to achieve optimal photovoltaic efficiency. For this, monomers have been built in which the central component is a π-conjugated energy donor/acceptor where the molecular organization of p-type and n-type semiconductors is controlled and, therefore, it would be possible to modulate and optimize the photophysical, photoconductive and photovoltaic properties of the system.



REFERENCES

1. Montoro-García,C. ; Camacho-García, J ; Lopez-Pérez, A. M. ; Bolbao, N. ; Romero-Pérez, S. ; Mayoral, M. J. ; González-Rodróguez, D. *Angew. Chem*. **2015**, 127, 6884.
2. Vázquez-González, V.; Mayoral, M. J.; Chamorro, R; Hendrix, M. M. R. M.; Voets, I. K.; González-Rodríguez, D. *J. Am. Chem. Soc*. **2019**, 41, 16432.
3. Vázquez-González, V.; Mayoral, M. J.; Aparicio, F.; Martínez-Arjona, P.; González-Rodríguez, D. *ChemPlusChem*. **2021**, 86, 1087-1096.

Synthesis, solubilization and cytotoxic activity of chlorinated lutetium(III) phthalocyanines

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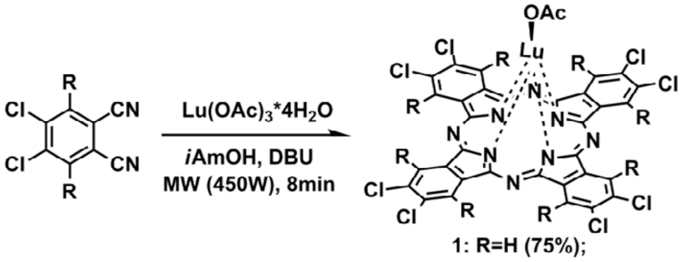
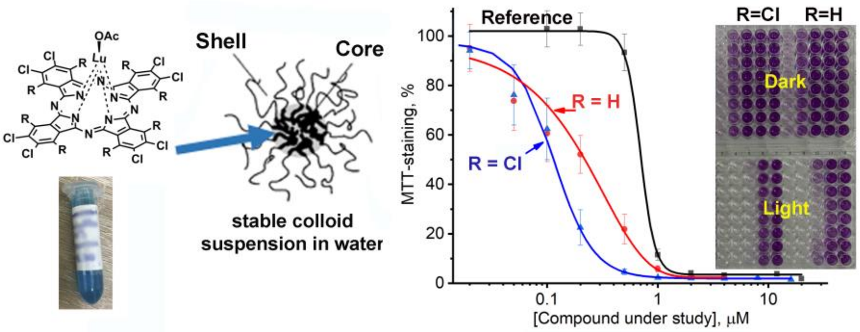
Halogen-substituted lanthanide(III) phthalocyanines are promising photosensitizers. Due to the heavy atom effect they are capable of efficient generation of singlet oxygen. The presence of electron-withdrawing halogen substituents results in high resistance to photoxidation. Octa- and hexadecachloro-substituted Lu(III) phthalocyanines **1** and **2** were obtained via MW-assisted template approach starting from the phthalonitriles [1].



1: R=H (75%);
2: R=Cl (78%)

Chloro-substituted complexes demonstrate moderate quantum yields of singlet oxygen generation (Φ_Δ=0.23-0.54). Moreover, they showed the ability to generate the superoxide anion radical ($O_2^{\bullet-}$) with higher efficiency compared to unsubstituted analog. The incorporation of chloro-substituted lutetium(III) phthalocyanine into polylactide micelles (PLAMs) results in the formation of stable colloid suspension that provides water solubility of the complex and makes it a promising photosensitizer for medical applications. Dark and photoinduced cytotoxic activity of chlorinated lutetium(III) phthalocyanines were tested using HeLa cell line to estimate their potential as photosensitizers for photodynamic therapy of cancer.



PLAMs with complex **1** showed effective phototoxic action – their IC$_{50}$ dose was 0.22 μM (higher than for chlorin e$_6$, its IC$_{50}$ dose was 0.7 μM). PLAMs with complex **2** showed even more effective phototoxic action (IC$_{50}$ = 0.11μM). The study was funded by RFBR, project number 20-33-90157.

REFERENCES

1. E.A. Gorbunova *et al.* // *Journal of Photochemistry & Photobiology, A: Chemistry*, 2022, 426, 113747.

2D/3D Covalent Organic Frameworks Based on Cobalt Corroles for CO Binding

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Corrole belongs to the family of porphyrinoids which is largely used for sensing applications [1]. We have shown that cobalt metallocorroles are able to bind carbon monoxide in the axial position with a high affinity even in the presence of nitrogen and dioxygen, the two main components of the atmosphere [2]. We have recently prepared sensing devices for low CO detection level (sub-ppm) using cobalt corroles deposited as films on a Surface Acoustic Wave device by spray coating [3]. Herein, we will describe the synthesis of new 2D and 3D porous materials belonging to the Covalent Organic Frameworks (COF) family based on cobalt corroles (Figure 1). Their synthesis and selective sorption properties for CO over N_2 and O_2 will be presented.

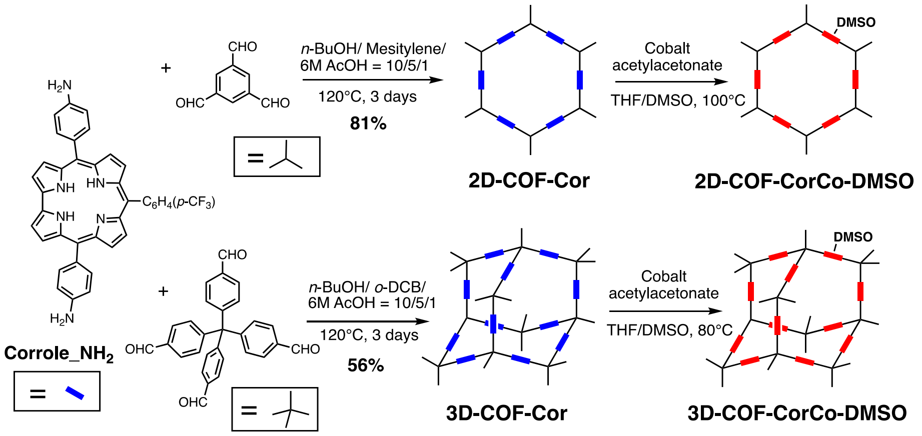

Fig. 1. Synthesis of 2D and 3D COFs

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REFERENCES

1. C. Di Natale, C. P. Gros and R. Paolesse, *Chem. Soc. Rev.,* **2022**, DOI: 10.1039/d1cs00662b, Advance article.
2. a) S. Brandès, V. Quesneau, O. Fonquernie, N. Desbois, V. Blondeau-Patissier, C. P. Gros, *Dalton Trans.* **2019**, *48*, 11651-11662 (*Cover*) b) M. Vanotti, C. Theron, S. Poisson, V. Quesneau, M. Naitana, V. Soumann, S. Brandès, N. Desbois, C. Gros, T.-H. Tran-Thi, V. Blondeau-Patissier, *Proceedings* **2017**, *1*, 444-447.
3. M. Vanotti, S. Poisson, V. Soumann, V. Quesneau, S. Brandes, N. Desbois, J. Yang, L. Andre, C. P. Gros and V. Blondeau-Patissier, *Sensors and Actuators B: Chemical*, **2021**, 129507.

Antipoxvirus Activity Evaluation of Optimized Corroles Based on Development of Autofluorescent ANCHOR Myxoma Virus

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We had previously shown that nitrocorroles could be used as potent anti-hCMV agent without acute toxicity in mice [1-3]. They therefore represent an excellent platform to perform Structure Activity Relationship (SAR) and increase efficiency or reduce toxicity [4].

A series of 43 antiviral corrole-based molecules have been tested on myxoma virus (Lausanne-like T1MYXV strain). An autofluorescent MYXV, with an ANCHOR cassette, has been used for the studies. The most promising compound displays a high selectivity index with the lowest IC50 (0.12 mM). Interestingly, the "Hit" corrole is easy to synthesize in an only two-step reaction [5]. Upscaling production up to 25 g has been carried out for in vivo tests.

In vivo studies on New Zealand white rabbits infected with myxoma virus show that symptoms are delayed and animal weight is increased upon treatment, while no acute toxicity of the corrole molecule was detected.

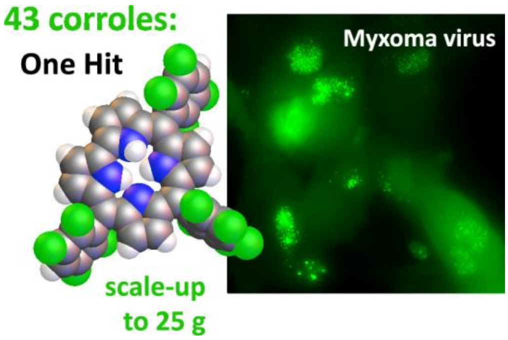

Figure 1

REFERENCES

1. C. P. Gros, N. Desbois, C. Michelin, E. Demilly, A.-F. Tilkin-Mariamé, B. Mariamé and F. Gallardo, *ACS Infectious Diseases* (Front Cover), **2015**, 1, 350-356.
2. L. Bucher, S. Kappler-Gratias, N. Desbois, K. Bystricky, F. Gallardo and C. P. Gros, *RSC Medicinal Chemistry* (Front Cover), **2020**, 11, 771-782.
3. S. Kappler-Gratias, L. Bucher, N. Desbois, Y. Rousselin, K. Bystricky, C. P. Gros and F. Gallardo, *RSC Medicinal Chemistry*, **2020**, 783-801.
4. C. Di Natale, C. P. Gros and R. Paolesse, *Chem. Soc. Rev.,* **2022**, DOI: 10.1039/d1cs00662b, Advance article.
5. S. Kappler-Gratias, L. Bucher, S. Top, C. Quentin-Froignant, N. Desbois, S. Bertagnoli, M. Louison, E. Monge, A. Bousquet-Melou, M. Lacroix, C. P. Gros and F. Gallardo, *ACS Infectious Diseases*, **2021**, 7, 2370-2382.

Photoswitchable molecular wires with SubPcs as photoactive compounds

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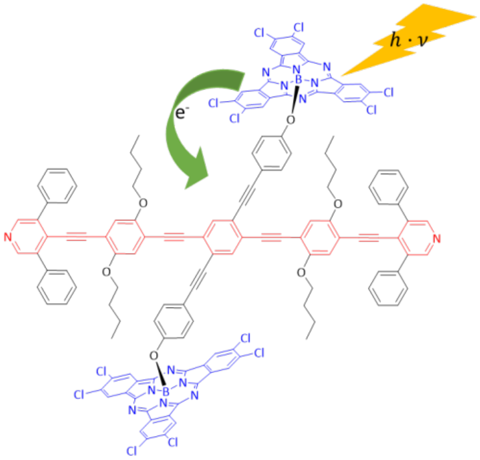

Molecular electronics is a diverse field of research aimed at replacing parts of the traditional electronics architecture by synthetic units [1]. Molecular wires are distinct organic molecules that have appreciable electric conductivity and can therefore serve as elementary building blocks for nanoscale devices [2]. In general, conductivity is achieved by applying a potential bias along a conjugated π-system [3].

The aim of our work is the synthesis and the characterization of a photoswitchable molecular wire with ethynyl phenylene backbone that is endcapped by pyridyl anchor groups for contacting common electrode materials. Light-induced modulation of the electron density along the main axis of the molecular wire will be achieved by the implementation of pending photoactive subphthalocyanines (SubPc) to the backboneSubPcs are well suited for this purposeas they are light-stable and can act as electron donors upon interaction with light. [4]. We will report here the synthesis and a preliminary photophysical characterization of first examples of these photoswitchable molecular wires.

REFERENCES

1. F. C. Grozema, L. D. A. Siebbeles, *Charge and Exciton Transport through Molecular Wires*, Wiley-VCH Verlag, 1. Ed., Weinheim, Germany, **2011**.
2. D. M. Guldi, H. Nishihara, L. Venkataraman, *Chem. Soc. Rev.* **2015**, 44, 842–844.
3. P. Moreno-García, M. Gulcur, D. Z. Manrique, T. Pope, W. Hong, V. Kaliginedi, C. Huang, *J. Am. Chem. Soc.* **2013**, 135, 12228–12240.
4. W. Chen, Z. Chen, S. Zheng, *Int. J. Quantum Chem.* **2020**, 120.

Investigation of Bis–Porphyrin–Functionalized Polycyclic Aromatic Hydrocarbon Model Compounds

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Over the past years, polycyclic aromatic hydrocarbons (PAHs) have gained great importance in the field of molecular materials, allowing us to get a comprehensive understanding of planar, as well as helical PAHs. [1] The planar hexa–*peri*–hexabenzocoronene (HBC), the non–planar [5]–helicene and the porphyrin have unique features on their own. [2-5] But what can we learn by preparing bis–porphyrin–functionalized model compounds? By optical and electrochemical investigation of these model compounds, interesting correlations are hoped to give more insight into the structure-property relationships defined by the geometrical orientation. [6] For a detailed insight into the electronic communication, the investigated bis–porphyrin model compounds were prepared with a ortho–, meta– and para–substitution pattern.

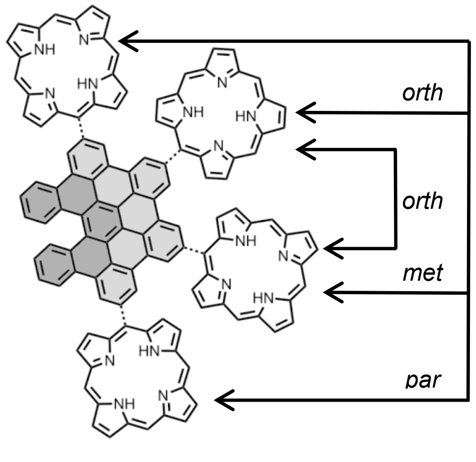

Figure 1. Schematic presentation of target model compound with a ortho–, meta– and para– substitution geometry.

REFERENCES

1. J. Wu, W. Pisula, K. Müllen, Chem. Rev. 2007, 107, 718–747. DOI: 10.1021/cr068010r.
2. M. D. Watson, A. Fechtenkötter, K. Müllen, Chem. Rev. 2001, 101, 5, 1267–1300. DOI: 10.1021/cr990322p.
3. R. Pathak, K. Vandayar, W. A. L. van Otterlo, J. P. Michael, M. A. Fernandes, C. B. de Koning, Org. Biomol. Chem. 2004, 2, 3504–3509. DOI:10.1039/b412932f.
4. K. M. Kadish, K. M. Smith, R. Guilard, The Porphyrin Handbook, 1999.
5. M. M. Martin, F. Hampel, N. Jux, Chem. Eur. J. 2020, 26, 10210–10212. DOI: 10.1002/chem.202001471.
6. M. M. Martin, D. Lungerich, P. Haines, F. Hampel, N. Jux, Angew. Chem. Int. Ed. 2019, 58, 8932–8937. DOI: 10.1002/anie.201903654.

Axially substituted silicone phthalocyanines: Synthesis, characterization, photochemical and photophysical, antioxidant activity, DNA cleavage and antimicrobial PDT properties

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Pc derivatives have been extensively studied as antioxidant agent [1-3]. Multidrug resistance of human pathogenic microorganism to commercial anti-microbial drugs lead to investigation of more effective alternative molecules like metal complex derivatives [4]. In recent years, studies on antimicrobial [5, 6] and antimicrobial PDT (aPDT) properties of the Pc derivatives have been increasing [7].

Suitable photopysical and photochemical properties have made silicon phthalocyanines (SiPcs) different from most other Pc derivatives by means of that SiPc macrocycle possess two additional axial bonds. These axially substitution reduce aggregation in solution and increase solubility thereby creating further scope for modulation of optical, chemical and electronic properties [8]. Considering the promising properties of the SiPc derivatives, it seemed reasonable to study on the SiPc derivatives. From this perspective, we have evaluated the possible antioxidant and antimicrobial capacities, DNA cleavage, cell viability, photodynamic therapy and biofilm inhibition properties of four different SiPc derivatives (**1**-**4**) consisting of two novel SiPc (**1**,**2**) and axially polyoxyethylene substituted **Polyoxo-SiPc** (**3**) and **$Si(OH)_2Pc$** (**4**) in order to evaluate the potential of these compounds as biological active molecule.

REFERENCES

1. Alici EH, Bilgicli AT, Gunset A, Arabaci G, Yarasir MN, *Dalton Trans*., **2021**;50: 3224
2. Li K, Dong W, Liu Q, Lv G, Xie M, Sun X, Qiu L, Jianguo L.*J Photochem Photobiol B Biol*. **2019**; 190:1–7.
3. Amaral GP, Puntel GO, Corte Dalla CL, Dobrachinski F, et.al. *Toxicology in Vitro* **2012**; 26: 125.
4. Günsel A, Bilgiçli AT, Barut B, Taslimi P, et al. *J. Molecular Struc.* **2020**; 1214: 128210
5. Özel A, Barut B, Demirbaş Ü, Biyiklioglu Z, J. *Photochem. Photobiol. B: Biology* **2016**; 157: 32.
6. Ağırtaş MS, Karataş C, ÖzdemirS., *Spectrochim. Acta Part A: Molecular and Biomol.* Spectroscopy **2015;** 135: 20.
7. Openda YI, Sen P, Managa M, Nyokong T, *Photodiagnosis and Photodynamic Therapy* **2020**; 29: 101607
8. Mitra K, Hartman MCT, *Org.Biomol.Chem*. **2021**; 19: 1168

Pathways to Early Transition Metal Corroles

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While the field of corrole complexes and their applications is ever growing, structures containing early transition metals have hitherto remained scarce.[1] Using already known corrole derivatives as a synthetic precursor may lead to new synthetic approaches. Lithium corroles may be a promising doorway due to their reactive nature and extraordinary cluster forming abilities.[2] The poster will present ongoing research and results of our path to unknown frontiers of early transition metal corrole chemistry.

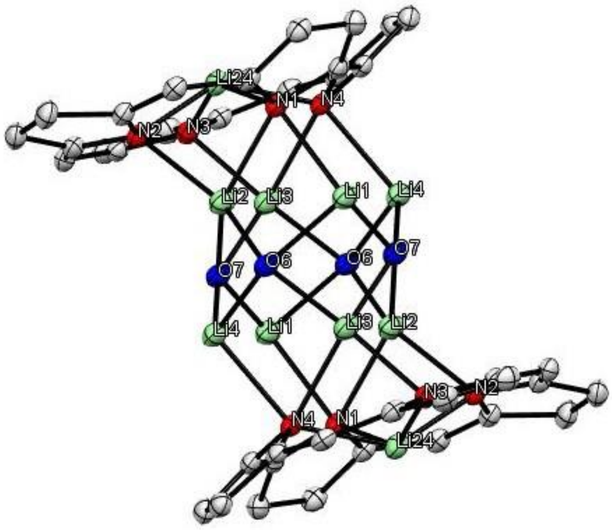

Figure 1 : Molecular structure of a Li corrole cluster obtained via X-ray diffraction. Substituents and solvent molecules where removed for better visibility.

REFERENCES

1. Barata, J.F., Neves, M. G. P., Faustino, M. A. F., Tomé, A. C., Cavaleiro, J. A. (2017). Strategies for Corrole functionalization. *Chem. Rev.,* 117(4), 3192-3253.
2. Buckley, H. L., Chomitz, W. A., Koszarna, B., Arnold, J. (2012). Synthesis of lithium corrole and its use as a reagent for the preparation of cyclopentadientyl zirconium and titanium corrol complexes. *Chem. Commun*., 48, 10766-10768.

Biological evaluation of peripherally crowded cationic phthalocyanines as photosensitizers for photodynamic therapy of tumours

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Phthalocyanines (Pc) are very promising second-generation photosensitizers (PS) for the eradication of solid tumours. These are synthetic macrocyclic dyes with optimal photophysical properties: strong absorption in the optical window of tissues (650-850 nm), high yields of singlet oxygen and very low inherent toxicity [1, 2]. In this study, novel peripherally crowded cationic Pcs containing 8 or 16 pyridyl moieties (neutral or quaternized) were synthesized and subsequently evaluated for photodynamic activity *in vitro* in cancer cell lines.

Cytotoxicity experiments were performed on several cell lines - malignant (HeLa, MCF-7) and non-malignant (3T3, EA.hy926), using neutral red uptake assay on 96-well plates. Both toxicity after irradiation (phototoxicity; EC_{50}) and toxicity in the absence of activating light (dark toxicity; TC_{50}) were assessed. Uptake of the PSs into the cancer cells was observed as an increase in fluorescence intensity of the dye in the cell lysate. Furthermore, subcellular localization was studied by the means of fluorescence microscopy. Mode of cell death was confirmed by real-time monitoring of Annexin V binding and the loss of cell membrane integrity.

The results of individual *in vitro* experiments have shown very high photodynamic activity after irradiation with EC_{50} up to 47 nM (MCF-7 cells) and exceptionally low inherent toxicity (in the dark) with TC_{50} > 600 000 nM. The Pcs were localized intracellularly, primarily in the endolysosomal compartment thus suggesting an endocytic mechanism of cellular uptake. Irradiation led to cell membrane rupture after activation of PSs and induced apoptosis with subsequent secondary necrosis.

This work has demonstrated that a bulky and rigid arrangement of peripheral cationic substituents is very efficient for providing high photodynamic activity in the development of novel PSs. This project is a part of extensive international project in which we studied the most active Pcs derivatives from renowned foreign scientific groups to assess their structure-activity relationship as a main outcome.

Acknowledgment: The work was supported from the project "Grant Schemes at CU" (reg. no. CZ.02.2.69/0.0/0.0/19_073/0016935), the Czech Science Foundation (19−14758Y) and Grant Agency of Charles University (1620219).

REFERENCES

1. Li, X., Zheng, B.-D., Peng, X.-H., Li, S.-Z., Ying, J.-W., Zhao, Y., Huang, J.-D., Yoon, J., Phthalocyanines as medicinal photosensitizers: Developments in the last five years. Coordination Chemistry Reviews 379, 2019, 147-160. https://doi.org/10.1016/j.ccr.2017.08.003
2. Liu, W., Jensen, T. J., Fronczek, F. R., Hammer, R. P., Smith, K. M., Grac, M., & Vicente, H., Synthesis and Cellular Studies of Nonaggregated Water-Soluble Phthalocyanines. Journal of Medicinal Chemistry. 48, 2005, Sv. 4, 1033–1041. http://doi.org/10.1021/jm049375b

Synthesis of Tetraaryl-Substituted 5,15-Dioxaporphyrin and its Oxidation to the Aromatic Dication

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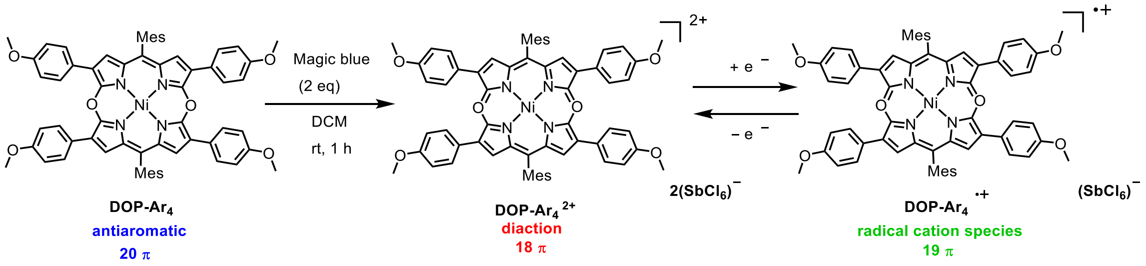
Heteroatom-containing porphyrin analogs have been attracting attention because of their unique optical and electrochemical properties. Among them, we have recently succeeded in the first synthesis of 5,15-dioxaporphyrin (DOP) by a nucleophilic aromatic substitution reaction of a nickel bis(α,α'-dibromodipyrrin) complex with benzaldoxime, followed by an intramolecular annulation of the α-hydroxy-substituted intermediate.[1] Owing to the introduction of the lone-pair electrons of oxygen atoms at *meso*-positions to the conjugated system of porphyrin, DOP exhibits 20π-antiaromatic characters. The electrochemistry of DOP in our previous work revealed a stepwise oxidation of the neutral 20π-antiaromatic state to the 19π-radical cation and further to the 18π-aromatic dication. However, due to the high reactivity at the β-pyrrolic positions of the 19π-radical cation species, chemical oxidation of DOP did not provide the 18π-aromatic dication species. Instead, a β,β-linked dimer was obtained. In this work, to prevent the dimerization reaction upon oxidation and isolated oxidized DOP species as stable forms, tetraaryl-substituted DOP (DOP-Ar_4) was synthesized and used for the chemical oxidation.

DOP-Ar_4 was synthesized by bromination of DOP and subsequent Suzuki-Miyaura coupling reactions. DOP-Ar_4 was oxidized with two molar equivalents of tris(4-bromophenyl)ammoniumyl hexachloroantimonate (Magic blue) in CH_2Cl_2 at room temperature for one hour to provide the dication species. The aromatic nature of the dication species was confirmed from the down-field shifts of the β-pyrrolic protons in the ^1H NMR spectrum. Finally, the structure was unambiguously elucidated by single crystal X-ray diffraction analysis. We also obtained the 19π radical cation species during the oxidation process. Their electronic structures were carefully investigated based on the UV/vis/NIR absorption spectra and theoretical calculations.

In this presentation, the synthesis of DOP-Ar_4 and its redox behaviors will be reported.



Scheme 1. Redox reactions of DOP-Ar_4

REFERENCES

1. A. Nishiyama, M. Fukuda, S. Mori, K. Furukawa, H. Fliegl, H. Furuta, S. Shimizu, *Angew. Chem. Int. Ed.* **2018**, *57*, 9728.

Synthesis and Characterization of Fluorinated Phthalocyanines as Hole Transporting Materials in Perovskite Solar Cells

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Perovskite solar cells (PSCs) are a good alternative to silicon cells thanks to their ease of preparation and low cost. Even more so now that they have achieved 25.7% efficiency.[1] However, to bring them to an industrial level, it is necessary to increase their stability and replace Spiro-OMeTAD with an economical and long-term stable hole-carrying material. Phthalocyanines (Pcs) are promising molecules for this role providing greater stability.[2,3]

In this communication, we will present the synthesis and characterization of novel ZnPcs (see Figure 1) as efficient, stable, and low cost HTMs in PSCs. The Pcs are substituted with p-methoxiphenylamino groups that possesses a very good solubility in a wide range of organic solvents, adequate HOMO LUMO levels and thus can be applied from solution processing in a wide range of perovskite solar cell devices. We will study how the number of substituents in the phthalocyanine ring, and the incorporation of a fluorine atom affect the photovoltaic properties of the PSCs.

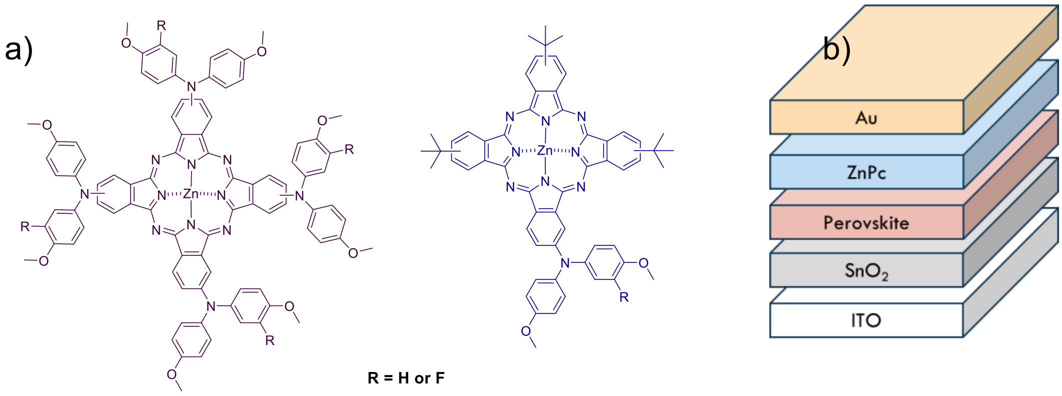

Figure 1. a) Different ZnPcs structures as HTMs in PSCs. b) Representation of a PSC device

REFERENCES

1. https://www.nrel.gov/pv/cell-efficiency.html, accessed: february 2022.
2. a) D. Molina, M. A. Ruiz-Preciado, F. Sadegh, M. João Álvaro-Martins, M. Grätzel, A. Hagfeldt, Á. Sastre-Santos*, J. Porphyr. Phthalocyanines*, **2019**, *23*, 546–553. d) D. Molina, M. A. Ruiz-Preciado, B. Carlsen, F. T. Eickemeyer, B. Yang, N. Flores-Díaz, M. J. Álvaro-Martins, K. Nonomura, A. Hagfeldt and Á. Sastre-Santos, *ChemPhotoChem*, **2020**, *4*, 307–314.
3. a) P. Huang, A. Hernández, S. Kazim, J. Ortíz, Á. Sastre-Santos, S. Ahmad *Sustainable Energy &Fuels.* **2020**, *4*, 6188-6195. b) P. Huang, A. Hernández, J. Follana-Berná, S. Kazim, J. Ortíz, Á. Sastre-Santos, S. Ahmad, *ACS Appl. Energy Mater.* **2021**, 4, *9*, 10124–10135.

Synthesis and strain-induced reactions of calix[3]pyrrole and related macrocycles

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Condensation reaction of pyrrole and carbonyl compounds under acidic conditions often lead to selective formation of tetrapyrrolic macrocycles such as porphyrin or calix[4]pyrrole. While ring-expanded analogues with five or more pyrroles are also synthesized by kinetic control, macrocycle with three pyrroles were never observed. The isolation and study of calix[3]pyrrole, a tripyrrolic macrocycle bearing three sp3-carbon linkage, might hold a key to explain the absence of tripyrrolic macrocycle. In this research, we have synthesized calix[3]pyrrole and discovered its strain-induced ring expansion reaction [1]. Besides, we have prepared core-modified analogues of calix[3]pyrrole and investigated the scope and reaction mechanism of the ring-expansion reaction [2].

Linear hexaketone 1 was converted into cyclic hexaketone 2 in 9% total yield over 5 steps, and Paal-Knorr pyrrole formation reaction of 2 gave calix[3]pyrrole 3 in 41% yield (Figure. 1a). Single crystal X-ray diffraction analysis and computational analysis indicated highly strained structure of 3 compared with other known calix[n]pyrroles (n = 4~6). This macrocyclic strain led to a rapid ring expansion reaction of 3 under acidic conditions to form calix[6]pyrrole 4 within 30 seconds (Figure. 1c). This rapid ring expansion reaction help to explain the absence of tripyrrolic macrocycles under classic oligopyrrole macrocycle synthesis.

Furthermore, calix[n]furan[3–n]pyrrole 5-7 (n = 1~3, Figure. 1b) were prepared in a similar manner to 3. Single crystal X-ray diffraction analysis and theoretical calculations suggested that the ring strain of 5-7 gets smaller as the number of inner NH sites decreases. When treated under acidic conditions, calix[1]furan[2]pyrrole 5 caused regioselective ring expansion reaction to give macrocycle 8 over 5 minutes while less strained analogues 6 and 7 was stable under the same conditions. The mechanism analysis revealed that the ring expansion reaction consists of regioselective ring cleavage and subsequent cyclodimerization. This unique reactivity of calix[3]-type macrocycles can facilitate efficient generation of new calix[6]-type macrocycles.

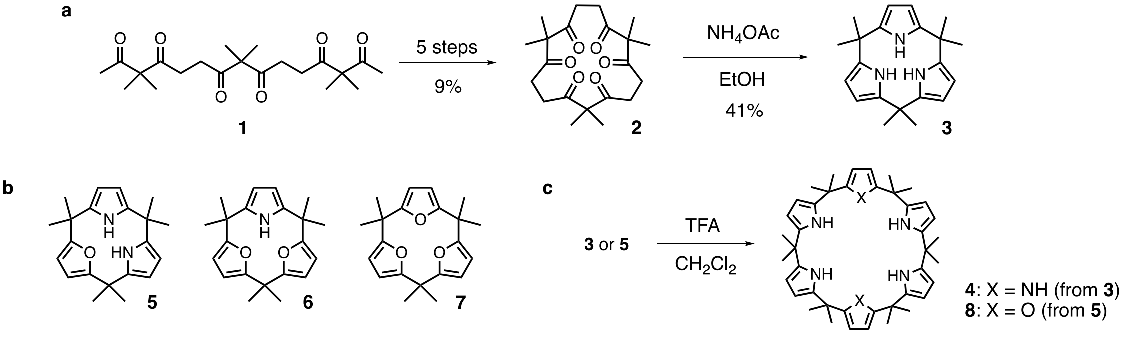

Figure 1. (a) Synthesis of calix[3]pyrrole **3**, (b) structures of **5-7**, and (c) ring expansion reaction of **3** and **5**.

REFERENCES

1. Y. Inaba, Y. Nomata, Y. Ide, J. Pirillo, Y. Hijikata, T. Yoneda, A. Osuka, J. L. Sessler, Y. Inokuma, *J. Am. Chem. Soc.* **2021**, *143*, 12355.
2. Y. Inaba, Y. Kakibayashi, Y. Ide, J. Pirillo, Y. Hijikata, T. Yoneda, Y. Inokuma, *Chem. Eur. J.* **2022**, *in press*.

Subphthalocyanines for Dye-Sensitized Solar Cells

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The low cost and easy fabrication processes, lightweight and flexible structure of dye-sensitized solar cells (DSSCs) make them promising alternatives to the conventional crystalline silicon solar cells. Among the many photosensitizers, porphyrinoid dyes (phthalocyanines, porphyrins) appear to be a good candidate because of their high chemical and optical stability and versatility. On the other hand, one of the main problems of these dyes is the planar aromatic structures leads to dye aggregation through the formation of π-π interaction between the cores, thus harming electron injection from the excited dye to the conduction band of the semiconductor. Subphthalocyanines (SubPcs) are nonplanar aromatic macrocycle, lower analogues of Pcs, constituted by three diiminoisoindole units N-fused around a central boron atom. SubPcs possess a peculiar conical structure, which provides them with relatively high solubility and a low tendency to aggregate.[2] SubPcs have recently received much attention as an effective light-harvesting material in the concept of artificial photosynthetic systems due to their strong absorption in the visible region (500–700 nm), chemical flexibility allowing modulating its electronic properties. SubPc derivatives have also been used as sensitizers in DSSCs, exhibited moderate power conversion efficiency of 1.3%.[3] The low power conversion efficiencies were attributed to the low-lying LUMO levels of SubPcs concerning that of the TiO_2 band edges.

In this study, a series of SubPc derivatives bearing electron-donating bulky peripheral substituents have been synthesized to tune their electronic and optical properties. The photovoltaic performance of novel SubPcs in DSSC devices will be tested.

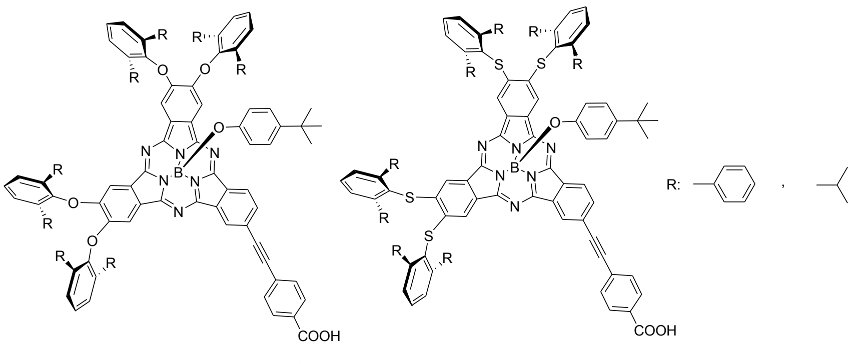

Figure 1. Molecular structure of SubPcs for DSSCs

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REFERENCES

1. A. Hagfeldt, G. Boschloo, L.Sun, L.Kloo, H.Pettersson, Chem. Rev., 2010, 110, 6595–6663.
2. C.G.Claessens, D. Gonzalez-Rodriguez, M.S. Rodríguez-Morgade, A. Medina, T. Torres, Chem Rev. 2014, 114,2192-277
3. M. Urbani, F. A. Sari, M. Grätzel, M. K. Nazeeruddin, T. Torres, M. Ince, *Chem. Asian J.* 2016, 11, 1223– 1231

Oxidation of cyclohexene by iron phthalocyanines: Effect of electron donating or electron withdrawing substituents

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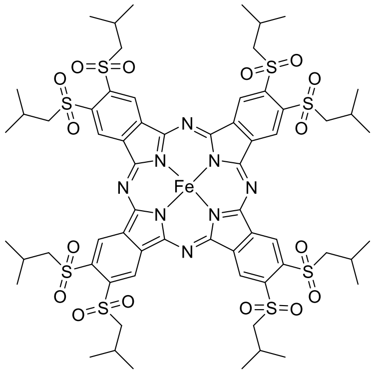
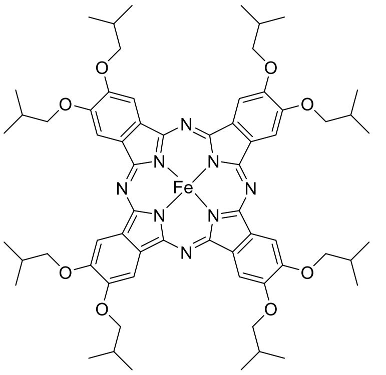
The catalytic oxidation of olefins is important for synthetic, industrial, and biological processes [1,2]. Phthalocyanines coordinating different metals such as iron, copper and manganese can oxidize olefins [3], such as a remarkably stable monomeric sulfonamide substituted iron phthalocyanine [4]. However, the effect of the macrocyclic substituents on oxidation reactions has not been deeply studied.

Two different iron phthalocyanines octa substituted either with electron-withdrawing isobutyl sulfonyl moieties or electron-donating isobutoxy moieties were prepared, characterized, and tested in oxidation of cyclohexene to evaluate substituents nature effect [5]. All results from oxidation reactions will be presented.





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REFERENCES

1. Y. Cao, H. Yu, H. Wang and F. Peng, *Catal. Commun.*, **2017**, *88*, 99-103.
2. T. Imahori, T. Tokuda, T. Taguchi and H. Takahata, *Org. Lett.*, **2012**, *14*, 1172-1175.
3. A. B. Sorokin, *Chem. Rev.* **2013**, *113*, 8152.
4. Ü. İşci, C. Caner, Y. Zorlu, A. G. Gürek, F. Dumoulin and V. Ahsen, *Dalton Trans.* **2014**, *43*, 17916.
5. C. Yüceel, Z. Şahin and Ü. İşçi. *J Porphyr Phthalocyanines*, 2022, https://doi.org/10.1142/S1088424621501285

Heteroleptic heterometallic μ-nitrido porphyrin-phthalocyanine complexes: Macrocycle vs metal variations on oxidation catalysis

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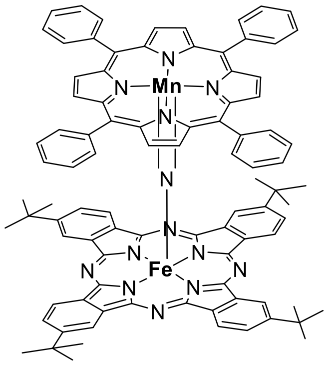
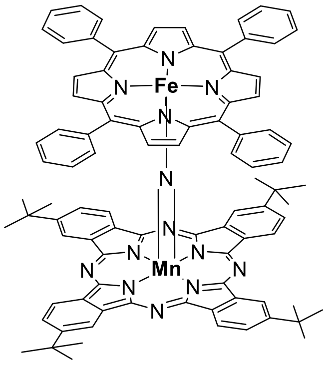
N-bridged μ-nitrido porphyrinoid complexes can act as powerful oxidation catalysts in various reactions such as the oxidation of methane, benzene, alkyl aromatics and olefins [1]. Different metals can also be used, mainly Fe and Mn. However, the importance of the role of the macrocycle vs the role of the metal has yet to be figured out, especially as we could demonstrate that minor structural variations can significantly affect their catalytic efficiency and other properties [2-5].

To this end, mixed heteroleptic and heterometallic μ-nitrido complexes involving one porphyrin and on phthalocyanine, metalated either with Mn or Fe, have been prepared and characterized by HRMS, MALDI-MS, UV-vis, FT-IR and EPR spectroscopies. Their catalytic activities will be compared in the light of their structural variations.





Acknowledgements: The Scientific and Technological Research Council of Turkey TUBITAK (project 217Z091) is gratefully acknowledged.

REFERENCES

1. A. B. Sorokin, *Chem. Rev.* **2013**, *113*, 8152.
2. Ü. İşci, P. Afanasiev, J.M.M. Millet, E.V. Kudrik, V. Ahsen, A.B. Sorokin, *Dalton Trans.* **2009**, 7410.
3. Ü. İşci, A. S. Faponle, P. Afanasiev, F. Albrieux, V. Briois, V. Ahsen, F. Dumoulin, A. B. Sorokin and S. P. de Visser, *Chem. Sci.* **2015**, *6*, 5063
4. Ü. İşci, F. Dumoulin, Vefa Ahsen, A. B. Sorokin, *J. Porphyrins Phthalocyanines* **2010**, *14*, 324
5. Ü. İşci, *J. Porphyrins Phthalocyanines* **2013**, *17*, 1022

Main group macrocyclic oligopyrrole complexes: outlook on synthesis and application

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The most 13, 14, 15 group elements form stable complexes with corrolles, porphyrins, phthalocyanines, and porphyrins in full agreement with the following requirements: 1) the metal cations should have an oxidation state corresponding to the low ionization potential and electronegativity sufficient for the cation to form covalent bonds; 2) correspondence of the inner coordination cavity bearing 4 nitrogen atoms to a metal cation dimension and its coordination polyhedron.

Few synthesis methodologies are used to form main group macrocyclic oligopyrrole complexes: the reaction of halides/acetates with free oligopyrrole bases; template assembly using nitrile (boron subphthalocyanines/subporphyrazines); treatment of tetrahalide by the corresponding dilithio complex (the tellurium porphyrin complexes); synthesis using an organometalic derivatives as $AlAlk_3$; axial modification of a ready-made main group porphyrin complex by a substitution or oxidative addition reaction. The structure of complexes varies from classic six/five coordinate with central atom in the mean porphyrin N_4 plane to never seen before as in the case of boron(III) or tellurium(IV) [1]. Unusual coordination geometries are the characteristic properties for porphyrin complexes of the period 6 main group elements. Therefore the preparation of main group oligopyrrole complexes can result in mixtures of various complexes which differ in the stoichiometry, a molecular structure, and the nature of axial ligands. The possibility of involving an aromatic macrocycle in the redox process during the synthesis of the complex is represented in our work by the examples of the indium and lead complexes [2].

The widest possibilities open up in the as yet little studied area of the chemistry of main group complexes with hemiporphyrazines, hemihexaphyrazine and others [3]. Taking into account the results in the theoretical and experimental studies of the deprotonated and anionic forms of these, the synthesis of their main group complexes is the achievement of the near future. Namely, the described in [4] trithiododecaazahexaphyrin forms lithium complexes which can be considered as precursors for main group ones.

The outlook on recent achievements in synthesis and application of the main-group polypyrrole complexes are represented.

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REFERENCES

1. P.J. Brothers. *J. Porphyrins Phthalocyanines* 2002; 6: 259-267.
2. T.N. Lomova. *Appl. Organomet. Chem*. 2021; e6254.
3. A.A. Otlyotov, Y.A. Zhabanov, A.E. Pogonin, A.S. Kuznetsova, M.K. Islyaikin, G.V. Girichev. *J. Mol. Struct.* 2019; 1184: 576e582.
4. D.I. Nazarov, S.S. Khasanov, I.A. Rompanen, E.N. Ivanov, O.I. Koifman, M.K. Islyaikin, D.V. Konarev. *Polyhedron* 2021; 202: 115198.

Synthesis and Redox Properties of Ag(III) and Ni(II) Complexes of Triply Fused N-Confused Porphyrin Dimers

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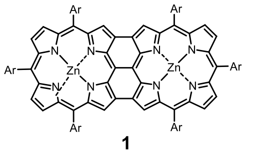
Fused porphyrin analogs (e.g., triply fused porphyrin dimer, **1**) have paid much attention due to the small HOMO-LUMO gap, rich redox features, and near-infrared nonlinear optical responses caused by highly perturbed electronic structures.[1] On the other hand, N-confusion modification of the porphyrin skeletons is an effective approach to modulating the distinct π-conjugated circuit and coordination capability at the inner NNNC cores of the typical porphyrins. In this regard, *meso-α* doubly fused N-confused porphyrin (NCP) dimer **2** was recently synthesized via metalation-coupled fusion reaction of the tetrabromo-substituted [36]octaphyrin.[2] Herein, we report the straightforward access to the genuine *α-α*', *meso-meso*', *β-β*' triply fused N-confused porphyrin tape (**3**) via the stepwise oxidative dimerization of 5-unsubstituted N-confused porphyrin.

Reflecting the NH tautomeric feature (2H vs. 3H forms in the core) of the N-confused porphyrins, coordination of silver(III) and nickel(II) ions of the triply fused NCP tape **3** yielded the corresponding bis-metal complexes, **Ag$_2$-3** and **Ni$_2$-3**, respectively. Exclusively, a local paratropic ring-current was realized on the benzo[*e*]pyrrolo[3,2-*g*]indole moiety in **Ag$_2$-3**. In contrast, a strong paratropic ring current emerged in **Ni$_2$-3** along with the distinct global Hückel antiaromaticity as inferred from the NMR spectroscopy and the DFT calculations. Corresponding reduced species (**rAg$_2$-3**) and oxidized species (**oNi$_2$-3**) will also be discussed in the presentation.



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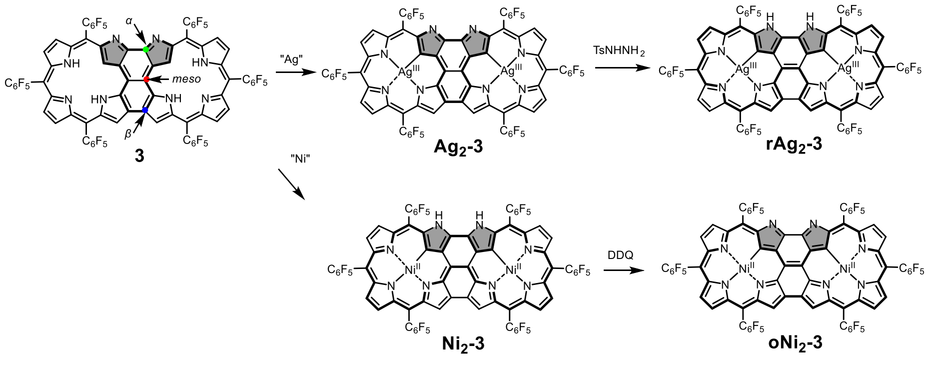
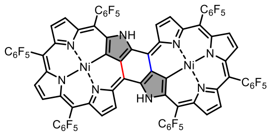
(Ar = 3,5-di-^{t}BuPh, C$_6$F$_5$)





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REFERENCES

1. A. Tsuda, H. Furuta and A. Osuka, *J. Am. Chem. Soc.* **2001**, *123,* 10304–10321; H. Mori, T. Tanaka, N. Aratani, B. S. Lee, P. Kim, D. Kim and A. Osuka, *Chem. Asian J.* **2012**, *7*, 1811–1816.
2. A. Nakai, J. Kim, T. Tanaka, D. Kim and A. Osuka, *Angew. Chem. Int. Ed.* **2021**, *60*, 26540–26544.

A photoimmunoconjugate for the treatment of breast cancer

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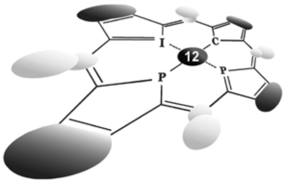
Finding biomarkers that allow the detection of neoplasms by illuminating them in real time in the operating room and combining it with photodynamic therapy (PDT) can be an advantage for the successful resection of the tumour. In this study, we chemically conjugated a water-soluble phthalocyanine with a monoclonal antibody to assess the selectivity for a cancer cell type. Photoimmunotherapy combine the antibody selectivity and the PDT properties of the photosensitiser. [1, 2, 3, 4]

One photoimmunoconjugate is presented, the antibody employed is Trastuzumab which has selectivity for HER-2 receptor and the moiety is IRDye® 700DX NHS. The *in vitro* assays were performed on two tumoral cells: BT-474 as a positive control and HeLa as a negative control. The biological *in vitro* assays show that this conjugate is able to photoinactivate cancerous mammalian cells that presents the receptor HER-2 at sub-micromolar concentrations. Furthermore, it is possible to differentiate the targeted cells by means of using a real-time fluorescence guided device adapted for this photoimmunoconjugate. *In vivo* studies are currently underway.

REFERENCES

1. Zhang, R. R.; Schroeder, A. B.; Grudzinski, J. J.; Rosenthal, E. L.; Warram, J. M.; Pinchuk, A. N.; Eliceri, K. W.; Kuo, J. S.; Weichert, J. P. Beyond the Margins: Real-Time Detection of Cancer Using Targeted Fluorophores. *Nat. Rev. Clin. Oncol.* 2017, 14 (6), 347–364.
2. Rosenthal, E. L.; Warram, J. M.; Boer, E. De; Basilion, J. P.; Biel, M. A.; Bogyo, M.; Bouvet, M.; Brigman, B. E.; Colson, Y. L.; DeMeester, S. R.; Gurtner, G. C.; Ishizawa, T.; Jacobs, P. M.; Keereweer, S.; Liao, J. C.; Nguyen, Q. T.; Olson, J.; Paulsen, K. D.; Rieves, D.; Sumer, B. D.; Tweedle, M. F.; Vahrmeijer, A. L.; Weichert, J. P.; Wilsopn, B. C.; Zenn, M. R.; Zinn, K. R.; van Dam, G. M. Successful Translation of Fluorescence Navigation During Oncologic Surgery: A Consensus Report. *J. Nucl. Med.* 2016, 57 (1), 144–150.
3. Photodynamic Medicine: From bench to clinic, edited by Herwig Kostron and Tayyaba Hasan, *The Royal Society of Chemistry, London,* 2016
4. Mitsunaga, M.; Ogawa, M.; Kosaka, N.; Rosenblum, L. T.; Choyke, P. L.; Kobayashi, H. Cancer Cell-Selective in Vivo near Infrared Photoimmunotherapy Targeting Specific Membrane Molecules. *Nat. Med.* 2011, 17 (12).



Towards self-assembling cationic phthalocyanines - synthetic strategies, challenges and progresses

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The self-assembly of amphiphilic molecules is governed by their amphiphilic balance and their overall shape, as well as microseggregation [1-2]. The porphysome nanotechnology developed by the Gang Zang group is a thrilling example of the self-assembly of amphiphilic porphyrins [3].

Our efforts to prepare amphiphilic phthalocyanines likely to form self-assembled supramolecular nanostructures will be presented, with the exploration of synthetic feasibility of two targeted phthalocyanines with either one or two alkyl chains, and one cationic function.

The Scientific and Technological Research Council of Turkey (TUBITAK) and the French Embassy in Turkey are gratefully acknowledged for the bilateral project Bosphorus 119R052 / 44754NA between Turkey and France.

REFERENCES

1. C. Tschierske, *J. Mater. Chem.,* 2001, 11, 2647-2671
2. F. Dumoulin, D. Lafont, T.-L. Huynh, P. Boullanger, G. Mackenzie, J. J. West, and John W. Goodby, *Chem. Eur. J.*, 2007, 13, 5585-5600.
3. J. F. Lovell, Ch. S. Jin, E. Huynh, H. Jin, C. Kim, J. L. Rubinstein, W. C. W. Chan, W. Cao, L. V. Wang & G.Zheng, *Nature Materials*, 2011, 10, 324-332

Supramolecular assembly of porphyrin derivatives having multiple ion binding sites

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Porphyrin derivatives are essential pigments in biological system. Owing to the versatile functionality of the porphyrin derivatives, various porphyrin-based functional materials have been designed. Recently, we have designed a triazole bearing strapped calix[4]pyrrole(1) which applied to selective extraction of lithium salts under an organic solvent condition. The bindings of LiCl and LiBr to 1 were confirmed by 1H NMR spectral studies, and a binding mode of LiCl⊂1, coordination with a triazole and water-assisted bridge, is confirmed by a single crystal X-ray crystallography and theoretical calculation. Furthermore, these lithium salts were successfully extracted to the organic solvent using 1 through liquid-liquid extraction and solid-liquid extraction. And then, lithium salts extracted by 1 could be isolated as the form of Li_2CO_3. In this symposium, we are going to report research on the porphyrin-based supramolecular architectures. A series of porphyrin derivatives having multiple ion-binding sites was prepared to build up supramolecular architecture through intermolecular hydrogen bonding. The details will be presented in the symposium.

REFERENCES

1. Hong, K. –I.; Kim, H.; Kim, Y. ; Choi, M. -G.; Jang, W. –D. Strapped calix[4]pyrrole as a lithium salts selective receptor through separated ion-pair binding. *Chem. Commun*. **2020**, *56*, 10541-10544.

Synthesis of Phthalocyanines for Supramolecular Interaction with Cucurbituril and Studying Their Properties

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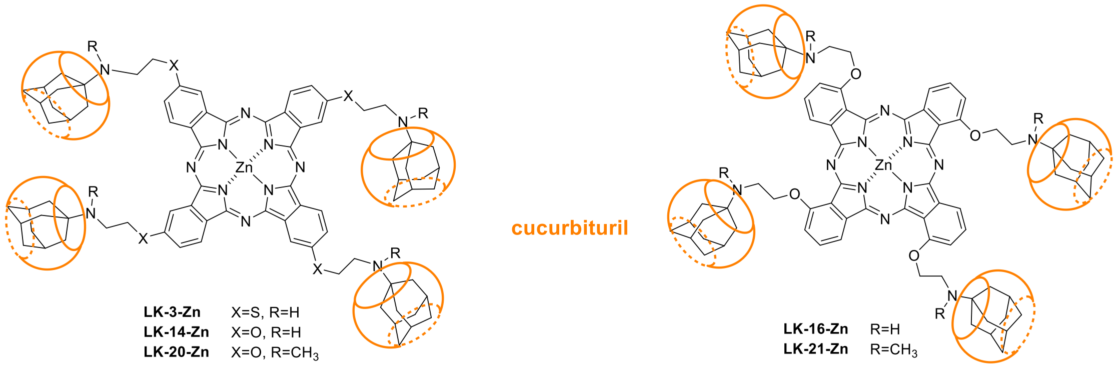
Phthalocyanines (Pcs) are macrocyclic compounds structurally related to porphyrins, which are used also as photosensitizers in photodynamic therapy. Because of their planar structure they form aggregates in water environment and therefore lose their desired photodynamic activity. Based on formation of a supramolecular complex with cucurbiturils (CBs), we can potentially improve solubility and decrease aggregation of Pcs in water. CBs are macromolecules composed of methylene bridged glycoluril monomers [1] with hydrophobic cavity and hydrophilic portals where they can bind appropriate guest molecules. In this project, we used one of the strongest reported supramolecular interactions between CB[7] and 1-aminoadamantane [2] as substituent on the Pc ring.
Seven zinc Pcs, peripherally or non-peripherally substituted with 1-aminoadamantane, were prepared. Their absorption spectra showed substantially improved (but not complete) monomerization in water after addition of four equivalents of CB[7]. This shows binding of one molecule of CB[7] with one molecule of 1-aminoadamantane which was also confirmed by NMR titration of phthalonitrile precursor and CB[7] complex formation. Higher quantum yields of fluorescence in water were also achieved after addition of four equivalents of CB[7]. Biological tests on HeLa cells did not show higher photodynamic activity of Pc-CB[7] complex even though higher monomerization should also result in higher activity. It was due to lower cell uptake of Pc-CB[7] complex.



LK-3-Zn X=S, R=H
LK-14-Zn X=O, R=H
LK-20-Zn X=O, R=CH_3

LK-16-Zn R=H
LK-21-Zn R=CH_3

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REFERENCES

1. Wiemann, M.; Jonkheijm, P. *Isr. J. Chem.* 58 (3-4), 2018, 314-325.
2. LIU, S. et al. *J. Am. Chem. Soc.* 127, 2005, 15959-15967.

Synthesis of unsymmetrical phthalocyanines for photoinduced drug release

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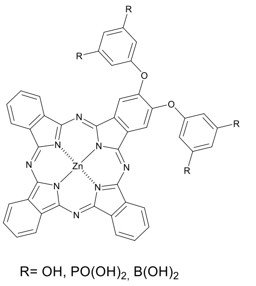
Phthalocyanines (Pcs) are group of organic dyes with promising photophysical properties (strong absorption in area over 600 nm and strong singlet oxygen production). Due to these properties, they can be used as photosensitizers (PSs) in photodynamic therapy (PDT).

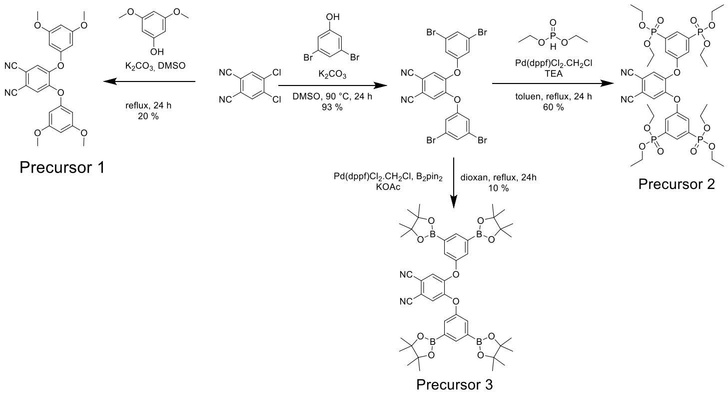
The aim of this project was to synthesize novel unsymmetrical Pcs with boronic acid, phosphonic acid and free hydroxy groups on the periphery. Due to their amphiphilic character, these Pcs can be incorporated into phospholipid bilayer of liposomes, which can serve as delivery systems carrying some cargo inside (e.g., hydrophilic anticancer drug). Upon light activation, the Pc releases reactive singlet oxygen that destroys liposomal membrane and releases cargo only in the irradiated area. The use of PS anchored in liposomes carrying antineoplastic drugs may thus cause double punch in the tumour tissue, since it allows combining of the benefits of targeted chemotherapy of the released drug and PDT caused by production of singlet oxygen.

Precursor 1 was obtained by nucleophilic substitution of 4,5-dichlorophthalonitrile by 3,5-dimethoxyphenol. Starting compound of precursors 2 and 3 was 4,5-bis(3,5-dibromophenoxy)phthalonitrile that was prepared by nucleophilic substitution of 4,5-dichlorophtalonitrile with 3,5-dibromophenol. 4,5-Disubstitued phthalonitrile was converted to precursor 2 by palladium-catalyzed cross coupling reaction with diethylphosphite. The phthalonitrile precursor 3 was obtained by Miyaura borylation.

Further work will be focused on synthesis of unsymmetrical magnesium complexes of Pcs by statistical condensation of phthalonitrile with 4,5-disubstituted precursor with magnesium butoxide as initiator. The reaction leads to the mixture of six different congeners. A required congener will be isolated and converted to zinc complex that has more favourable photophysical properties. After final deprotection of protective groups, three final amphiphilic Pcs should be obtained. These compounds will be further tested *in vitro* for their own photodynamic activity as well as the activity in the combination with hydrophilic drug incorporated in liposomal matrix.



R= OH, $PO(OH)_2$, $B(OH)_2$



Acknowledgement: This work was supported by Czech Science Foundation, grant. No. 20-09212S and SVV 260 547.

The influence of a solvent and a delivery system on a dissociation of the central metal of magnesium phthalocyanines and tetrapyrazinoporphyrazines in acidic media

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Magnesium complexes of phthalocyanines (Pc) and tetrapyrazinoporphyrazines (TPyzPz) are widely examined for their ability of strong photon emission. Magnesium as the lightest central cation stable in the macrocycle explains the strong fluorescence of such complexes. [1] On the other hand, the instability of magnesium complexes in acidic environment (demetallation to metal-free ligands) decreases the various usage of these fluorescent dyes and may influence their *in vitro* as well as *in vivo* testing. This project evaluated more closely the demetallation process of these compounds at various pH and considered possible protection. Pcs and corresponding TPyzPzs substituted with alkylsulfanylperipheral substitution were involved in the study (Fig. 1e). The progress of the reaction was monitored by absorption spectroscopy where characteristic splitting of the Q-band occurs after demetallation. Water-soluble compounds were tested in buffers at five different pH ranging 1 – 7.4 for 24 h or less. Lipophilic derivatives were examined in anhydrous benzene by titration with differently strong acids and subsequently in time-dependent study for 24 h. A mechanism of demetallation was confirmed in organic solvent as well as in water. The mechanism of demetallation in organic solvent was proved as acidoprotolytic, in water on the other hand as solvoprotolytic. [2] Moreover, lipophilic compounds were incorporated into two delivery systems (liposomes and microemulsions) to test their protection ability. Interestingly, the use of liposomes as a delivery system resulted in high level of protection where no changes in absorption spectra of TPyzPz were detected even after 24 h at tpH=1. Moreover, magnesium complexes of TPyzPzs were more stable than corresponding Pcs, either free molecules in solvent or incorporated in both delivery systems.

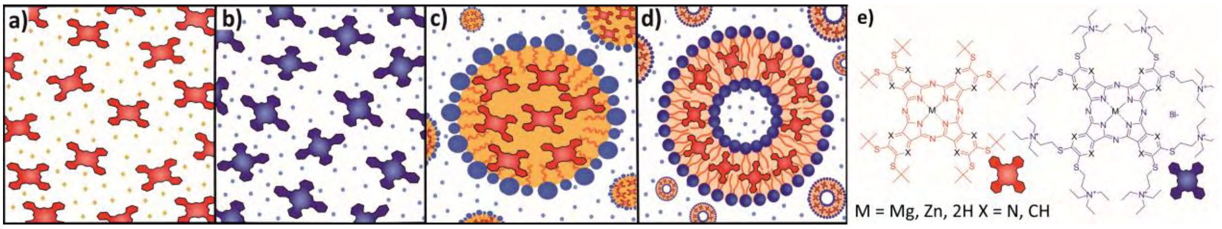

Figure 1. Studied systems a) Organic solvent b) Water c) Microemulsion d) Liposome e) Structures of Pcs and TPyzPzs

REFERENCES

1. Novakova, V., Donzello, M. P., Ercolani, C., Zimcik, P., Stuzhin, P. A. Coord. Chem. Rev., 2018, 361, 1-73.
2. Berezin, B. D., Shukhto, O.V., Berezin, D.B. A new type of metal porphyrin dissociation reaction. Russ. J. Inorg. Chem. 2002, 47, 1763-1768.

Porphyrin-Based (Chir)Optical Sensing of Amino-Functionalized Thiourea Organocatalysts

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Metalloporphyrins can act as Lewis acids capable for strong axial binding of Lewis base-type ligands, e.g., amines. Due to the axial binding properties and unique spectral characteristics, porphyrins are widely used as chemical sensors [1]. Takemoto's catalyst [2] (**1a**, Figure 1) and similar amino-functionalized thioureas are widely used chiral organocatalysts. Environmental pollution with chiral organic compounds is an emerging problem which is requiring innovative sensing methods. Environmental safety data and detection methods are currently absent for **1**.

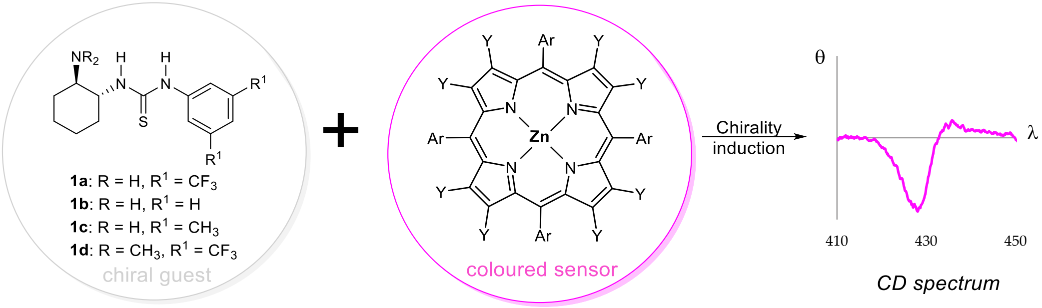

Figure 1. Amino-functionalized thiourea organocatalysts studied as model pollutants (left) and an example CD signal they induce in zinc porphyrins (right).

Our ecotoxicology studies with Vibrio fischeri bacteria revealed ecotoxic properties for 1a and 1d. To develop a detection method for these chiral pollutants, a range of zinc porphyrins were tested as plausible chemical sensors [3, 4]. In nearly all cases axial ligation of guests 1 to porphyrin hosts resulted in induction of system-specific (chir)optical signals. In total, 24 host-guest complexes have been characterized with UV-Vis and CD spectroscopies. Additional single crystal X-ray diffraction analysis and computational studies were performed for the selected complexes to characterise the geometries of the complexes.

REFERENCES

1. Paolesse, R.; *et al. Chem. Rev.* **2017**, 117, 2517-2583.
2. Okino, T.; *et al. J. Am. Chem. Soc.* **2003**, 125, 12672–12673.
3. Konrad, N.; *et al. J. Porphyr. Phthalocyanines* **2019**, 24, 840–849.
4. Konrad, N.; *et al. Chemosensors* **2021**, 9, 278.

Polypeptide oligomers comprised of corroles – hydrogen bonding provides "short-circuit" coupling pathways for electron transfer

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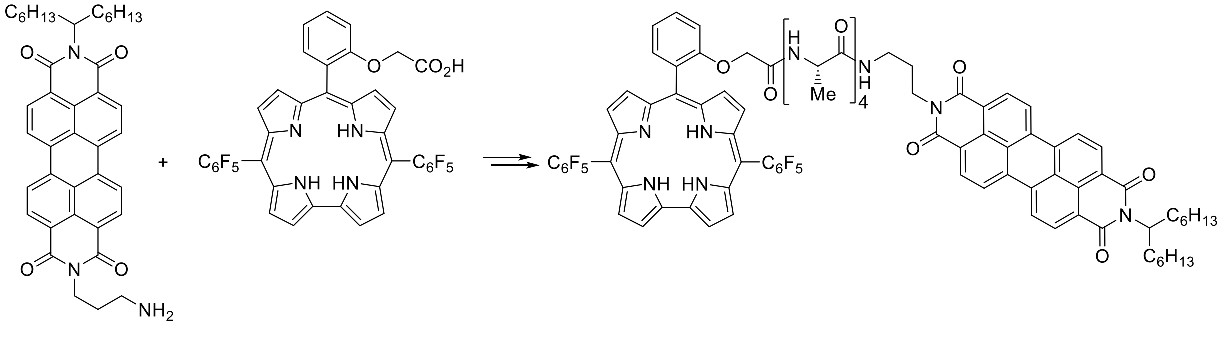
Electron flow through proteins is a crucial factor, which decides about their multiple functions in living organisms. Incorporating polypeptides as bridges in donor-bridge-acceptor (DBA) conjugates allows for examining how various structural features in proteins affect the kinetics of the CT processes they mediate. Based on the premise that hydrogen-bonds formation could serve to modify geometry and special orientation of donor and acceptor scaffolds in covalently linked bichromophoric system we designed and synthesized series of dyads comprised of perylene-bisimide and free-base corrole. Specifically, the object of the study was hydrogen-bonded discrete assemblies of corroles possessing core-NH as hydrogen bond donor and amide groups located at position *meso*-10 as hydrogen bond acceptor [1,2]. The three dyads differ in type and number of bridging aminoacids' moieties: *L*-alanine and *L*-phenylalanine and one or four respectively. These complex corroles were prepared *via* synthesis of perylenebisimide-amino acid conjugate possessing free NH_2 group followed by amidation of COOH-corrole. Combined steady-state and time-resolved photophysical studies identified that electron-transfer occurs in all four bichromophoric systems. Our focus was on alanine tetramer that is long enough not to mediate too efficiently through-bond CT. A corrole moiety serves as an electron donor, and a perylenediimide as an acceptor. The picosecond rates of electron transfer suggests that the electronic-coupling pathways cannot be through-bond and most likely involve through-hydrogen bond interaction.



REFERENCES

1. Orłowski, R.; Vakuliuk, O.; Gullo, M. P.; Danylyuk, O.; Ventura, B.; Koszarna, B.; Tarnowska, A.; Jaworska, N.; Barbieri, A.; Gryko, D. T. *Chem. Commun.* **2015**, *51*, 8284-8287.
2. Orłowski, R.; Cichowicz, G.; Staszewska-Krajewska, O.; Schilf, W.; Cyrański, M. K.; Gryko, D. T. *Chem. Eur. J.* **2019**, *25*, 9658-9664.

Photodynamic therapy with water-soluble phthalocyanines and their efficacy against 3D tumor multicellular spheroids

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Nowadays, cancer is one of the most common fatal diseases, so it is desirable to improve treatment methods. Photodynamic therapy is non-invasive form of cancer treatment. This non-invasive method is based on the combination of three elements – photosensitizer (PS), light and molecular oxygen. PS is a non-toxic molecule which absorb the light of a specific wavelength and initiates the formation of reactive oxygen species that cause cell death.[1,2] This study is mainly focused on the research of novel PSs, which should provide better efficacy against tumours and lower toxicity to non-malignant tissue.[2] Phthalocyanines studied in our work belong to the group of modern promising PSs. In the commonly used and somewhat "standard" 2D cultures, cells grow in monolayer and inadequately reflect the complexity of *in vivo* environment. Three-dimensional (3D) cultures should help better mimic tumour microenvironment, cell-cell and cell-matrix interactions.[3,4] 3D tumour spheroids derived from MCF 7, CT-26 or HeLa cell lines were generated by an ultra-low adhesion plates. The photodynamic activity of original amphiphilic and hydrophilic (aza)phthalocyanine PSs (cationic and anionic) was determined on 3D tumour multicellular spheroids by two separate methods – fluorescence measurement of resorufin formation and luminescence measurement of ATP. We have also studied the invasive behaviour of spheroids after PDT with the studied compounds. The distribution of PSs in spheroids was evaluated by confocal microscopy after cryomicrosectioning. The amphiphilic cationic PS provided highest phototoxicity against all cell lines. Invasive potential to extracellular matrix was detected only for spheroids derived from CT-26 cell line. Invasive behaviour of these spheroids exposed to all PSs has been reduced after irradiation, nevertheless, for cationic (aza)phthalocyanines more than for anionic. Despite the fact, that invasive behaviour has been reduced, viability of spheroids could not be completely reduced after irradiation. The work was supported by Charles University PRIMUS/20/SCI/013 and “Grant Schemes at CU” (CZ.02.2.69/0.0/0.0/19_073/0016935).

REFERENCES

1. Białkowska, K., Komorowski, P., Bryszewska, M., & Miłowska, K. (2020). Spheroids as a type of three-dimensional cell cultures—examples of methods of preparation and the most important application. *International Journal of Molecular Sciences*, 21(17), 1–17. https://doi.org/10.3390/ijms21176225
2. Pereira, P. M. R., Berisha, N., Bhupathiraju, N. V. S. D. K., Fernandes, R., Tomé, J. P. C., & Drain, C. M. (2017). Cancer cell spheroids are a better screen for the photodynamic efficiency of glycosylated photosensitizers. *PLoS ONE*, 12(5), 1–21. https://doi.org/10.1371/journal.pone.0177737
3. Roguin, L. P., Chiarante, N., García Vior, M. C., & Marino, J. (2019). Zinc(II) phthalocyanines as photosensitizers for antitumor photodynamic therapy. *International Journal of Biochemistry and Cell Biology*, 114(May), 105575. https://doi.org/10.1016/j.biocel.2019.105575
4. Shen, H., Cai, S., Wu, C., Yang, W., Yu, H., & Liu, L. (2021). Recent advances in three-dimensional multicellular spheroid culture and future development. *Micromachines*, 12(1), 1–21. https://doi.org/10.3390/mi12010096

PorphyStruct – Structural Analysis of Porphyrinoids

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While the non-planar displacements of porphyrins and their consequences on both chemical and physical properties were investigated using the NSD method of J. A. Shelnutt and its reimplementation by C. J. Kingsbury and M. O. Senge, such a method did not exist for other porphyrinoids, like corroles, for a long time. [1]
PorphyStruct is a digital tool for the quantitative analysis of out-of-plane distortion modes for a variety of porphyrinoids. [2] An analysis of the vibrational normal modes obtained by DFT calculations showed that the established non-planar vibrational modes of porphyrins - Doming, Saddling, Ruffling, Waving (X, Y) and Propellering, are also observable in the less symmetric porphyrinoids. These are used describe and quantify the conformations of corroles and other macrocycles. As in the NSD method, the minimal basis is formed from the first set of the 6 vibrational modes - the extended basis includes another set of the 6 vibrational modes.

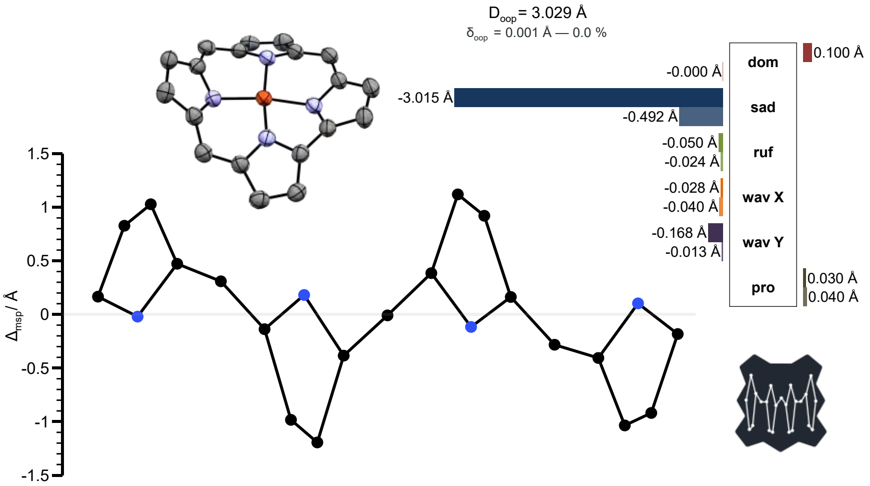

Figure 1 : « *Supersaddling* » in Copper Corrole *OVEVAN* (CCDC 815952)[3]. Substituents omitted for clarity.

An examination of already published corroles showed a peculiarity in copper corroles - they can only be described with the extended basis and show a substantial amount of both saddling variants – we called this phenomenon "*Supersaddling*".

REFERENCES

1. a) W. Jentzen, J.-G. Ma, J. A. Shelnutt, *Biophys. J.,* **1998**, *74*, 753–763; b) W. Jentzen, X.-Z. Song, J. A. Shelnutt, *J. Phys. Chem. B,* **1997**, *101*, 1684–1699; c) C. J. Kingsbury, M. O. Senge, Coord. *Chem. Rev*., **2021**, *431*, Article 213760.
2. J. Krumsieck, M. Bröring, *Chem. Eur. J.*, **2021**, *27*, 11580-11588.
3. K. E.Thomas, J. Conradie, L. K. Hansen, A. Ghosh, *Eur. J. Inorg. Chem*., **2011**, *2011*, 1865-1870.
4. Download & Sourcecode: https://github.com/JensKrumsieck/PorphyStruct

Metalloisoporphyrins

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Isoporphyrins represent a tautomeric form of porphyrins where one NH proton shifts to a *meso* position, resulting in the break-up of the macrocyclic π conjugation. Isoporphyrins feature intense Q bands in the NIR region between 700 and 1000 nm (Fig. 1) and act as a monoanionic ligand after deprotonation.

Isoporphyrins and phlorins, which themselves exhibit tautomerism to porphodimethenes, are formally separated by a $2e^-/2H^+$ redox step (Fig. 1). An electrochemical gateway to the isoporphyrin/phlorin redox step has been proposed in [1].

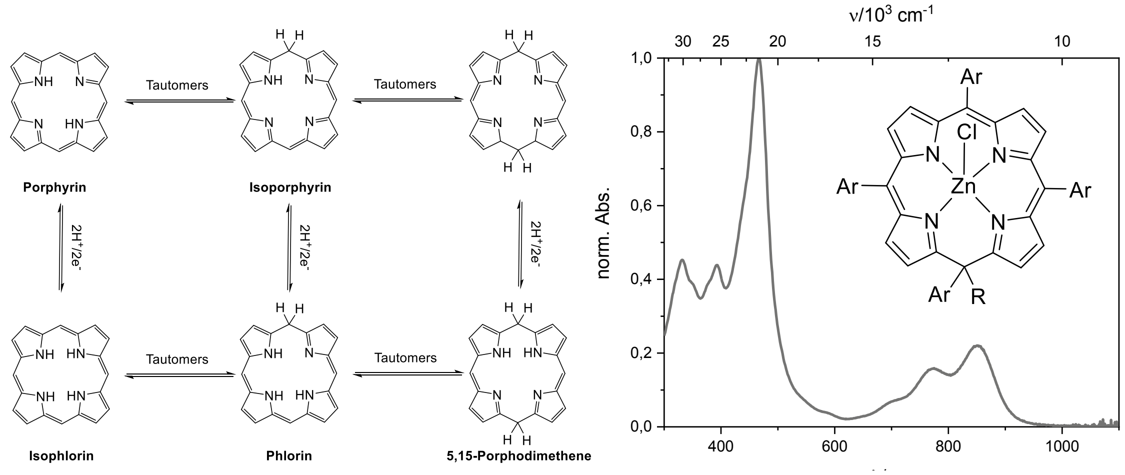

Figure 1 : Isoporphyrin and its relatives (left) – UV/Vis Spectrum of a zinc-isoporphyrin complex (right)

Zinc- and Cadmium-meso-Aryl-Isoporphyrins carrying a pyrrolyl or dipyrrinyl residue can be obtained by a two-step one-pot procedure using pyrrole and aromatic aldehydes [1,2]. Complexes from other metal ions can be obtained from these zinc or cadmium complexes and will be presented on the poster.

REFERENCES

1. Ç. Baş, J. Krumsieck, W.-D. Möller, D. Körner, M. Bröring, *Chem. Eur. J.*, **2021**, *27*, 8021 – 8029.
2. P. Schweyen, M. Hoffmann, J. Krumsieck, B. Wolfram, X. Xie, M. Bröring, *Angew. Chem. Int. Ed.*, **2016**, *55*, 10118-10121.

Synthesis of the parent corrole and catalytic applications of the corresponding metal complexes

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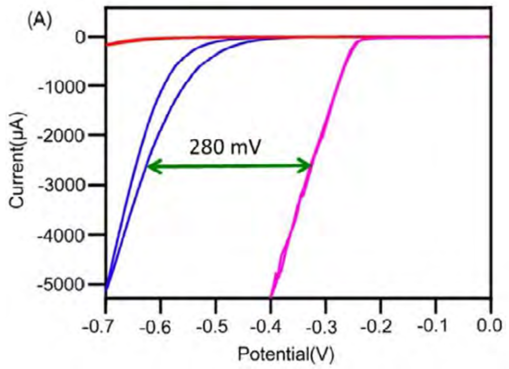
Corrole chemistry has constantly gained popularity amid its stable and easily accessible derivatives. In particular, the metal complexes of these macrocycles has been proved beneficial for mankind due to their drug carrying efficiency and catalytic properties for several sustainable energy processes. Despite so many applications, the puckered structure of this macrocycle has sometimes been a setback as it does not allow full elucidation of many fundamental properties of corroles. With this in mind,0 we now report the substituent-free corrole following conceptually different reaction pathways. Five metal complexes of this novel corrole were also synthesized and characterized. The molybdenum complexes, including that of the parent corrole, were utilized for exploring their catalytic properties for the hydrogen evolution reaction.



REFERENCES

1. A. Kumar, P. Yadav, M. Majdoub, I. Saltsman, N. Fridman, S. Kumar, A. Kumar, A. Mahammed, Z. Gross, *Angew. Chemie* **2021**, *133*, 25301–25307.

Strong Two-photon Absorption and Ultrafast Dynamics in *Meso*-Functionalized "Push-Pull" *Trans*-A_2BC Porphyrins

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Porphyrins and their analogues possess high thermochemical stability, aromatic delocalized π-system, and small HOMO-LUMO gap which are essential to have good NLO response and utilized in the various potential technological applications as optoelectronic devices for telecommunication devices for telecommunications, information storage, optical switching, signal processing, and light frequency converter [1]. Herein, we report two new series of *trans*-A_2BC "Push-Pull" type porphyrins having mesityl groups, the phenothiazine moiety (electron donor) and nitrophenyl moiety (electron acceptor) on *meso*-position (Figure 1). These *trans*-A_2BC "Push-Pull" porphyrins with a strong dipole moment have been prepared *via* [2+2] MacDonald method and their metallation by Zn(II), Cu(II) and Ni(II) find possible use in photonic and two-photon imaging applications. These *trans*-A_2BC porphyrins were characterized by UV-vis, fluorescence, and NMR spectroscopic techniques and, mass spectrometry, cyclic voltammetry, single-crystal X-ray diffraction analysis, and DFT studies.

The synthesized *trans*-MA_2BC porphyrins (M = 2H, Zn(II), Cu(II) and Ni(II)) exhibited marginal redshift in their electronic spectra as compared to corresponding MTPPs. In cyclic voltammetry, these *trans*-A_2BC porphyrins have shown cathodic shift for first oxidation potential and anodically shifted for the first reduction potential as compared to MTPPs possibly due to destabilization of HOMOs in the case of *trans*-A_2BC porphyrins. These porphyrins adopt planar conformation of macrocyclic core revealed by single crystal X-ray analysis. Femtosecond nonlinear optical (NLO) studies performed with kHz pulses at 800 nm revealed strong two-photon absorption coefficients and cross-sections for these push-pull porphyrins.

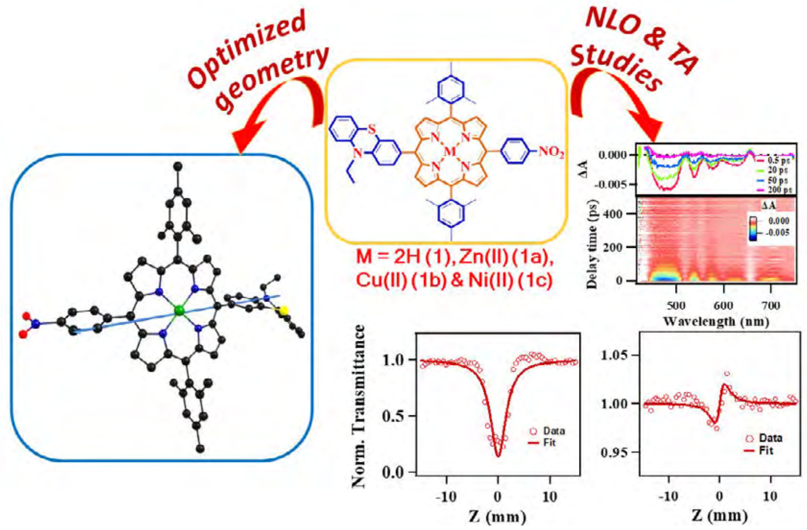
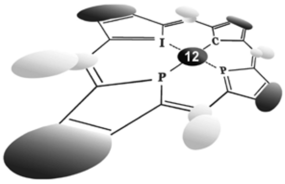


Figure 1. The molecular structure and optimized geometry of *trans*-A_2BC "Push-Pull" porphyrins and its non-linear optics (NLOs) and transient absorption (TA) studies.

REFERENCES

1. (a) Kumar, S.; Acharyya, J. N.; Banerjee, D.; Soma, V. R.; Prakash, G. V.; Sankar, M. *Dalton Trans.* **2021**, *50*, 6256-6272. (b) Rohal, R. K.; Acharyya, J. N.; Shanu, M.; Prakash, G. V.; Sankar, M. *Inorg. Chem.* **2022**, *61*, 1297-1307. (c) LeCours, S. M.; Guan, H. W.; DiMagno, S. G.; Wang, C. H.; Therien, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 1497-1503. (d) Ji, W.; Wang, T.-X.; Ding, X.; Lei, S.; Han, B.-H. *Coord. Chem. Rev.* **2021**, *439,* 213875.



Stable Glucose Conjugated aza-BODIPY-Platinum Supramolecular Metallocage

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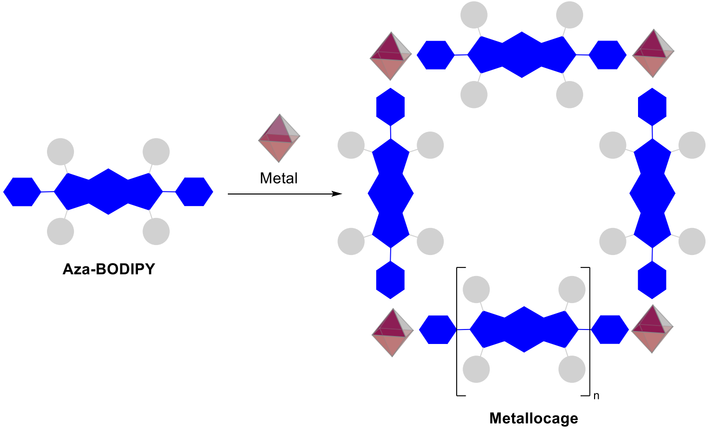
In the recent past, BF_2-chelated dipyrromethenes (BODIPYs)[1] have drawn major attention because of their broad range of applications as laser dyes, fluorescent stains and labels in imaging, indicator dyes in sensors and chemosensors, photodynamic therapy agents, and building light-energy-converting donor-acceptor systems.[2] The properties of the BODIPY can be altered by simple modifications at the appropriate positions of the BODIPY core. One of the modifications on the BODIPY core is the replacement of meso carbon by imine-type nitrogen atom resulting in a new derivative often known as azaBODIPY.[3] Compared to BODIPYs, the azaBODIPYs exhibited red-shifted absorption and emission spectra with high molar absorption coefficients and fluorescence quantum yields, which has captured the attention of researchers to construct azaBODIPY-based photosynthetic model compounds. Moreover, BODIPYs and AzaBODIPYs-Pt(II) derivatives have attracted considerable attention in the field of nanomedicine, including cancer therapy, bioimaging, and bioanalysis.[4]

The present work is aimed at developing new 2D amphiphilic supramolecular coordination complexes through coordination driven self-assembly of pyridyl-functionalized azaBODIPYs to Pt(II) metal centers. Furthermore, these chromophores are functionalized with glucose units, providing the molecule with the necessary amphiphilic character, water-solubility, and biocompatibility, together with improved uptake features by the tumor tissues. The Pt(II)-metallocage were thoroughly characterized by a combination of techniques: ^{11}B-, ^{19}F-, ^{195}Pt- and ^{1}H-NMR, ESI-TOF-MS, and absorption and emission spectroscopies.



REFERENCES

1. A. Treibs, F.-H. Kreuzer, *Ann. Chem.* **1968**, *718*, 208-223.
2. A. Turksoy, D. Yildiz, E.U. Akkaya, *Coord. Chem. Rev*. **2019**, *379*, 47-64.
3. M. Tasior, D. F. O'Shea, *Bioconjugate Chem.* **2010**, *21*, 1130-1133.
4. G. Gupta, Y. Sun, A. Das, P. J. Stang, C. Y. Lee, Coord. *Chem. Rev*. **2022**, *452*, 214308.

Synthesis, Spectral, and Electrochemical Studies of *β*-Tetracyanobutadiene Appended *π*-Extended Porphyrins

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Porphyrins and their analogues are used as a model compounds of biological importance and potential material applications due to their interesting properties, such as high chemical and thermal stability, strong absorption in the visible region, and flexible architectural modification to tailor physicochemical and optoelectronic parameters [1]. Herein, we have synthesized a new series of *β*-substituted 1,1,4,4-tetracyano-buta-1,3-diene (TCBD) porphyrins (Figure 1) and their metal complexes (M-TCBD, where M = 2H, Co(II), Ni(II), Cu(II), and Zn(II)) from 2,3-diphenylethynyl-12-formyl-*meso*-tetraphenylporphyrin and characterized by various spectroscopic techniques. This reaction is highly regioselective and proceeds *via* [2+2] cycloaddition, followed by the reteroelectrocyclization reactions of tetracyanoethylene (TCNE) with one of the phenylethynyl group because TCNE acts as a powerful dienophile for electron-rich alkenes and alkynes and form donor-acceptor (D-A) appended π-conjugated chromophores, which possess strong electrical conductivity and optical properties [2]. These type of porphyrins have ideal response toward nonlinear optical (NLO) properties/features, because due to modulation in their aromatic delocalized π-system, high thermochemical stability, smaller HOMO−LUMO gap, tuneable molecular conformation, and redox properties. DFT studies showed nonplanar conformation of the resultant complexes w.r.t. macrocyclic core due to the steric repulsion among the *β*-and *meso*-substituents extended π-conjugation. The UV-visible spectrum of these complexes exhibited a broadening of the Q bands in the visible region. These features could be utilized in material applications like photonics, optical limiters and magnetic wires. In this presentation, we will discuss about the synthesis and spectral properties and their utilization in nonlinear optics (NLO) in detail.

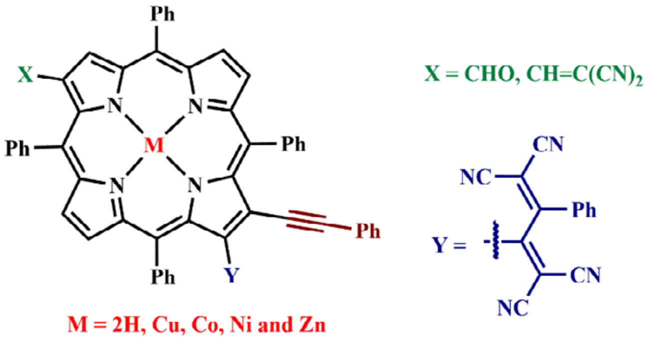

Figure 1. Molecular structures of *β*-TCBD appended π-Extended Porphyrins.

REFERENCES

1. (a) S. Kumar *et al*., *Dalton Trans*. **2021**, *50*, 6256-6272. (b) M. de-Torres *et al*., *Chem. Commun*. **2015**, *51*, 2855-2858.
2. (a) R. K. Rohal *et al*., *Inorg. Chem.* **2022**, *61*, 1297-1307. (b) B. Sekaran *et al*., *Chem. Eur. J.* **2021**, *27*, 14335-14344.

The influence of the nature of a metal atom on the electronic and geometric structures of the complexes with tetrabenzoporphyrin

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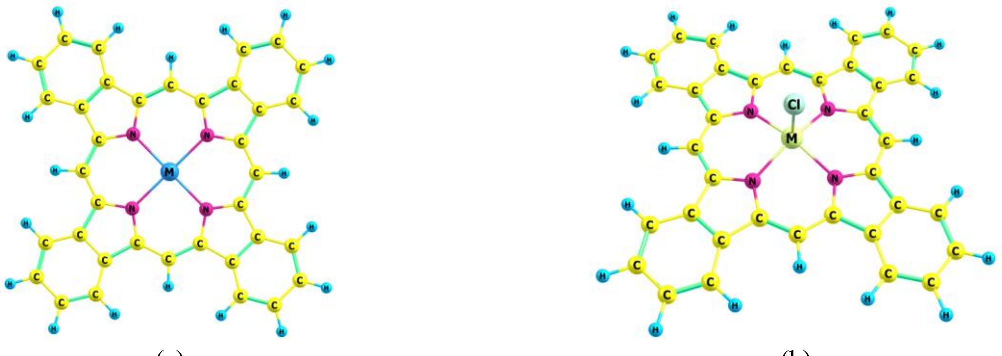
Tetrapyrrole macroheterocycles are widely used in various fields owing to the possibility of fine-tuning their properties. The nature of a central metal determines a number of properties of the molecules, e.g. efficiency of the singlet oxygen generation, fluorescence, coordination or catalytic activity.
The electronic and geometrical structure of metal-free tetrabenzoporphyrin (TBP) and its complexes with Zn, Cd (Fig. 1a), Al, Ga, In (with an axial -Cl ligand, Fig. 1b) were investigated by DFT calculations followed by natural bond orbital (NBO) analysis of the electron density distribution.



(a) (b)

Figure 1. Molecular models of the metal complexes of tetrabenzoporphyrin: MTBP (M = Zn, Cd) (a) and MClTBP (M = Al, Ga, In) (b).

The equilibrium structure of metal-free H_2TBP was found to possess D_{2h} symmetry, while metal complexes are either planar (MTBP, D_{4h} point group), or exhibit doming distortion (MClTBP, C_{4v} point group). It should be noted that the nature of a metal atom only slightly affects the geometry of the macrocyclic skeleton. The distance M-N correlates with ionic radii of metals [1] and these bonds possess predominantly ionic character with a noticeable covalent contribution according to the results of the NBO analysis. Strong interactions between natural bond orbitals of the types LP(N) → *ns*(M), LP(N) → *np*(M) (and an additional favorable overlap LP(N) → np_z(M) for complexes with Al, Ga and In), where *n* is a principal quantum number, contribute to stabilization of the complexes.
This work was supported by the Russian Science Foundation grant 21-73-10126.

REFERENCES

1. Shannon, R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr. Sect. A 1976, 32, 751–767.

Redox properties of nanostructured LS films of vitamin B_{12} derivative

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[c] *Institute of Pharmacoinformatics, Federal Research Center "Computer Science and Control" of Russian Academy of Sciences, Moscow, Russia*

Nanoparticles of a derivative of vitamin B_{12} – aquacyanocobyrinic acid heptabutyl ester (AC) in the layers at air-water interface and Langmuir-Schaefer (LS) films were formed. Characteristics of the structure and properties of the layers were determined with the method of quantitative analysis of compression isotherms [1].

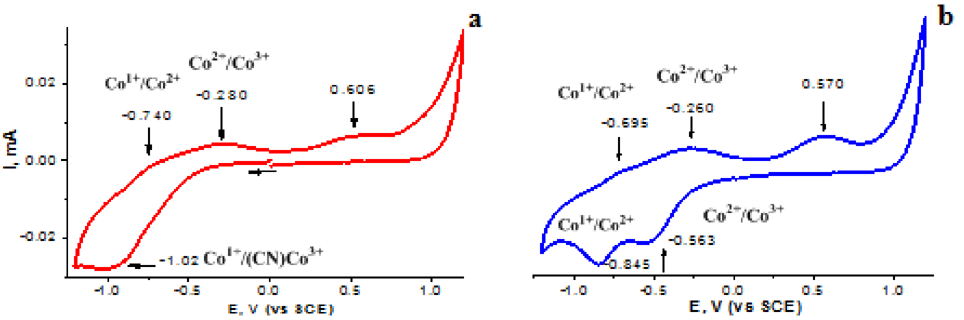

Figure 1. CV of the first (a) and second (b) cycles of LS film on ITO electrode in 0.1 m KCL aqueous solution.

The LS films demonstrate the significant difference of electrochemical responses of the first and the second cycles (figs. 1a and b). During the first cycle, a two-electron reduction leads to forming cyanide free AC nanoparticles in the LS film with yielding Co^{1+} (reduction peak current at –1.02 V, Co^{3+}/ Co^{1}, fig. 1a). After reverse of potential scan the oxidation waves at –0.740 V (Co^{1+}/Co^{2+} oxidation), –0.280 V (Co^{2+} /Co^{3+} oxidation), 0.606 V and >0.750 V (deprotonation of Co ion-linked water molecules) are observed. The first cycle leads to accumulation of aquahydroxo forms of the nanoparticles which are observed as Co^{3+}/Co^{2+} RedOx response at –0.563 V and Co^{2+}/Co^{1+} RedOx response at –0.845 V during the second cycle (fig. 1b). The potential of Co^{3+}/Co^{2+} couple for AC nanoparticles is more negative than that for aqua form of vitamin B_{12} monomers, so it should be expected the stronger reducing properties of Co^{2+} in LS films.

The work was financially supported by the grant of the RSF (20-12-00175, film formation and study), ISUCT, and Ministry of Science and Higher Education of the RF (FZZW-2020-0008, synthesis of the compounds).

REFERENCES

1. Maiorova LA. et al. *Prot. Met. Phys. Chem.* 2015, 51, 85-92; Vu T.T. et al. *Macroheterocycles* 2016, 9(1), 73-79; Valkova LA. et al. *Bull. Russ. Acad. Sci.: Phys.* 1997, 61, 631; Petrova M.V. et al. *Macroheterocycles* 2014, 7, 267-271; Kharitonova N.V. et al. *JPP* 2018, 22(6), 509-520.

Artificial cofactors in heme proteins

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Proteins are key components in functional biological systems and many of these proteins rely on cofactors modulating their activity. Hence the exchange of the natural cofactor by artificial analogues allows for investigations concerning not only their properties, but also to establish a detailed understanding of the structure-function relationship in respecting metal proteins. Furthermore, the knowledge derived from these investigations can be utilized to modify the reactivity and substrate specificity in order to design tailored functionality.[1,2,3]

Figure 1. Reconstitution of Myoglobin with artificial cofactor [4].

A promising class of artifical cofactors to be explored is represented by corroles, which resemble the natural porphyrine cofactors, while maintaining a unique coordination chemistry.[5] Therefore, a new method facilitating the preparation of amphipolar *meso*-free metal corrole derivatives was developed and the reconstitution to heme apo-proteins explored. The poster provides an overview of first results.

REFERENCES

1. L. Fruk, C.-H. Kuo, E. Torres, C. M. Niemeyer, *Angew. Chem. Int. Ed.* **2009**, *48*, 1550-1574.
2. T. Hayashi, H. Dejima, T. Matsuo, H. Sato, D. Murata, Y. Hisaeda, *J. Am. Chem. Soc* **2002**, *124*, 11226-11227.
3. C. Shirataki, O. Shoji, M. Terada, S.-I. Ozaki, H. Sugimoto, Y. Shiro, Y. Watanabe, *Angew. Chem.* **2014**, *126*, 2906-2910.
4. K. Chu, J. Vojtchovský, B. McMahon, R. M. Sweet, J. Berendzen, I. Schlichting, *Nature* **2000**, *403*, 921-923.
5. K. Oohora ,T. Hayashi, Methods in Enzymology **2016**, *580*, 439-446.

Aryloxyphosphorus(V) tetrapyrazinocorrolazines as fluorescent sensors and switchable photosensitizers

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Reaction of free-base porphyrazines with phosphorus(III) halides leads to contraction of the macrocycle due to expulsion of one of the meso-nitrogens and formation of P^V corrolazine complex having a wide range of unique features. They possess intense absorption both in the 600-700 nm region, inheriting this property from porphyrazines, and intense absorption in the 400-500 nm region, acquiring this property from the contraction of the macrocycle. In addition, phosphorus(V) corrolazines exhibit intense fluorescence with high quantum yields, as well as a high ability to generate singlet oxygen [1].

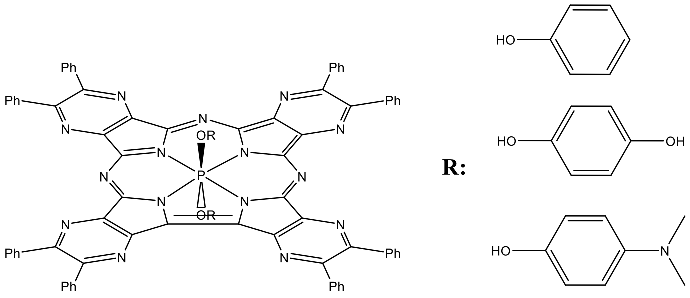

Figure 1. Left – investigated complexes; Right – Decomposition of DPBF by p-(dimethylamino)phenoxy-derivative during irradiation of light.

Axial modification of macroheterocyclic compounds allows tuning of their luminescence properties and can endow them with sensor features. For example, the sub-phthalocyanines and their analogs bearing axial phenolic ligands change their fluorescence properties depending on the acidity of the medium [2]. The prescence of deprotonated hydroxy or dimethylamino groups in para-position of axial phenoxy groups enables PET process to proceed, which results in a switchable fluorescence and its strong dependence on the solvent properties and medium acidity.

In this work we have synthesized the first examples of phosphorus (V) corrolazines bearing axial aryloxy ligands. The fluorescent and photosensitizing properties, as well as their sensitivity to additions of acid or base, was investigated in different media. Influence of pyrazine annulation to corrolazine ring is discussed.

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REFERENCES

1. X. Zhang, Coord. *Chem. Rev.,* 2015, **285**, 52-64.
2. I. Skvortsov, P. Zimcik, P. Stuzhin, V. Novakova, *Dalton Transactions,* 2020, **49**, 11090-11098.

Hexaphyrin-cyclodextrin hybrids: The story so far

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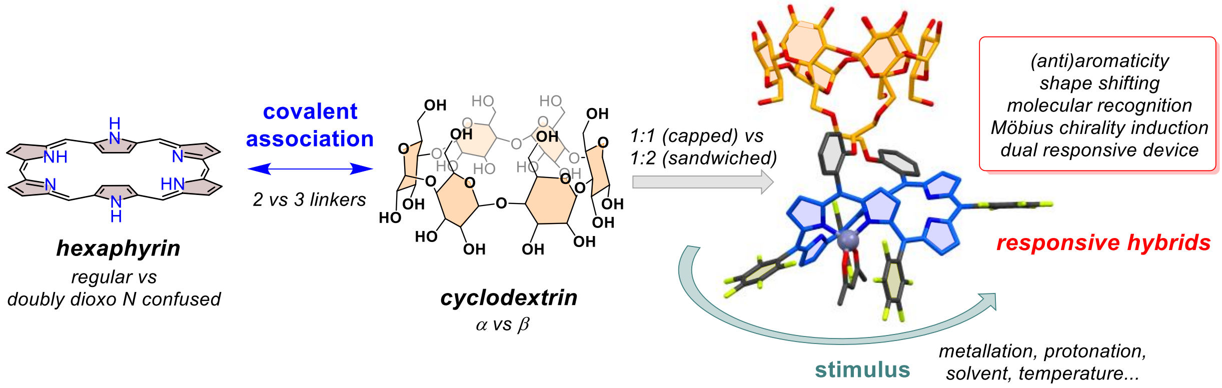
In the last two decades, the flourishing chemistry of azaannulenic systems larger than porphyrins has witnessed an ever-growing diversity of scaffolds. Beyond β- and meso-functionalization, isomeric, core-modified, fused, π-extended, twisted, among other types of congeners, afford a huge set of possibilities for the emergence of novel π-functional systems. Besides, conformational flexibility, coordination/organometallic chemistry, aromaticity, inherent chirality, are key interlinked features of expanded porphyrins. Orchestrating these features with appropriate external stimuli opens the way to ever-complex adaptive systems.

Until recently, a particular domain of engineering consisting in the coupling of an expanded porphyrin with an hydrophobic cavity has remained under-explored. Considering the previous work achieved with porphyrin-cyclodextrin conjugates bringing selectivity in molecular recognition and catalysis, the emergence of novel properties was expected to arise from the controlled association of larger porphyrin congeners with such cavities. With this idea in mind, the covalent assembly of hexaphyrin and cyclodextrin subunits was recently developed by our groups leading to the so-called family of hexaphyrin-cyclodextrin hybrids.[1, 2, 3, 4, 5] This presentation will give an overview of the story so far.



REFERENCES

1. Ménand, M.; Sollogoub, M.; Boitrel, B.; Le Gac, S. *Angew. Chem. Int. Ed.* **2016**, *55*, 297-301.
2. Le Gac, S.; Boitrel, B.; Sollogoub, M.; Ménand, M. *Chem. Commun.* **2016**, *52*, 9347-9350.
3. Ménand, M.; Sollogoub, M.; Boitrel, B.; Le Gac, S. *Chem. Eur. J.* **2018**, *24*, 5804-5812.
4. Benchouaia, R.; Cissé, N.; Boitrel, B.; Sollogoub, M.; Le Gac, S.; Ménand, M. *J. Am. Chem. Soc.* **2019**, *141*, 11583-11593.
5. Robert, F.; Boitrel, B.; Ménand, M.; Le Gac, S. *J. Porphyrins Phthalocyanines* **2021**, *25*, 1022-1032.

Möbius Zn(II)-hexaphyrins bearing a chiral coordinating arm: a chiroptical switch featuring P/M twist inversion controlled by achiral effectors

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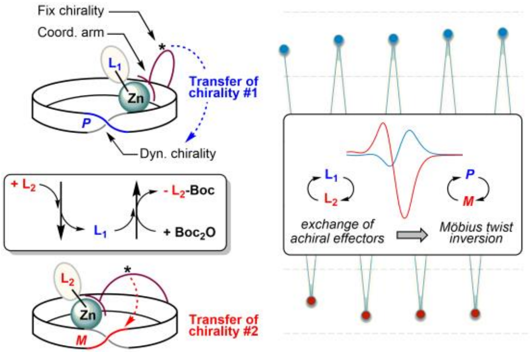
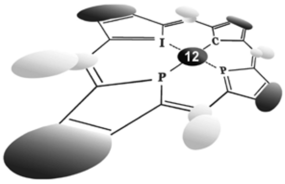
Möbius rings are inherently chiral objects (topological chirality),[1] mirror images being generated by twisting the Möbius band according to a right or a left screw sense (respectively *P* and *M* configurations). Compared to other sources of chirality, Möbius chirality has been scarcely investigated at the molecular level and thus constitutes an innovative stereogenic element. Chirality is an important added value to π-conjugated systems opening to a wide range of functions with potential technological applications.[2] Considering the importance of chiroptical switches in many fields of science,[3] designing Möbius-type chiroptical switches represents a real challenge with great opportunities.

Currently, a major obstacle remains the asymmetric preparation of Möbius compounds with only two examples described in the literature. Focusing on the Möbius [28]hexaphyrin scaffold, our group has investigated an original approach for chirality induction taking advantage of the dynamic character of the twisted π system. Indeed, this conformationally flexible scaffold undergoes rapid *P* ↔ *M* equilibrium in solution,[4] thus exhibiting a dynamic Möbius chirality. In the present contribution, we have extended our dynamic approach[5] to a situation where a source of fix chirality is part of a covalently attached coordinating arm.[6] The arm allows straightforward formation of labile monometallic Zn(II) complexes with an exogenous ligand, either a carboxylato or an amino with opposite *inwards*/*outwards* orientations relative to the Möbius ring. As a corollary, the chiral coordinating arm is constrained over the ring or laterally, inducing opposite *P* and *M* Möbius configurations with unprecedented high stereoselectivity (diast. excess greater than 95 %). By tuning the transfer of chirality, these achiral effectors generate electronic circular dichroism spectra with bisignate Cotton effect of opposite signs. Switching between distinct chiroptical states was ultimately achieved in mild conditions owing to ligand exchange, with high robustness (10 cycles).



REFERENCES

1. R. Herges, *Chem. Rev.* **2006**, *106*, 4820-4842.
2. J. R. Brandt, F. Salerno, M. J. Fuchter, *Nat. Rev. Chem.* **2017**, *1*, 0045.
3. B. L. Feringa, R. A. van Delden, N. Koumura, E. M. Geertsema, *Chem. Rev.* **2000**, 100, 1789-1816.
4. J. Sankar, S. Mori, S. Saito, H. Rath, M. Suzuki, Y. Inokuma, H. Shinokubo, K. Suk Kim, Z. S. Yoon, J.-Y. Shin, J. M. Lim, Y. Matsuzaki, O. Matsushita, A. Muranaka, N. Kobayashi, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2008**, *130*, 13568-13579.
5. H. Ruffin, G. Nyame Mendendy Boussambe, T. Roisnel, V. Dorcet, B. Boitrel, S. Le Gac, *J. Am. Chem. Soc.* **2017**, *139*, 13847-13857.
6. H. Ruffin, A. Fihey, B. Boitrel, S. Le Gac, *Angew. Chem. Int. Ed.* 10.1002/anie.202113844.



Formation of Tetrapyrrolic Macrocycle-based Supramolecular Assembly

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Porphyrins and chlorophylls are often self-assembled into nanoscale superstructures to perform many essential functions, such as light harvesting and electron transport. From the inspiration of the natural light harvesting systems, a variety of porphyrin-based nanoarchitectures, such as nanofibers, nanosheets, nanoparticles, and nanorings have been fabricated for applications in various research fields including photonics, catalysis, and electronics. The mimicry of light harvesting system is a very important subject, not only form a scientific viewpoint, but also for its possible contribution to sustainable utilization of energy resources. As mimic of natural light harvesting system, we recently have designed several porphyrin-based artificial models including porphyrin dendrmers, self-assembled nano-ring, and supramolecular receptors. We are going to report recent advances in our research on the porphyrin-based supramolecular architectures. A series of porphyrin derivatives having multiple carboxylic acid groups was prepared to build up supramolecular architecture through intermolecular hydrogen bonding. The obtained nanostructures were successfully analyzed by X-ray crystallography. The details will be presented in the symposium.

REFERENCES

1. H. Kim, K.-I. Hong, J. H. Lee, P. Kang, M.-G. Choi and W.-D. Jang. *Chem. Commun.* **2018**, *54*, 10863-10865.

Cannabinoid detection and speciation with phthalocyanine-based organic thin-film transistor sensors

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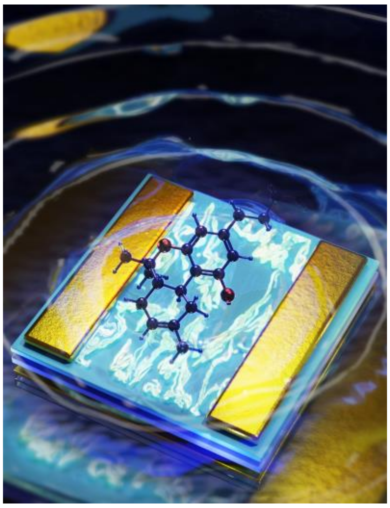

With a growing international trend of Cannabis legalization, there is a present need for on-the-spot, low cost, and rapid differentiation of cannabinoids. The two primary cannabinoids, Δ9-tetrahydrocannabinol (THC) and cannabidiol (CBD), obtained from *Cannabis*, elicit very different pharmacological effects necessitating consumer and industry methods for their detection and rapid speciation. CuPc and F_{16}-CuPc, well characterized p- and n-type semiconductors respectively, are used as the OTFT semiconducting layer in combination with a cannabinoid-sensitive chromophore allowing for 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. Spectroelectrochemistry was used to probe molecular interactions between cannabinoids with and without a cannabinoid sensitive chromophore against a variety of Pcs. Spectroelectrochemical changes to the Q-band region of the Pc spectra in the presence of analytes was related to modified ratios of Pc-Pc orientations in solution, streamlining material selection, reducing manufacturing burden, and expediting sensor development. 2D-NMR was used to further elucidate unique Pc-Pc and Pc-analyte interactions, providing additional insight on atomic level interactions. Through altered Pc-Pc orientations, analytes can induce physical alterations to Pc thin-film morphology and structure, consequently, modifying electrical performance beyond charge trapping effects. Pc peripheral and axial substitutions allow an additional level of Pc tunability and their relationship with analyte interactions, film structure, and OTFT sensing performance was explored.

We established relationships between thin-films of phthalocyanines (Pcs) with a variety of central, peripheral, and axial substituents and their response to THC. X-Ray diffraction and UV–vis absorption spectroscopy measurements demonstrate significantly altered film morphologies and the formation of new crystal orientations in response to analytes, which are corroborated by scanning electron microscopy. With exposure to THC, aluminium chloride Pc generates the largest physical film changes as well as the largest changes in OTFT performance. These findings have implications for Pc-based OTFT sensor design, suggesting that the semiconducting Pc thin-film morphologies are not static in the presence of analytes, and that the sensing response is driven both by strong analyte-Pc coordination and bulk film restructuring to accommodate these interactions.

REFERENCES

1. *Advanced Functional Materials*, **2021**, ASAP, doi:10.1002/adfm.202107138
2. *ACS Appl. Mater. Interfaces,* **2020**, 12, 45, 50692–50702
3. *ACS Sensors,* **2019**, 4, 10, 2706-2715.

Corrinated Glucagon to treat Hypoglycemia

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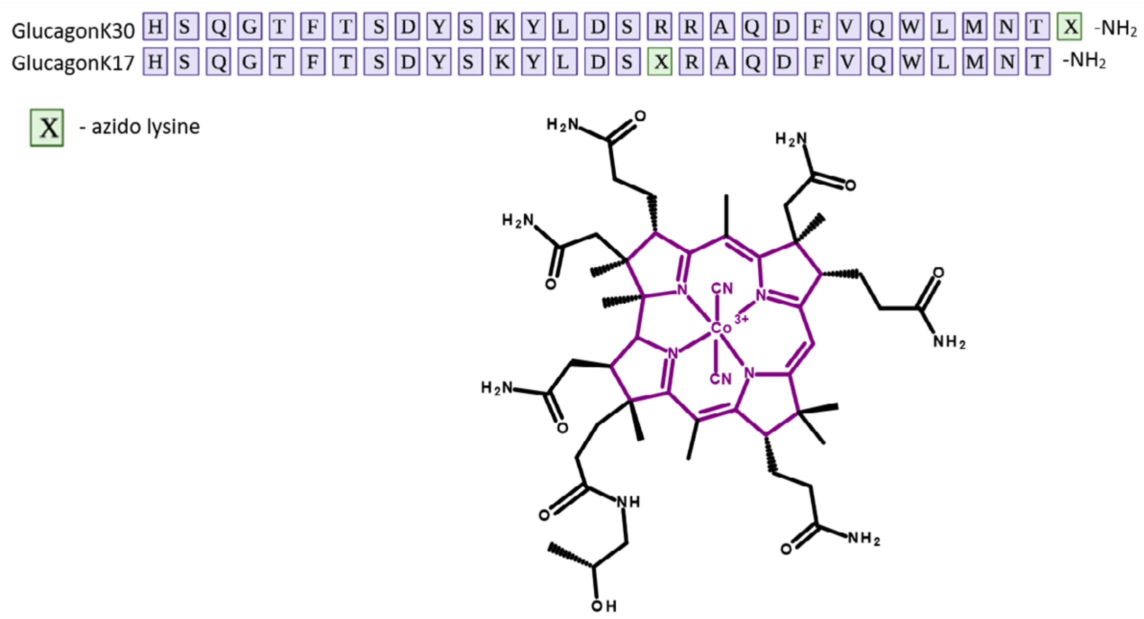
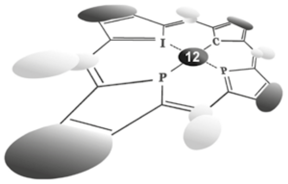
Glucagon is a 29-amino acid pancreatic hormone responsible, in part, for the regulation of glucose. This regulation is imperative when it comes to patients with insulin-dependent diabetes, as glucose can have large fluctuations in these patients. Current treatments consist of solubilizing the glucagon immediately prior to administration, however, is poorly soluble and prone to aggregation in its native state. Developing a modified glucagon that is shelf stable and readily soluble would improve the current treatment. The Doyle group has coined the term 'corrination' [1, 2] to describe the conjugate modification of a compound/peptide/protein with a corrin ring containing compound such as dicyanocobinamide (Cbi). Herein, we describe the corrination of glucagon with the highly water-soluble Cbi via copper catalysed azide-alkyne cycloaddition. The effects of corrination position on the peptide on solubility, stability, aggregation, and function at the glucagon receptor is described.



REFERENCES

1. T. Borner *et al.*, "Corrination of a GLP-1 Receptor Agonist for Glycemic Control without Emesis," *Cell Rep.*, vol. 31, no. 11, p. 107768, Jun. 2020, doi: 10.1016/j.celrep.2020.107768.
2. I. C. Tinsley *et al.*, "Synthesis, Optimization, and Biological Evaluation of Corrinated Conjugates of the GLP-1R Agonist Exendin-4," *J. Med. Chem.*, vol. 64, no. 6, pp. 3479–3492, Mar. 2021, doi: 10.1021/acs.jmedchem.1c00185.



Realization of Stacked-Ring Aromaticity in a Water-Soluble Micellar Capsule

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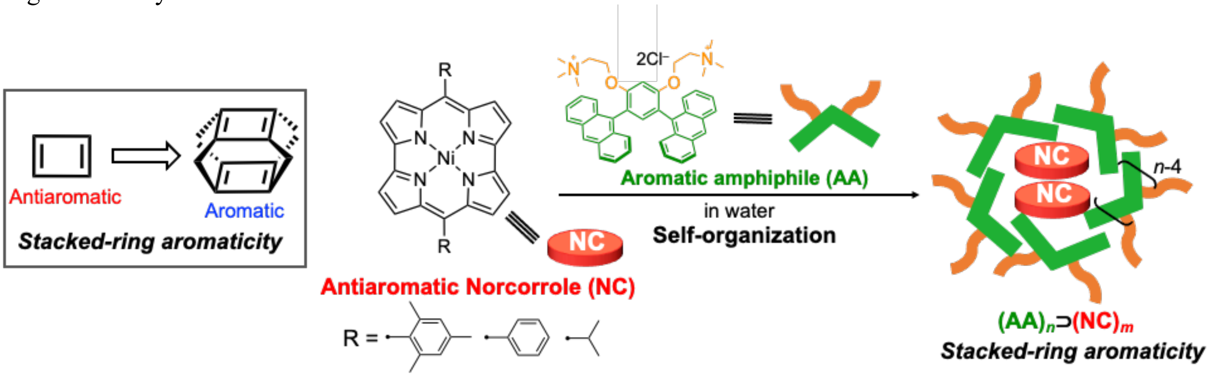
The interaction between stacked antiaromatic π-systems has recently attracted considerable attention. Schleyer and Fowler theoretically proposed that stacking of two antiaromatic systems in methano-bridged superphanes eliminates their antiaromaticity, which originates from their effective orbital interactions [1]. This phenomenon has been known as stacked-ring aromaticity [2]. Recently, our group have achieved stacked-ring aromaticity experimentally by tethering two antiaromatic norcorrole units using covalent linkers. These norcorrole dimers with remarkably short interplanar distances (< 3.4 Å) exhibit characteristic absorption bands in the near infrared (NIR) region [3]. However, the current strategy to achieve stacked-ring aromaticity consists only of the tethering approach, which requires the elaborate synthesis of norcorrole dimers.

Here, we demonstrate the realization of stacked-ring aromaticity by a rational supramolecular approach. Several norcorroles were subjected to the encapsulation in a micellar capsule composed of bent polyaromatic amphiphiles [4]. The encapsulation resulted in the appearance of a broad absorption band in the NIR region, which is characteristic of face-to-face staked norcorrole dimers. Importantly, 5,15-diisopropylnorcorrole, which does not exhibit π-staked orientation even in a concentrated organic solvent and crystalline phase, adopted π-stacking in the micellar capsule. These results demonstrate the power of supramolecular chemistry for the realization of stacked-ring aromaticity.



REFERENCES

1. a) Corminboeuf, C.; Schleyer, P. v. R.; Warner, P. *Org. Lett.* **2007**, *9*, 3263; b) Bean, D. E.; Fowler, P. W. *Org. Lett.* **2008**, *10*, 5573.
2. Aihara, J.-i. *J. Phys. Chem. A* **2009**, *113*, 7945.
3. a) Nozawa, R.; Tanaka, H.; Cha, W.-Y.; Hong, Y.; Hisaki, I.; Shimizu, S.; Shin, J.-Y.; Kowalczyk, T.; Irle, S.; Kim, D.; Shinokubo, H. *Nat. Commun.* **2016**, *7*, 13620; b) Nozawa, R.; Kim, J.; Oh, J.; Lamping, A.; Wang, Y.; Shimizu, S.; Hisaki, I.; Kowalczyk, T.; Fliegl, H.; Kim, D.; Shinokubo, H. *Nat. Commun.* **2019**, *10*, 3576.
4. Kondo, K.; Suzuki, A.; Akita, M.; Yoshizawa, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 2308.

Polar, columnar Subphthalocyanine-based supramolecular structures: Design, synthesis and characterization

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Over the past decades, columnar-organized structures obtained from π-conjugated bowl-shaped molecules have gained increased attention. As a result of their molecular structure, these systems can form unconventional polar organizations that significantly improve the charge transport, which is of outmost importance in most of state-of-the-art technological devices.

Among the molecular building blocks able to form such columnar assemblies, **Subphthalocyanines** (**SubPcs**; Figure 1a) are particularly attractive on account of their outstanding structural and photophysical properties (*i.e.*, intense absorption and/or emission in the UV-vis and near-infrared (NIR) region, excellent charge transport properties, and a wide chemical versatility). [1] Thus, these aromatic macrocycles, with their singular non-planar structure, have demonstrated a great capability to form columnar assemblies both in solid-state, solution and liquid crystal (LC) phases. [2] Herein we report the synthesis and characterization of SubPc columnar materials which, depending on the molecular design, behave as lyotropic/thermotropic liquid crystal or form columnar polymers in solution. The factors that govern such an unusual organization are studied by a combination of several experimental techniques and theoretical calculations.

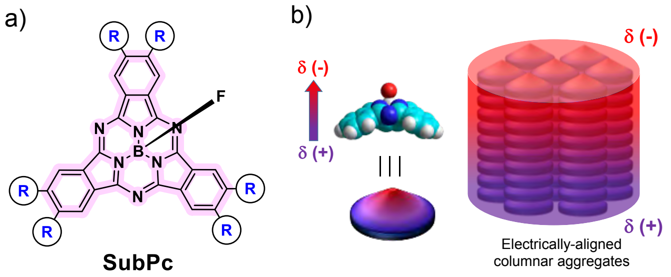

Figure 1. a) Molecular structure of SubPcs, b) columnar structures resulting from the assembly of SubPc molecules.

REFERENCES

1. Claessens, C. G.; Gonzalez-Rodriguez, D.; Rodriguez-Morgade, M. S.; Medina, A.; Torres, T. Chem. Rev. 2014, 114, 2192-2277.
2. a) Guilleme, J.; Arago, J.; Ortí, E.; Cavero, E.; Sierra, T.; Ortega, J.; Folcia, C. L.; Etxebarria, J.; Gonzalez-Rodríguez, D.; Torres, T. A columnar liquid crystal with permanent polar order. J. Mater. Chem. C. 2015, 3, 985−989. b) Mayoral, M. J.; Guilleme, J.; Calbo, J.; Arago, J.; Aparicio, F.; Orti, E.; Torres, T.; Gonzalez-Rodriguez, D. J. Am. Chem. Soc. 2020, 142, 21017-21031.

Positively charged styryl pyridine substituted Zn (II) Phthalocyanines for Photoantimicrobial Chemotherapy: Effect of the number of charges

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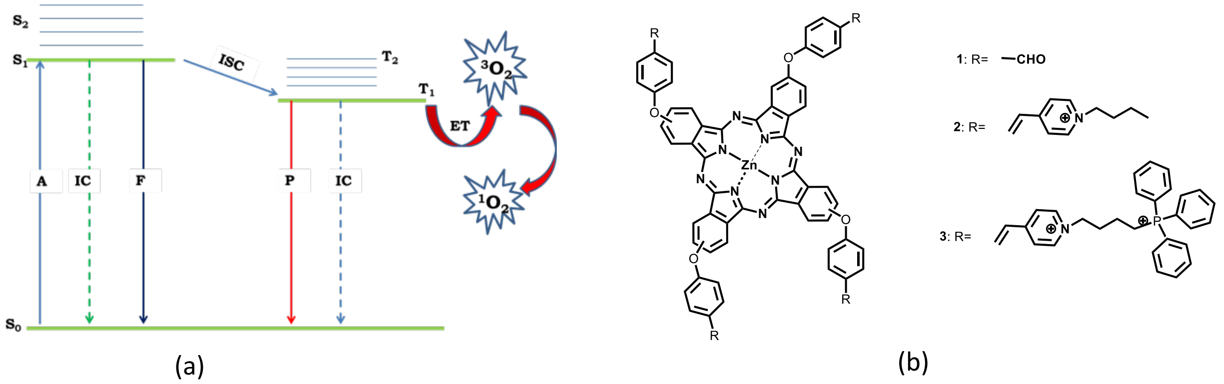
Photo antimicrobial chemotherapy (PACT) is a therapeutic modality to pathogenic bacteria [1] based on the administration of a non-toxic photosensitizer (PS), which after activation by visible light of an appropriate wavelength in the presence of molecular oxygen, produces reactive oxygen species (ROS) including singlet oxygen (figure.1a), that cause irreversible photodamage to bacteria cells, leading to cell death [2]. Phthalocyanines (Pcs) are second-generation photosensitizers that possess impressive photophysical and photochemical properties and an aptitude for several structural modifications on the Pc ring (fig.1b) making them and ideal candidate for antibacterial molecules. Attributes for an effective PS for use in PACT include low toxicity in the dark and strong light absorption in the optical window of biological tissues, that is, in the range of 650−800 nm. In this work, cationic styryl pyridine triphenylphosphonium-based Pcs are synthesized and applied in PACT on *E. coli*. We present ZnPc containing styryl pyridinoxy (containing four positive charges) and styryl triphenylphosphine (containing eight positive charges). The effect of number of charges on the PACT activity will be evaluated.

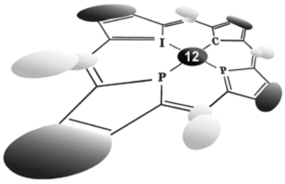


(a) (b)

Figure 1. (a) Electronic energy transfer from suitable photosensitizers to molecular oxygen to produce reactive oxygen species (ROS) (b) Phthalocyanine photosensitisers

REFERENCES

1. A. Galstyan, U. Dobrindt, *J. Mater. Chem. B*, 2018, 6, 4630-4637.
2. B. Zheng, X. Jiang, T. Lin, M. Ke, J. Huang, *Dyes Pigm.*, 2015, 112, 311.



The small molecules reactivity of homologous cytochrome *bd* oxidases from *E.coli*

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Cytochrome *bd* oxidases are unique terminal oxidases from prokaryotic respiratory chains that catalyse the reduction of molecular oxygen in water and oxidation of quinols. Three heme cofactors, namely heme *d*, heme b_{558} and heme b_{595} are buried in the scaffold of these bacterial enzymes. Catalytic reduction of O_2 takes place at the high spin d-type heme in all cyt *bd* oxidases that is also the binding site for small uncharged signalling molecules such as CO, H_2S and NO. In particular, it was demonstrated that *bd* oxidases enhance the bacterial survival under oxidative and nitrosative stress [1]. The understanding of the NO binding with cyt *bd* oxidase might help to evaluate the relevance of this reaction for microbial pathogenicity.

E. coli contains two highly comparable cytochrome *bd* oxidases [2], *bd-I* and *bd-II*. Despite the high similarity in sequence and structure, there are differences in accessibility of the active site through the gas channel that may cause the differences in binding to the small gaseous molecules. In this study we focus on the NO binding mechanism of *bd-I* and *bd-II* oxidases from *E. coli*. On the basis of an essay based on bioelectrochemical sensor the inhibitory effect of nitric oxide on the enzyme electrocatalysis with oxygen and the respective IC_{50} values were determined for both enzymes [3]. Additionally, the UV-Vis spectroscopic study of the NO binding and release was studied. It can be shown that cyt *bd-I* and *bd-II* have a different pH dependence concerning both, the enzymatic turnover and the sensitivity towards NO. It is suggested that the presence of the two *bd* oxidases is necessary to ensure the activity of *E.coli* for a broader pH range.

REFERENCES

1. A. Giuffrè, V.B. Borisov, M. Arese, P. Sarti, E. Forte, Cytochrome bd Oxidase and Bacterial Tolerance to Oxidative and Nitrosative Stress, *Biochim. Biophys. Acta, Bioenerg.* 1837 (2014) 1178-1187.
2. Grauel, A., Kägi, J., Rasmussen, T., Makarchuk, I., Oppermann, S., Moumbock, A., Wohlwend, D., Müller, R., Melin, F., Günther, S., Hellwig, P., Böttcher, B., and Friedrich, T. (2021) *Nat. Commun*., 12:6498.
3. A. Nikolaev, I. Makarchuk, A. Thesseling, J. Hoeser, T. Friedrich, F. Melin, P. Hellwig, Stabilization of the Highly Hydrophobic Membrane Protein, Cytochrome bd Oxidase, on Metallic Surfaces for Direct Electrochemical Studies, Molecules 25 (2020) 3240.Safarian, S., Rajendran, C., Müller, H., Preu, J., Langer, JD., Ovchinnikov, S., Hirose, T., Kusumoto, T., Sakamoto, J., Michel, H. (2016) *Science,* 352 (6285): 583-586.

Sustainable approaches to the synthesis and functionalization of state-of-art and novel phthalocyanines for technological applications

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In recent decades, particular attention has been paid to the issue of sustainability by encouraging the development of technologies with low environmental and economic impact. It is a transversal approach that is gaining momentum in all sectors of industry, especially in the chemical industry and research. Given the extreme versatility and technological importance of phthalocyanines, the design and study of alternative synthetic approaches to the conventional ones have gained importance in the last few years. Phthalocyanines are commonly synthesized on lab-scale by tetramerization of phthalonitriles with lithium alcolates or strong organic bases in environmentally impacting reaction media like alkyl alcohols or aromatic organic solvents. Further state-of-the-art protocols exploit melting methods from phthalic anhydride at high temperatures (200-300 °C), microwave-assisted processes, synthesis in ionic liquids and syntheses performed at room temperature catalyzed by strong organic bases such as lithium diisopropylamide (LDA). [1, 2, 3] Even though moving towards an increased sustainability, these alternative synthetic routes often suffer from lack of scalability, thus may result difficult to realize on a large scale. In this context, the idea of approaching the synthesis of phthalocyanines exploiting classical solution processes by applying green chemistry principles was developed.

In this contribution, the use of more sustainable solvents and purification methods [4] as well as the rational design of electron-rich symmetrically substituted phthalocyanines by means of pot-economical approaches will be shown and discussed, along with an estimation of the environmental and economic impact with respect to the related established procedures. Optoelectrochemical characterizations of the synthesized materials hint at the possibility of their application in the field of organic electronics and perovskite solar cells.

REFERENCES

1. W. Zheng, C. Z. Wan, J.X. Zhang,, C.H. Li, X. Z. You, X.Z.*Tetrahedron Lett.,* 2015, 56, 4459–4462.
2. Ö. Koyun, S. Gördük, B. I. Keskin, A. Çetinkaya, A. I. Koca, U. Avciata, *Polyhedron*, 2016,113, 35–49.
3. P-C. Lo, D. Y. Y. Cheng, D. K. P. Ng, *Synthesis*, 2005, 7, 1141-1147.
4. G. Zanotti, P. Imperatori, A. M. Paoletti, G. Pennesi, *Molecules*, 2021, *26*, 1760.

Electronic properties of N-confused metalloporphyrins

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Porphyrin derivatives can be found in several biological molecules,[1] usually in enzyme cofactors, and have inspired the synthesis of many chemicals with properties that are useful for mankind.[2] Transition metal complexes of the N-confused NCP-2H isomer of porphyrin, in particular, have been shown to have anti-cancer activity,[3] be able to fixate and functionalize CO_2[4] and work as molecular probes.[5] Their understanding is thus of the utmost urgency.

While the optical and electronic properties of these molecules have been tentatively rationalized with analyses of their molecular orbital diagrams in the frontier region (HOMO-LUMO),[6] they are still unclear to this day as the spin and oxidation state of the complexes is elusive due to the porphyrinate ring non-innocence. These complexes have also been obtained with different structural features[7] and it would be useful to understand the rationale behind the preference for different coordination modes and numbers.

Here, we use state-of-the-art Density Functional Theory methods[8] to study the electronic properties of [M(2H-NCP)$^{2-}$], M = transition metal complex with varying oxidation state, type complexes with varying *d*-electron populations to understand how they can be used to modulate the properties of porphyrin into more useful scenarios and how they react to redox phenomena. We hope to provide guidelines for the rational design of this class of porphyrin derivatives.

Figure 1. NCP-2H metalloporphyrin structure.

REFERENCES

1. S. E. J. Bowman, K. L. Bren, *Nat. Prod. Rep.* **2008**, *25*, 1118-1130
2. C. M. Drain, A. Varotto, I. Radivojevic, *Chem. Rev.* **2009**, *109*, 1630-1658
3. N. Halder, L. U. Dzhemileva, I. R. Ramazanov, V. A. D'Yakonov, U. M. Dzhemilev, H. Rath, *ChemMedChem* **2020**, *15*, 632-642
4. J. B. dela Cruz, C.-H. Hung, *Catal. Sci. Technol.* **2021**, *11*, 2144-2154
5. N. Grover, M. Sankar, *Chem. As. J.* **2020**, *15*, 2192-2197
6. S. Sripothongnak, C. J. Ziegler, M. R. Dahlby, V. N. Nemykin, *Inorg. Chem.* **2011**, *50*, 6902-6909
7. a) T. Miyazaki, T. Yamamoto, S. Mashita, Y. Deguchi, K. Fukuyama, M. Ishida, S. Mori, H. Furuta, *Eur. J. Inorg. Chem.* **2018**, *2018*, 203-207. b) C.-H. Yang, S. J. Dzugan, V. L. Goedken, *J. Chem. Soc., Chem. Commun.* **1986**, 1313-1315
8. M. Swart, *Chem. Phys. Lett.* **2013**, *580*, 166-171

On-surface Synthesis and Atomic-scale Characterization of [3]Triangulene-fused Porphyrins

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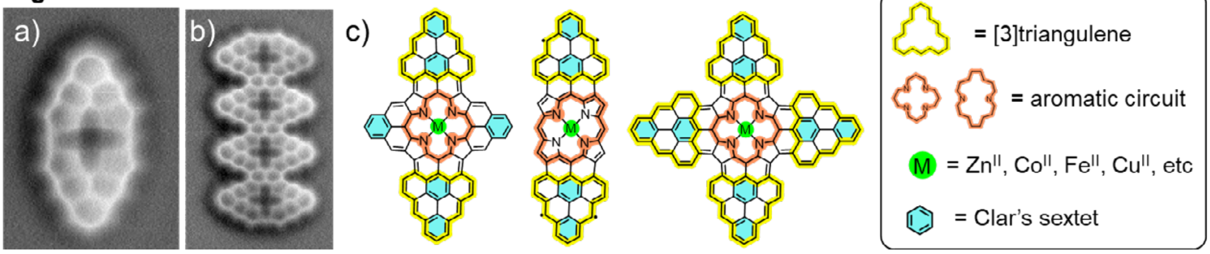
On-surface synthesis under ultra-high vacuum (UHV) conditions has emerged as an appealing strategy for the fabrication of surface-supported nanostructures [1]. Moreover, the resulting nanoarchitectures can directly be accessed by local-probe techniques such as scanning probe microscopy, allowing for their in situ structural and electronic characterization with sub-molecular resolution. Among such nanostructures, π-extended porphyrins (Pors) represent an interesting target due to the unique structural and optoelectronic features these macrocycles have.

Recently, our group has reported the fabrication and atomic-scale characterization of some novel phenalenyl-based π-extended Pors (Figure 1a) [2]. These nanostructures were obtained on Au(111) via on-surface cyclodehydrogenation reaction at 300 °C from suitable Por precursors and showed an open-shell electronic character. Interestingly, further thermal annealing (i.e., 325 °C) of the latter surface-supported monomeric Pors triggered an intermolecular coupling reaction leading to the formation of π-extended Por nanotapes (Figure 1b) which retained the open-shell character of the precursor [3].

As an extension of that work, we aim here at investigating the effect of further increasing the π-extension of the surface-supported Pors by "fusing" them to [3]triangulene moieties (Figure 1c). Such nanostructures will be achieved through cyclodehydrogenation reaction of adequate Por precursors bearing two or four 9-(2,6-dimethylphenyl)anthryl moieties at their meso position and will be characterized by STM and nc-AFM. Furthermore, the effect of the nature of the inner metal center on the electronic features of the resulting Por nanostructures will also be explored.

Figure 1



REFERENCES

1. Clair, S.; de Oteyza, D. G., *Chem. Rev.* **2019**, *119*, 7, 4717-4776.
2. a) *J. Am. Chem. Soc.* **2020**, *142*, 42, 18109-18117; b) Sun, Q.; Mateo, L. M.; Robles, R.; Ruffieux, P.; Bottari, G.; Torres, T.; Fasel, R., Lorente, N.; *Adv. Sci. under revision.*
3. Sun, Q.; Mateo, L. M.; Robles, R.; Lorente, N.; Ruffieux, P.; Bottari, G.; Torres, T.; Fasel, R., *Angew. Chem. Int. Ed.* **2021**, *60*, 16208-16214.

Porphyrin based self-assembled nanocages

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Natural systems represent a source of inspiration when it comes to the processing of energy and matter. At the core of many of these processes are metalloporphyrinoids, which are found in many of the organized enzymatic machineries that harvest solar energy and catalyse relevant chemical processes [1]. Enzymes also teach us that the catalytic sites around the metal centres must remain accessible to the relevant substrates to optimize catalytic performance and embedded in a well-defined compartment to enhance selectivity. These complex natural systems have inspired chemists to design various porphyrin-based nanocages, making use of both covalent and noncovalent interactions [2]. Notably, in these synthetic systems, discrete cofacial porphyrin-based systems, where two porphyrin units are arranged in a parallel conformation with the help of rigid covalent spacers, have proven unique advantages over their monomeric analogues [3].

In this context, we target the construction of nanocages whose simple preparation relies on the development of a new self-assembly strategy that will allow us to cofacially arrange metalloporphyrinoids at tailored interstitial distances, thus creating accessible (photo/electro) catalytic compartments.

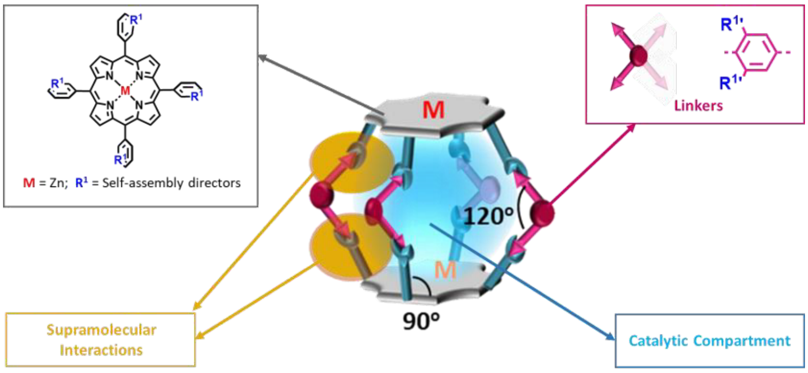
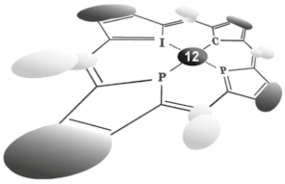


Figure 1. Schematic representation of a nanocage and its components.

To this aim, metalloporphyrinoids macrocycles have been tetra-functionalized at the periphery with arenes bearing self-assembling motifs R^1 disposed at 120º angle (i.e. meta position). This metalloporphyrnoids will be fused, thanks to the linkers bearing a complementary self-assembling motif $R^{1'}$.

REFERENCES

1. I. Oroz-Guinea, E. Garcia-Junceda, *Curr. Opin. Chem. Biol.*, 2013, **17**, 236-249.
2. R. D. Mukhopadhyay, Y. Kim, J. Koo, K. Kim, *Acc. Chem. Res.* 2018, **51**, 2730−2738.
3. J. P. Collman, P. S. Wagenknecht, J. E. Hutchison, *Angew. Chem., Int. Ed.*, 1994, **33**, 1537-1554.
4. J. Rosenthal, D. G. Nocera, *Acc. Chem. Res.*, 2007, **40**, 543-453.



Photophysics and Photostability of Porphycenes Bearing Electron-Donating and Accepting Moieties

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Porphycene and its derivatives have been of interest to researchers due to their established applications in information storage, studies of tautomeric equilibria, and photodynamic therapy (PDT) [1]. The deployment of porphycenes, structural isomers of porphyrin, in cancer phototherapy was motivated by photophysical and photobiological properties of these compounds, which make them excellent candidates for PDT. These properties include high molar absorptivity in the red region of the spectrum (which penetrates deeper into tissues), low dark cytotoxicity, high yield of triplet state formation, high quantum yield of singlet oxygen generation, and fast cellular uptake. Reports of successful use of porphycenes in PDT are present in the literature [2]. Although there are several records on the photophysical properties of porphycenes [3], studies of photostability are rare, which calls for more research in this area. Therefore, our group has focused on the investigation of photostability in porphycenes and recently reported photostability of selected porphycenes on a single molecule level [4].

Although photophysical properties are fundamental in the choice of photosensitizers, photostability is equally a significant factor that determines the suitability and durability of sensitizers in PDT. The present study reports the photophysics of selected porphycenes substituted with electron-donating amino and electron-withdrawing nitro groups. The influence of *tert-butyl* substituents on the photophysics is also evaluated. The bulky *tert-butyl* groups present a significant influence on the fluorescence quantum yields and lifetimes. We also report influence of electron-donating and electron-withdrawing substituents on the photophysics and photostability. Two of the studied porphycenes demonstrate dual fluorescence bands, assigned to emission from two tautomeric forms.

REFERENCES

1. Stockert J C, Cañete M, Juarranz A., Villanueva, A, Horobin R W, Borrell, J I, Teixidó, J, Nonell, S. *Curr. Med. Chem.* 2007, 14, 997.
2. Toledano H, Edrei R, Kimel S. J. Photochem. Photobiol. B. 1998, 42, 20; Guardiano, M, Biolo, R, Jori G, Schaffner K. *Cancer Lett*. 1989, 44, 1.
3. Waluk J. Chem. Rev. 2017, 117, 2447; Braslavsky S E, et al. J. Photochem. Photobiol. B 1997, 40, 191; Aramendia P, et al. J. Photochem. *Photobiol.* 1986, 44, 555.
4. Bednarz A, Kamińska I, Jamrozik A, Zielonka K, Listkowski A, Waluk J. *Methods Appl. Fluoresc.* 2021, 9, 035004.

Carbonic Anhydrase Inhibitors Featuring a Porphyrin Scaffold

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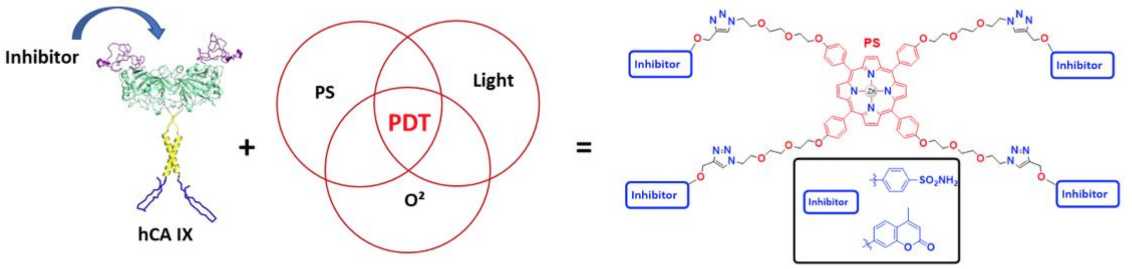
Cancer is a multifaceted disease and one of the leading causes of death worldwide, responsible for 9.6 million deaths and affecting almost 18.1 million new cases in 2018.[1] Among the therapeutic armamentarium against cancer, photodynamic therapy (PDT) has attracted much enthusiasm due to its minimal invasiveness, implementation, low systemic toxicity and high efficiency.[2] This type of treatment is based on tumoral specific accumulation of a photosensitizing agent that can be activated by light source at a specific wavelength to produce locally reactive oxygen species (ROS), leading to a cascade of reactions, which could trigger cancer cells death by necrosis or apoptosis.[3] However, the PDT efficacy is largely impaired by the deficient oxygen supply in solid tumours where hypoxia commonly exists. To overcome this limitation, recent approaches based on synergistic combination of tumor-targeted PDT and inhibition of the transmembrane solid tumor-associated carbonic anhydrase IX (hCA IX) which is overexpressed under hypoxia, have recently emerged and proved their effectiveness.[4-6] In this context, we will describe in this presentation the synthesis, the characterization, the optical and biological properties of innovative tetrafunctionalized zinc(II) porphyrins bearing carbonic anhydrase (CA) inhibitors in sulfonamide and coumarin series.



REFERENCES

1. https://www.who.int/news-room/fact-sheets/detail/cancer.
2. A. Merabti, M. Roger, C. Nguyen, A. Nocentini, P. Gerbier, S. Richeter, M. Gary-Bobo, C. T. Supuran, S. Clément, J.-Y. Winum, *Eur. J. Org. Chem*. **2022**, *In press*, doi: 10.1002/ejoc.202101538
3. U. Chilakamarthi, L. Giribabu, *Chem. Rec.* **2017**, *17*, 775-802.
4. H. S. Jung, J. Han, H. Shi, S. Koo, H. Singh, H.-J Kim, J. L. Sessler, J. Y. Lee, J.-H. Kim, J. S. Kim, *J. Am. Chem. Soc*. **2017**, *139*, 7595-7602.
5. Y. Jiang, J. Li, Z. Zeng, C. Xie, Y. Lyu, K. Pu, *Angew. Chem. Int. Ed. Engl*. **2019**, *58*, 8161-8165.
6. W. Zhu, Y. Liu, Z. Yang, L. Zhang, L. Xiao, P. Liu, J. Wang, C. Yi, Z. Xu, J. Ren, *J. Mater. Chem. B* **2018**, *6*, 265-276.

Efficiency of Strain Promoted Azide-Alkyne Cycloaddition of Azaphthalocyanine Fluorescence Quencher and BODIPY Fluorophore with Oligonucleotides

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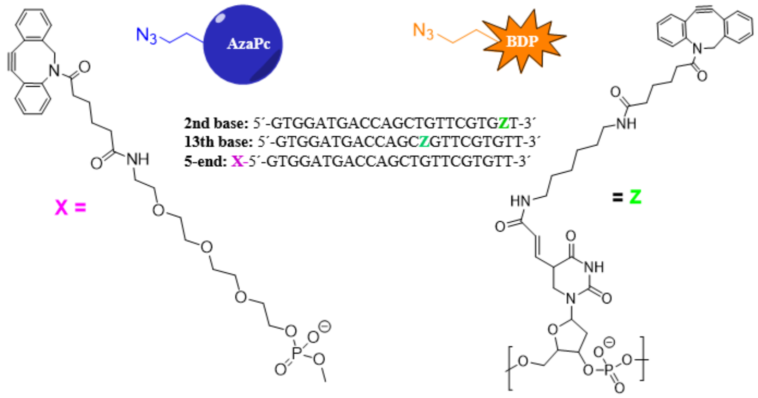
Functionalized synthetic oligonucleotides are object of intense interest in the field of natural sciences, as well as nanotechnologies and related fields. They contribute to proceedings in area of genetic diagnosis as well as therapeutic approaches like antisense and SiRNA technologies.[1] There is a great potential also in development of aptamer-drug conjugates.[2] The development of highly reliable and efficient methods for the modification of synthetic and native nucleic acids is therefore an important issue. The solid phase post-synthetic labelling employing "click" type reaction - Strain Promoted Azide Alkyne Cycloaddition (SPAAC) [3] is one of the most convenient approaches. Since the reaction efficiency on solid phase depends on position in the oligonucleotide chain, size and character of the conjugated molecule, and also the solid phase character, we have performed a comparative study with azaphthalocyanine (AzaPc) fluorescence quencher and BODIPY (BDP) fluorophore to reveal more regularities of this process.



An oligonucleotide synthesized and bound on various supports, modified with dibenzoazacyclooctyne (X, Z) in various positions was "clicked" with azido derivatives of the above mentioned molecules. The reactions outcomes were evaluated by HPLC chromatography.

REFERENCES

1. Biessen E.A.L, Van Berkel T.J.C. *Arterioscler. Thromb. Vasc. Biol.* 2021, 41, 2855-2865.
2. Kim D.H., Seo J.M., Shin K.J., Yang S.G. *Biomaterials Research* 2021, 25, 42.
3. N. J. Agard, J. A. Prescher and C. R. Bertozzi, *J. Am. Chem. Soc.,* 2004, 126, 15046-15
4. The study was supported by Czech Science Foundation Grant No. 21-14919J.

Novel A₃B-type Phthalocyanine with Terminal Thioacetate Group for Self-assembled Monolayers on a Gold Surface

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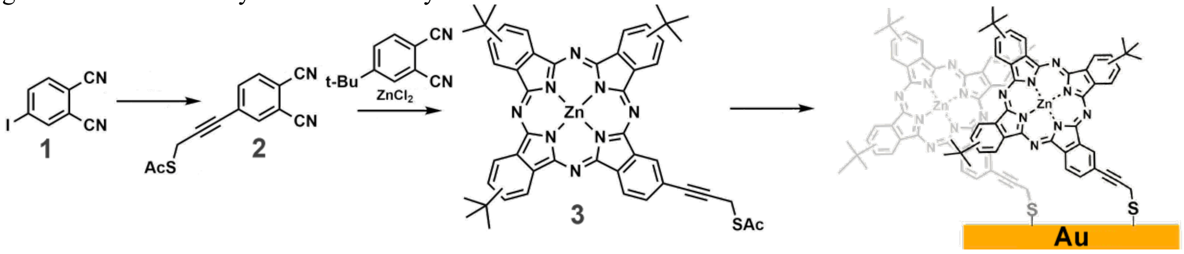
Low-symmetry phthalocyanines containing peripheral thiol groups are prospective compounds for covalent bonding on the gold surface. They can form self-assembled monolayers (SAMs) for different applications: modified electrodes for electrochemical sensors; capping agents for tuning of gold nanoparticles (GNPs) for drug delivery [1,2]. Although functionalization of gold surfaces with phthalocyanines has been previously reported, free peripheral thiols or amines were employed [3]. The use of acetate-protected thiols can be superior due to the stability of the functional group and the possibility of the direct attachment to gold [4]. By changing the structure of macrocycles, one can control the orientation of the self-assembled layer (edge-on or face-on arrangement of phthalocyanine with respect to the substrate). A_3B-type phthalocyanines with only one functional linker attach to gold surfaces in strictly vertical macrocycle orientation and exclude the formation of cross-linked structures.



In this work, a three-stage synthesis of low-symmetry mono-(prop-2-ynyl thioacetate)-substituted zinc phthalocyanine starting from 4-iodophthalonitrile was conducted. Initial 4-iodophthalonitrile was obtained according to an alternative synthetic protocol recently described [5]. A_3B-type phthalocyanine was obtained by the reaction of mixed cyclization between 4-*tert*-butyl- and 4-(prop-2-ynyl thioacetate)-substituted phthalonitriles. Phthalocyanine **3** was employed in the surface modification reaction of a gold electrode and GNPs. Two modification procedures were performed. The removal of the acetate group was more efficient than the reaction without deprotection. The obtained self-organized monolayers were studied by cyclic voltammetry and chronoamperometry. The number of phthalocyanine molecules adsorbed to the electrode surface was calculated.

Novel phthalonitrile **2** was characterized by nuclear magnetic resonance (NMR), infrared (IR) spectroscopy and electrospray ionization (ESI) mass spectrometry. Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry, NMR and IR spectroscopy were used to characterize the targeted phthalocyanine **3**. The composition and texture of the modified gold surface were characterized by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Functionalized GNPs were confirmed by UV-Vis spectroscopy.

We are grateful for financial support from the Russian Foundation for Basic Research Grant № 21-33-70004.

REFERENCES

1. Tamara V. Basova and Asim K. Ray. ECS J. Solid State Sci. Technol. 2020. **9** (6), 061001.
2. Ghosh, P., Han, G., De, M., Kim, C. K., & Rotello, V. M. Adv. Drug Deliv. Rev. 2008. **60** (11), 1307-1315.
3. Ozoemena, K. I., Nyokong, T. Talanta. 2005. **67**(1), 162-168.
4. Kind, M., & Wöll, C. Prog. Surf. Sci. 2009. **84** (7-8), 230-278.
5. Moiseeva E.O., *et. al*. Inorg. Chim. Acta. 2022, DOI: 10.1016/j.ica.2022

Synthesis, Photochemical Properties and *in vitro* Cytotoxicity of Substituted Boron Subphthalocyanines

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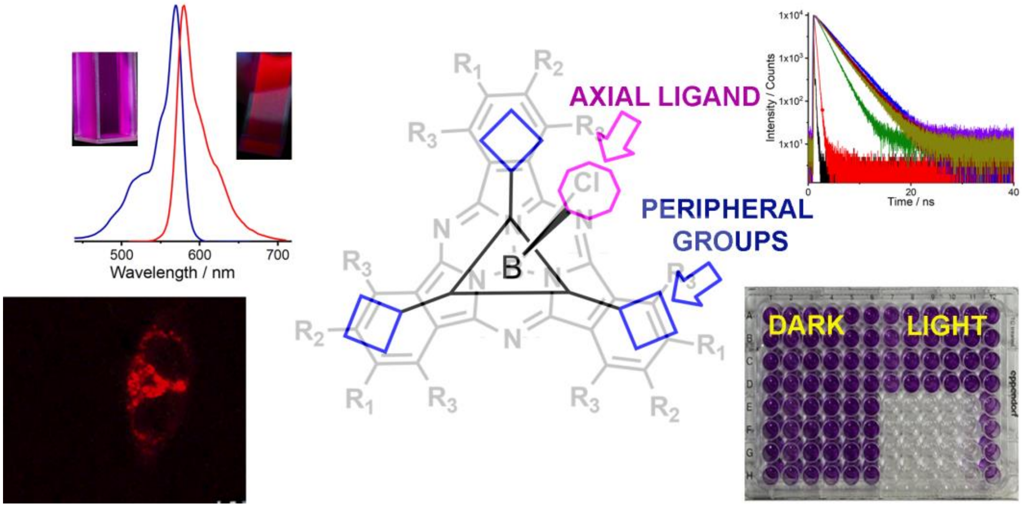
Boron subphthalocyanines bearing aryl, aryloxy, alkyl and halogen peripheral functional groups were tested as a photosensitizers and fluorophores. Synthetic protocols to novel 4-ethoxycarbonylphenoxy-substituted subphthalocyanine and phenoxy-substituted subphthalocyanine boron phenolate were presented.

The results of flesh photolysis measurements predicted the good ability of target boron subphthalocyanines to singlet oxygen formation and it was supported by the measurements of $^1O_2$ quantum yields (Φ_Δ=0.44÷0.85). Satisfactory yields of fluorescence (Φ_f=0.13-0.28) were observed for the main part of subphthalocyanines. The fluorescence decay kinetics was studied to determine the fluorescence lifetimes and confirm the regularities obtained for fluorescence yields.



Good fluorescent properties allowed investigating the distribution of boron subphthalocyanines in endoplasmic reticulum. The binding constants with bovine serum albumin were determined. Tetra-*tert*-butyl- and iodo-substituted subphthalocyanines demonstrate remarkable photocitotoxicity to human epidermoid carcinoma cells at micromolar concentrations. At the same time target boron subphthalocyanines exhibited low dark cytotoxicity and no oxidative stress without irradiation.

Acknowledgements: We thank RFBR 21-33-70004 mol_a_mos for financial support.

Perovskite Solar Cells with Diethynyl-Conjugated Zinc-Phthalocyanine Dimers as Hole-Transporting Materials for Improved Stability

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Perovskite solar cells (PSCs) are promising candidates to reach the market to complement the current offer of photovoltaic cells although for such a thing they still have to overcome some challenges such as long-term stability. The hole transporting layer (HTL) is a crucial component in n-i-p PSC, since it must favor an adequate movement of charges and protect the perovskite layer from environmental conditions. In this sense, the commonly used HTL, spiro-OMeTAD, does not provide PSCs with sufficient stability and is too expensive. Cheaper molecular materials such as metallophthalocyanines are proving to be a good alternative, as they provide greater stability.[1]

In this comunication, both the synthesis of new dimers based on zinc phthalocyanines (ZnPc) and their study as HTL in n-i-p PSCs are exposed. These dimers (**ZnPc-t-DPP-t-ZnPc 1**,[2] **ZnPc-t-t-ZnPc 2**,[3] **ZnPc-t-Spiro-t-ZnPc 3**, Figure 1) are connected by different groups through ethynyl bridges. PSCs containing **ZnPc-t-Spiro-t-ZnPc 3** yielded an efficiency of 18.32%, higher than the state-of-art spiro-OMeTAD (17.42%). Furthermore, ZnPc dimers showed improved long stability under different stress conditions such as moisture and thermal.[4]

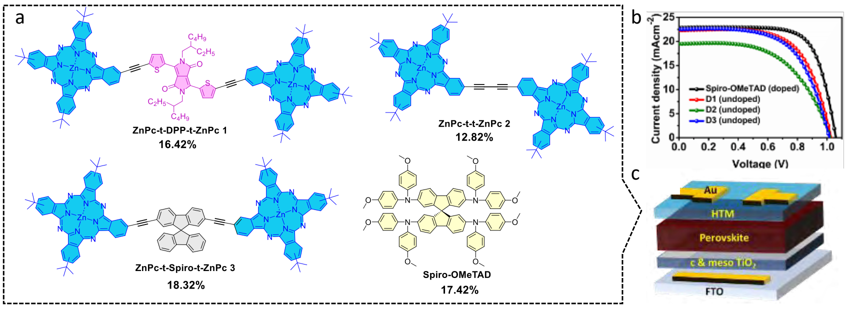

Figure 1. a) Chemical structure of the HTMs under study, b) *J*-V curves and c) representation of an n-i-p PSC device.

REFERENCES

1. a) M. Urbani, M. E. Ragoussi, M. K. Nazeeruddin, T. Torres, *Coord. Chem. Rev.* **2019**, *381*, 1-64; b) P. Huang, A. Hernández, S. Kazim, J. Ortíz, Á. Sastre-Santos, S. Ahmad *Sustainable Energy &Fuels.* **2020**, *4*, 6188-6195. c) D. Molina, M. A. Ruiz-Preciado, F. Sadegh, M. João Álvaro-Martins, M. Grätzel, A. Hagfeldt, Á. Sastre-Santos*, J. Porphyr. Phthalocyanines*, **2019**, *23*, 546–553. d) D. Molina, M. A. Ruiz-Preciado, B. Carlsen, F. T. Eickemeyer, B. Yang, N. Flores-Díaz, M. J. Álvaro-Martins, K. Nonomura, A. Hagfeldt and Á. Sastre-Santos, *ChemPhotoChem*, **2020**, *4*, 307–314. e) P. Huang, A. Hernández, J. Follana-Berná, S. Kazim, J. Ortíz, Á. Sastre-Santos, S. Ahmad, *ACS Appl. Energy Mater.* **2021**, 4, *9*, 10124–10135.
2. D. Molina, M. E. El-Khouly, M. El-Kemary, S. Fukuzumi, F. Fernández-Lázaro, Á. Sastre-Santos, *Chem. Eur. J.* **2016**, *22*, 17800-17807.
3. H. Yoshiyama, N. Shibata, T. Sato, S. Nakamura, T. Toru, *Chem. Commun.* **2008**, 1977-1979.
4. D. Molina, M. Pegu, M. João Álvaro-Martins, L. Ferrer, M. Castillo, S. Kazim, S. Ahmad, Á. Sastre-Santos, submitted.

Mono and Metallo-substituted porphyrins as antimicrobial agents against gram-positive and gram-negative bacteria

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Infectious diseases are the leading cause of death worldwide, particularly in developing countries [1]. The development of alternative technologies to overcome microbial resistance is necessary and PACT is one such attractive approach [2,3]. This study aimed to synthesize asymmetrically meso-substituted porphyrin H_2BPMPP containing two different types of meso-substituents and to enhance the photodynamic antimicrobial properties by inserting Zinc and Indium metals to their peripheral to form H_2BPMPP, ZnBPMPP, and ClInBPMPP. Photophysical properties were determined by measuring the UV-Vis absorption, singlet oxygen quantum yields, and Fluorescent quantum yields. The PACT activity of the photosensitizers was evaluated on both gram-positive (Staphylococcus aureus) and gram-negative bacteria (E.Coli).). The $\Phi\Delta$ values for H2BPMPP, ZnBPMPP and ClInBPMPP were 0.5705, 0.6734, 0.756 and ΦF values of 0.011, 0.007, 0.004 respectively. In all the photosensitizers there was reduced bacterial survival in S. aureus than in E. coli. ZnBPMPP and InBPMPP gave better inhibition compared to H2BPMPP. These results indicate that meso metalloporphyrin complexes can have a good antimicrobial activity after illumination than the free base porphyrin.

Antimicrobial activity of $H_2TBnOPP$, ZnBPMPP, and ClInBPMPP against *E. coli* was also done and discussed in this work.

REFERENCES

1. X. Fu, Y. Fang, and M. Yao, “Antimicrobial Photodynamic Therapy for Methicillin-Resistant Staphylococcus aureus Infection,” *Biomed Res. Int.,* vol. 2013, pp. 1–9, 2013.
2. F. Fayyaz, R. Rahimi, M. Rassa, and R. Hedayat Yaghoobi, “Photodynamic antimicrobial chemotherapy, a pathway for photo-inactivation of bacteria by porphyrins compounds,” *Proc. 1st Electron. Conf. Mol. Sci.,* no. October, p. b003, 2015.
3. A. Almeida and A. Cunha, “Photodynamic inactivation of Penicillium chrysogenum conidia by cationic porphyrins Photodynamic inactivation of Penicillium chrysogenum conidia by cationic,” no. November 2014, 2011.

Iron- and heme-mediated regulation of the nickel uptake system of *Vibrio cholerae* and physiological significance

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For most bacteria, Fe^{2+} is an essential element for their survival, and in response to Fe^{2+}, many iron metabolism proteins were regulated by a transcription factor, Ferric uptake regulator (Fur). Fur regulates downstream gene expression by binding to the specific DNA sequence, Fur box. Interestingly, we found a Fur box sequence just upstream of the *nik* operon encoding proteins for the nickel uptake system in *Vibrio cholerae*, suggesting that the *nik* operon is regulated by Fe^{2+} via Fur. To examine the Fur box binding of Fur from *V. cholerae* (*Vc*Fur) in the presence of Fe^{2+}, the titration of *Vc*Fur against the 6-FAM-modified Fur box was performed, showing a biphasic binding curve (Fig. 1, black circles). The addition of Salmon sperm DNA (SalDNA), which non-specifically binds to the Fur box sequence, resulted in disappearance of the low-affinity binding process at [*Vc*Fur] > 10 mM, indicating that the low-affinity binding process was non-specific binding (Fig. 1 black triangles). On the other hand, the high affinity binding process at [*Vc*Fur] < 10 mM, which was independent of the concentration of SalDNA (Fig.1 black circles and triangles), corresponds to the specific binding of Fur to Fur box. The value of K_d for the Fur-Fur box binding was 1 mM. This value is 20-50 times larger than that of Fur from other species. The fluorescence anisotropy measurements in the presence of Ni^{2+} showed that, unlike the case of Fe^{2+}, the addition of SalDNA shifted the entire plot to the right, and non-specific DNA binding of Fur was observed. (Fig. 1 red circles and triangles).

Interestingly, Fe^{2+}-induced Fur box binging in *Vc*Fur was inhibited by the addition of heme. As clearly shown in Fig. 2, the fluorescence anisotropy was decreased by the addition of heme, indicating that Fur was dissociated from the Fur box. The decreased anisotropy was restored when apo-myoglobin (Fig.2 red triangles) was added to extract heme from *Vc*Fur. These results suggest that the Ni^{2+} uptake system in *V. cholerae* is regulated by iron and heme, but the physiological function of Ni^{2+} in *V. cholerae* is not reported. Therefore, it is more plausible that the *nik* operon of *V. cholerae* has a function other than the uptake of nickel. One of the *nik* operon protein, NikA of *Escherichia coli* (*Ec*NikA) has been reported to bind heme, suggesting that it is involved in the heme metabolism. VCA1098, a homologue of *Ec*NikA, is present in the *nik* operon of *V. cholerae*. As we expected, VCA1098 was found to bind heme with low affinity (K_d = 1.3 μM). The K_d value is about 100 times larger than that of proteins binding heme as the active center. The heme binding to VCA1098, therefore, functions as a regulator of nickel uptake or heme transporter in *V. cholerae*.

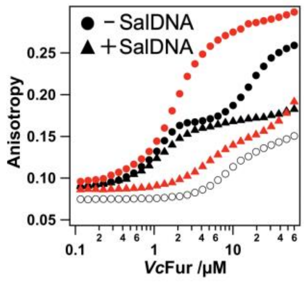


Fig. 1. Evaluation of Fur box binding of VcFur in the presence of 1 mM Fe2+ or Ni2+

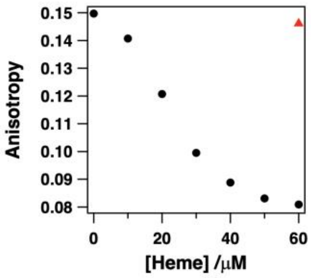
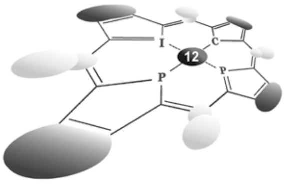


Fig. 2. Inhibition of Heme binding by *Vc*Fur.



On-surface Porphyrin Transmetalation with Pb/Cu Redox Exchange

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Metal surfaces and interfaces functionalized with metal complexes play important roles in modern technologies such as catalysis, sensors, and organic electronics. Since the chemical and (opto-)electronic properties of the complexes are partly determined by their central metal atoms, stability with respect to metal exchange at the interface is a crucial issue. Here, we studied a model transmetalation reaction, i.e., the exchange of the central atom of a complex, between Pb(II) tetraphenylporphyrin (PbTPP) and Cu atoms from a Cu(111) surface.[1] X-ray photoelectron spectroscopy (XPS) showed that the Pb/Cu exchange starts around 380 K and is complete at 600 K. The identity of the reaction product, CuTPP, was confirmed by mass spectrometry. Scanning tunneling microscopy (STM) uncovers structural changes accompanying the metal exchange and additional reactions of the ligand. Our study reveals that metal exchange reactions of complexes at interfaces can proceed already at moderate temperatures and thus can affect the operational stability of functionalized hetero interfaces.

REFERENCES

1. J. Herritsch, S. R. Kachel, Q. Fan, M. Hutter, L. J. Heuplick, F. Münster, J. M. Gottfried, *Nanoscale*, 2021, **13**, 13241–13248.

Tetrabromo[36]octaphyrin: A Promising Precursor of Directly Fused Porphyrin(2.1.1.1) Dimer and *meso-α* Fused N-Confused Porphyrin Dimer

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Porphyrin tapes have been targets of extensive studies because of their remarkably red-shifted absorptions, multi-charge responsibility, and electric conductivity.[1] A variety of porphyrin tape variants have also been created to display perturbed photophysical properties being characteristic of constituent porphyrin(oid) units. Such tape-like porphyrinoid arrays are synthesized mostly by oxidative fusion of the corresponding singly-linked precursors.
Here we found that tetrabromo[36]octaphyrin was transformed into novel fused porphyrin dimers such as porphyrin(2.1.1.1) dimer **2** and N-confused porphyrin dimer **3** through metalation-induced transannular C–C bond formation. Tetrabromo[36]octaphyrin **1** was synthesized as a nonaromatic *meso*-free type octaphyrin. Zn(II) complexation of **1** afforded bis-Zn(II) complex **2** through C_{meso}–C_{meso} bond formation. The complex **2** exhibited a diatropic ring-current effect due to its 36π Möbius aromaticity.[2] On the other hand, Ni(II) complexation of **1** caused C_{meso}–C_{β} bond formation with concomitant debrominations to afford bis-Ni(II) complex **3**, which showed a paratropic ring-current effect due to its global 36π Hückel antiaromaticity.

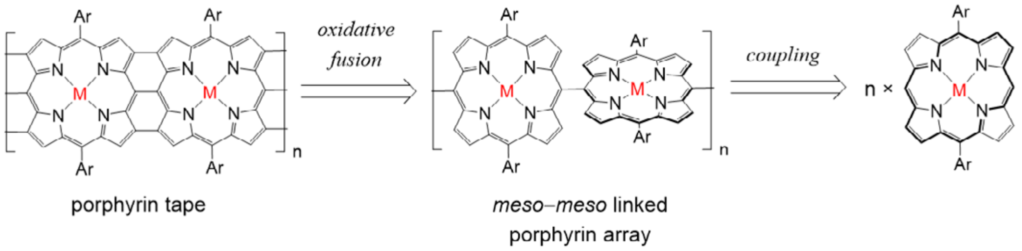
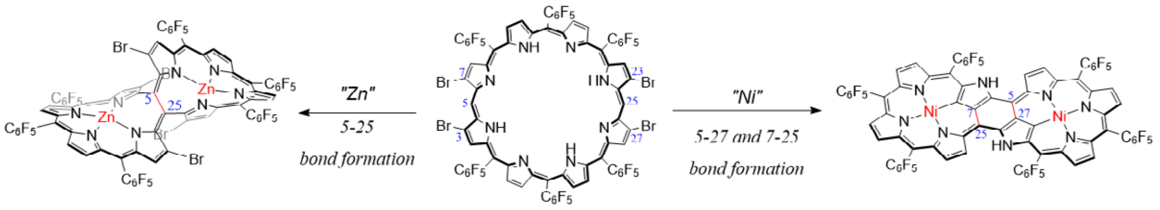


Figure 1. Typical synthetic route of porphyrin tape.



2
36π Möbius aromatic

[36]octaphyrin **1**
nonaromatic

3
36π antiaromatic

Scheme 1. Synthesis of **2** and **3**.

REFERENCES

1. T. Tanaka, A. Osuka, *Chem. Soc. Rev.* **2015**, 44, 943.
2. a) T. Tanaka, A. Osuka, *Chem. Rev.* **2017**, 117, 2584
   b) D. Kim, A. Osuka *et al. Angew. Chem. Int. Ed.* **2008**, 47, 681.
3. For the details of this work, see; A. Nakai, J. Kim, T. Tanaka, D. Kim, A. Osuka, *Angew. Chem. Int. Ed. in press.* (DOI: 10.1002/anie.202112023)

Formation of a stable compound I in the peroxidase activity of heme bound Aβ complexes associated with Alzheimer’s disease

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Colocalization of heme rich deposits in the senile plaque of Aβ in the cerebral cortex of Alzheimer’s disease (AD) brain along with altered heme homeostasis and heme deficiency symptoms in AD patients have invoked the association of heme in AD pathology [1-3]. Heme binds to Aβ to form heme-Aβ complex and depending on the concentration of the complex or peptide to heme ratio it exhibits an equilibrium between a high spin mono-His bound peroxidase-type active site and a low spin bis-His bound cytochrome b type active site [4-6]. The high spin heme-Aβ complex shows higher peroxidase activity than free heme where compound I is the reactive oxidant [6-7]. It is also capable of oxidizing neurotransmitters like serotonin in the presence of peroxide, owing to the formation of compound I [6-7]. The low spin bis-His heme-Aβ complex on the other hand shows enhanced peroxidase activity relative to high spin heme-Aβ. It reacts with H_2O_2 to produce two stable intermediates compound 0 and compound I which are characterized by absorption, EPR and resonance Raman spectroscopy. The stability of compound I of low spin heme-Aβ is accountable for its enhanced peroxidase activity and oxidization of the neurotransmitter serotonin. The effect of second sphere Tyr10 residue of Aβ in the formation and stability of the intermediates of low spin heme-Aβ has also been investigated. The higher stability of compound I for low spin heme-Aβ indicate that in contrast to the high spin form Tyr10 [6-7] in this case is redox inactive possibly due to its involvement in H-bonding interactions at the distal pocket.

REFERENCES

1. J. Flemmig, M. Zámocký and A. Alia, *Neural Regen. Res.,* 2018, **13**, 1170–1174.
2. T. Kimpara, A. Takeda, T. Yamaguchi, H. Arai, N. Okita, S. Takase, H. Sasaki and Y. Itoyama, *Neurobiol. Aging,* 2000, **21**, 551–554.
3. H. M. Schipper, S. Cissé and E. G. Stopa, Ann. *Neurol.,* 1995, **37**, 758–768.
4. D. Pramanik and S. Ghosh*, J. Am. Chem. Soc.,* 2011, **133**, 81–87.
5. C. Ghosh, S. Mukherjee, M. Seal and S. Ghosh, *Inorg. Chem*., 2016, **55**, 1748–1757.
6. M. Roy, I. Pal, A. K. Nath and S. G. Dey, *Chem. Commun.,* 2020, **56**, 4505–4518.
7. I. Pal, A. K. Nath, M. Roy, M. Seal, C. Ghosh, A. Dey and S. G. Dey, *Chem. Sci.,* 2019, **10**, 8405–8410.

Screening a Wide Range of Porphyrin Luminophores for Novel Pressure Sensitive Paint Formulations

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Pressure Sensitive Paint (PSP) is a new method of measuring pressure distribution over an aircraft model in a wind tunnel using optical oxygen sensors, known as luminophores. The field settled early on platinum(II) 5,10,15,20-tetrakis-(2,3,4,5,6-pentafluorophenyl)porphyrin (figure 1) as the main luminophore, as it has ideal photo physical properties suited for oxygen sensing [1]. These compounds are formulated into paint formulations with an oxygen permeable binder such as various polymers [2], porous substrates [3] and polymer ceramic formulations [4]. When excited the luminophores phosphoresce, which can be quenched by the presence of local oxygen and so the intensity of phosphorescence decreases and therefore is proportional to the partial pressure of oxygen in the air. When the model is placed into a wind tunnel, the varying pressure caused by air currents causes a dynamic quenching environment that can be imaged and processed to generate a global pressure map. The PSP method is easy to apply to the model, provides global coverage and has a much higher resolution than pressure tap measurements.

There are to date few publications describing the effect of the luminophore identity on the paints characteristics. Porphyrins are a rich family of strong light absorbing compounds and there is a great variety of halogenated metalloporphyrins [5] and metallobenzoporphyrins [6] that are being developed for other oxygen sensing platforms. Therefore, this work aims to synthesise and characterise a large variety of metalloporhyrins and benzometalloporphyrins and study the effect of these compounds chemical structure and identity of the central metal ion on the performance of PSP formulations.

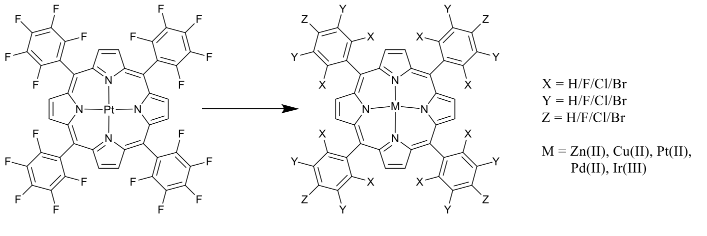

Figure 1: The current luminophore (right) and the structure of luminophores studied in this work (left).

REFERENCES

1. N. Hasebe, K, Suzuki, H. Horiuchi, H. Suzuki, T. Yoshihara, T. Okutsu, S. Tobita, *Anal. Chem.*, 2015, **87**, 2360-2366
2. Y. Takeuchi, Y. Amao, in *Frontiers in Chemical Sensors,* G. Orellana, M. Moreno-Bondi, Springer, Switzerland, Vol 1, 2005, ch 10, 303-322
3. H. Zare-Behtash, L. Yang, N. Gongora-Orozco, K. Kontis, A. Jones, *Measurement*, 2012, **45**, 1902-1905
4. D. Peng, F. Gu, Y. Li, Y. Liu, *Sensor. Actuat. A-phys.*, 2018, **279**, 390-398
5. C. Arunkumar, F. R. Kooriyaden, X. Zhang, S. Sujatha, J. Zhao, *New. J. Chem.*, 2017, **41**, 4908 4917
6. S. M. Borisov, G. Nuss, I. Kilmat, *Anal. Chem.*, 2008, **80**, 9435-9442

Nanographene-Fused Porphyrins

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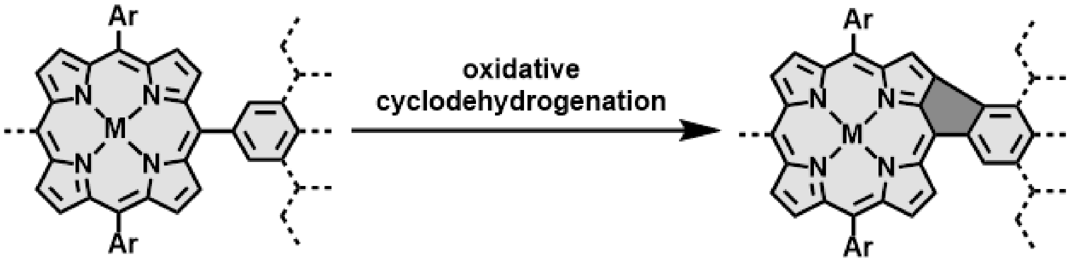
The application of porphyrins as a main element for the design of extended carbon-based frameworks gained increasing popularity in recent years [1]. The fusion of aromatic hydrocarbons of various sizes to the *β*- and *meso*-positions of porphyrins emerged hereby as a particularly convenient strategy for an effective expansion of the aromatic network [2]. The here presented extension of the π-system leads to substantial alterations in optical and electrochemical features. These changes involve a bathochromic shift in the absorption spectrum, increased absorption in the NIR range as well as a profound decrease of the HOMO-LUMO gap [3].



REFERENCES

1. Borissov A, Maurya YK, Moshniaha L, Wong W-S, Żyła-Karwowska M and Stępień M. Chem. Rev. 2022; **122**: 565–788.
2. Martin MM, Oleszak C, Hampel F and, Jux N. *Eur. J. Org. Chem.* 2020; **40**: 6578-6762.
3. Oleszak C and Jux N. Manuscript in preparation.

Constructing cytochrome *c* with enhanced dye-decolorizing activity

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Dye-decolorizing peroxidase (DyP) is an enzyme that can degrade compounds difficult to be decomposed such as anthraquinone dyes [1]. To examine the possibility of the application for environmental purification, we constructed an *Escherichia coli* (*E. coli*) strain expressing DyP. However, the dye-degradation activity of the strain was not so high, due to the low heme contents of DyP in cells. Thus, we tried to design an artificial peroxidase based on cytochrome *c* (cyt *c*), whose heme is covalently bound to the protein.

In the presence of an artificial dye, reactive blue 19 (RB19), significant dye-decolorizing activity (k_{cat}/K_m = 44 $s^{-1}mM^{-1}$), 60 % of DyP at pH 4.5 (Table 1), was detected for cyt *c* under the high H_2O_2 concentration (20 mM) conditions, but the turnover under low H_2O_2 concentration (200 μM) conditions was ~1/60 that of DyP at pH 4.5, suggesting the low affinity of cyt *c* to H_2O_2. To enhance the affinity of H_2O_2 to cyt *c*, we prepared a mutant lacking one of the axial heme ligands by replacing Met80 with Val (M80V) (Fig. 1). However, the activity of M80V was only 1.5 times larger than that of wild type protein (WT) (Table 1), and the lack of a heme axial ligand did not result in the drastic improvement of the dye-degrading activity. Another factor to increase the dye-decolorizing activity is improvement of low binding affinity of the dye substrate (Table 1). We focused on aromatic amino acid residues on the protein surface since they are function as the substrate binding site as well as the active center in DyPs [2]. Considering that introduction of Trp to the myoglobin surface significantly increased the dye-degrading activity by π-π stacking interaction between Trp and RB19 [3], we replaced Pro76, located on the protein surface near the putative substrate binding sites, with Trp (P76W). The k_{cat}/K_m value of the mutant was 138 $s^{-1}mM^{-1}$, which was ~3-fold larger than that of WT cyt *c*. However, the *E. coli* strain expressing the mutant failed to degrade RB19. The UV/vis spectrum of the cyt *c* mutant in *E. coli* indicated the heme iron was reduced to form reduced cyt *c* in cells, which is inactive to H_2O_2. To stabilize the oxidized form of cyt *c*, we replaced Gly29 near His18 with Asp (G29D) (Fig. 1) to form a hydrogen bond between axial His and Asp, which stabilizes the ferric state of the heme iron and promotes the reaction with H_2O_2 as found for many peroxidases [4]. The mutation resulted in the drastic enhancement (~80-fold) of the dye-decolorizing activity (Table 1). In summary, we found that cyt *c* can decompose the artificial dye and the activity was drastic improved by the formation of the hydrogen bond with the axial histidine. We are now trying to construct an effective dye-degradation system in *E. coli* based on this mutation.

		RB19			
		K_m	k_{cat}	k_{cat}/K_m	turnover
protein	pH	μM	s^{-1}	s^{-1} mM^{-1}	min^{-1}
WT	7.0	53 ± 6	2.3 ± 0.1	44 ± 5.9	0.7 ± 0.1
M80V	7.0	49 ± 3	3.4 ± 0.1	70 ± 5.1	–
P76W	7.0	25 ± 2	3.4 ± 0.1	138 ± 12	–
G29D	7.0	0.70 ± 0.09	2.5 ± 0.05	3825 ± 483	–
DyP	4.5	30 ± 3	2.3 ± 0.1	77 ± 11	36 ± 0.3

Table 1. DyP activity of DyP and cyt *c*

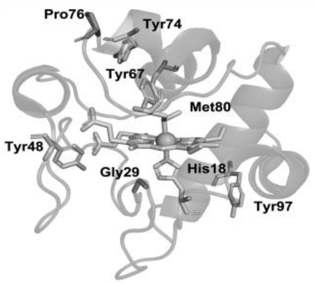

Fig. 1. The structure of cyt *c*

REFERENCES

1. Sugano *et. al*., (1999) *J. Biosci. Bioeng*., **87** (4), 411-417
2. Uchida *et al*., (2021) *J. Inorg. Biochem*., **219**, 111422
3. Zhang *et. al*., (2019) *ACS Catal.,* **9** (9), 7888-7893
4. Goodin (1996) *JBIC*., **1**, 360-363

meso-tetra-dihydro benzocyclobutacenaphthylene free-base porphyrin: synthesis and characterization

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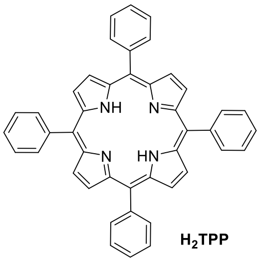
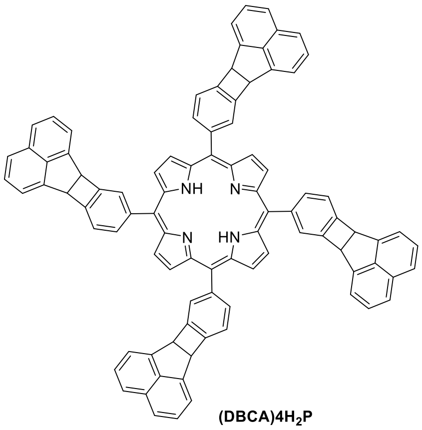
Porphyrin $(DBCA)_4H_2P$ which has 8(9)-6b,10b-dihydrobenzo[j]cyclobut[a]acenaphthylene units directly on the meso positions of the porphin core has been synthesized. Its photophysical, photochemical and electrochemical properties, as well as its frontier orbitals and the HOMO–LUMO gaps, have been determined and compared to those of tetraphenylporphyrin [1].



H_2TPP



$(DBCA)4H_2P$

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REFERENCES

1. Ü. İşci, S. Z. Topal, E. Önal, İ. Fidan, S. Berber, V. Ahsen, C. Parejo, A. Sastre-Santos and F. Dumoulin, J. Porphyrins Phthalocyanines, 2018; 21: 173–180

Porphyrin-cubane/BCP arrays as sensor for metal perchlorates

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In nature, many proteins contain metal ions as cofactors. The selection of a particular metal in a specific oxidation state is crucial for the biological function.[1] The amide linkage in proteins offers two potential binding sites, oxygen for the interaction with protons, and nitrogen for the metal ions binding. Tetrapyrroles and their derivatives represent a class of chromophoric systems that have been widely used for metal ion recognition processes, due to their remarkable photophysical and electrochemical properties.[2;3]

To this end, porphyrin-cubane/BCP arrays [BCP = bicyclo(1.1.1)pentane] featuring a combination of BCP/cubane units and a semi-rigid amide linkage (Figure 1a) were investigate for their suitability as receptors for transition metals in form of their perchlorate salts.[4] A spectroscopic investigation revealed that these porphyrins **1** and **2** possesses both strong anion and cation recognition sites.

The complexes formed were studied using UV-Vis, fluorescence (FL), time-correlated single photon counting (TCSPC), and ^{1}H NMR spectroscopy. In particular, the stoichiometry of binding and limit of detection (LOD) were calculated using UV-Vis, and fluorescence spectroscopy (Figure 1b). NMR spectroscopy was employed to investigate the mode and site of complex formation. Also, circular dichroism (CD) spectroscopy was used to study a conformational switch upon formation of supramolecular complexes. These spectroscopic investigations suggest that the coordination of $MClO_4$ can act as a driving force to control the conformation of the porphyrin unit. The supramolecular architectures formed, indicate the possibility to mimic a protein structure due to the sp^3 rigid aliphatic hydrocarbon scaffolds (BCP or cubane) that exhibit the essential conformational space for protein function while simultaneously providing amide bonds for molecular recognition. Reversible photophysical changes indicate that these dimeric systems act like switchable porphyrin tweezers.

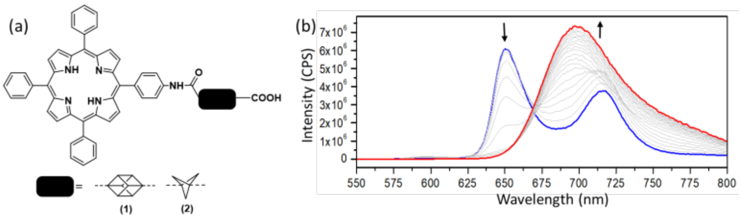

Figure 1: a) Chemical structure of porphyrin arrays; b) fluorescence spectral titration of porphyrin-BCP array in presence of $Fe(ClO_4)_2$ in $CHCl_3$.

REFERENCES

1. K. J. Waldron, J. C. Rutherford, D. Ford, N. J. Robinson, Nature, 2009, 460, 823–830.
2. Y. Ding, W.-H. Zhu, Y. Xie, Chem. Rev., 2017, 117, 2203–2256.
3. S. Bettini, R. Pagano, L. Valli, G. Giancane, J. Phys. Chem. C, 2014, 118, 23, 12384–1239.
4. (a) N. Grover, G. M. Locke, K. J. Flanagan, M. H. R. Beh, A. Thompson, M. O. Senge, Chem. Eur. J. 2020, 26, 2405–2416; (b) N. Grover, M. O. Senge, *Synthesis*, 2020, 52, 3295–3325.

Alkali Metal Ion Capture Using Cyclic Polyketones and Application to Reactions

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Cyclic compounds with selective and reversible binding of metal ions have been applied to ion adsorption and catalytic reactions. We have reported that linear polyketones **1** composed of 3,3-dimethylpentane-2,4-dione as a repeating unit has lithium-ion conductivity [1]. On the other hand, cyclic polyketones **2**-**5** consisting of the same repeating unit are capable of binding alkali metal ions depending on their ring size (**Figure 1**). In this study, we apply the metal-ion binding property of these cyclic hexa- to dodeca-ketones **2**-**5** to catalyze reactions and for the design of new alkali metal ion capture molecules [2].

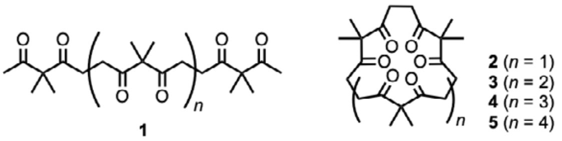
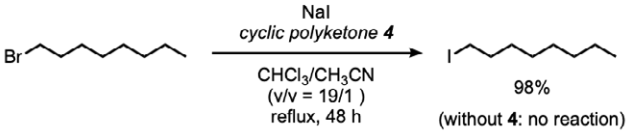


Figure 1. Linear and cyclic polyketones.

Association constants of cyclic polyketones **2**-**5** with Na^+ ion were investigated by NMR titration experiment in mixture of $CDCl_3/CD_3CN = 9/1$ (v/v). Na^+ ion capture was observed for cyclic polyketones **3**-**5**, while cyclic deca-ketone **4** showed the highest association constant ($K = 9.2 \times 10^3\ M^{-1}$). Alkali ion-binding hosts **3**–**5** exhibited catalytic activity for the Finkelstein reaction in low-polarity solvents. The observed positive correlation between catalytic activity and sodium ion binding constants (**Scheme 1**). Since no interaction with alkali metal ions was observed in the linear octa-ketone, we attempted to functionalize the molecular terminal sites in expectation of changing the binding properties. Linear compound **6** with pyrenes at the terminal sites induced a pseudo-cyclic structure due to π-π interactions, and showed high association ability with Na^+ ion ($K = 6.4 \times 10^2\ M^{-1}$), which is almost 6.5 times higher than the cyclic octa-ketone **3** ($K = 9.8 \times 10^1\ M^{-1}$) (**Figure 2**). The optimized structure of **6**•Na^+ obtained from the theoretical studies revealed that the pseudo-cyclic conformation is stabilized by five C=O•••Na^+ coordination bonds with pyrene moieties no longer showing π-stacking interactions. The terminal functionalization of linear polyketones can change the ring size and the association constant with alkali metal ions.



Scheme 1. Finkelstein reaction catalyzed by cyclic polyketones **2**-**5**.

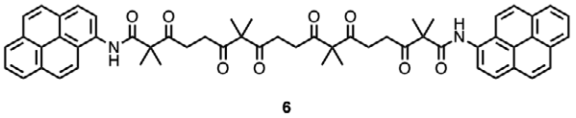


Figure 2. Linear compound **6** with pyrene units.

REFERENCES

1. T. Eriksson, A. Mace, Y. Manabe, Y. Yoshizawa-Fujita, Y. Inokuma, D. Brandell, J. Mindemark, *J. Electrochem. Soc.*, **2020**, *167*, 070537.
2. N. Ozawa, K. I. Shivakumar, M. Murugavel, Y. Inaba, T. Yoneda, Y. Ide, J. Pirillo, Y. Hijikata, Y. Inokuma, *Chem. Commun.*, **2022**, *in press*.

Green and fast synthesis of porphyrin-Ag nanostructured adducts for photocatalytic applications

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Porphyrins constitute a ubiquitous class of molecules largely employed in different application fields [1]. In order to enhance the performance of porphyrin-based devices, tetrapyrrolic compounds are often coupled to metallic nanoparticles. It has been demonstrated that the singlet oxygen production can be maximized when porphyrin derivatives are opportunely coupled to plasmonic metal. Furthermore, porphyrin-nanoparticle hybrid nanostructures have been used to enhance light harvesting [2] for photodegradation of different organic compounds [3]. In this work, supramolecular adducts formed by a commercial porphyrin derivative and silver nanoparticles have been obtained using exclusively light as an external trigger that is able to promote the formation of the plasmonic nanostructures. In particular, a water-soluble porphyrin, i.e. tetrakis(4-carboxyphenyl)porphyrin, has been used. We demonstrate that, by means of light illumination, it is possible to tune the porphyrin aggregation state. Furthermore, when the monomeric form of the organic macrocycle is induced and a controlled amount of $AgNO_3$ is simultaneously dissolved, it is possible to promote the formation of silver nanostructures using visible light. The proposed eco-friendly mechanism allowed porphyrin derivatives/Ag hybrid nanostructures to be obtained without using a chemical reducing agent. The porphyrin derivative simultaneously acts as reducing agent when irradiated by visible light and as a capping agent for the silver nanostructures. The organic/inorganic adduct was characterized by means of steady-state fluorescence that highlights a strong energetic or electronic communication between the two species. XRD and SEM investigations evidence that silver nanoparticles are formed without using any reducing agent. Radical Oxygen Species (ROS) production under visible light was finally preliminary tested.

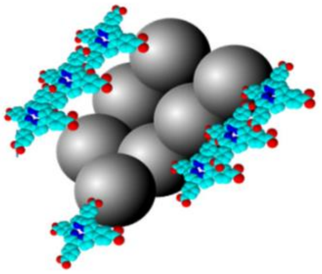
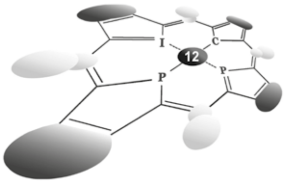


Figure 1 Schematization of proprphyrin/Ag adducts.

REFERENCES

1. Urbani M, De La Torre G, Nazeeruddin MK and Torres T. *Chem. Soc. Rev.* 2019; 48: 2738–2766.
2. Kundu S and Patra A. *Chem. Rev.* 2017; 117: 712–757.
3. Shee N. K. , Kim M,. K. and Kim H. *Nanomaterials* 2020, 10: 2314



YfeX– A New Platform for Carbene Transferase Development with High Intrinsic Reactivity

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Biocatalysts containing transition metals have been shown to synthesize carbon-carbon and carbon-nitrogen bonds stereospecifically through carbene insertion reactions, generating few by-products.[1-3] Typically, industry uses metallo- and organocatalysts to perform carbene insertion reactions; however, these catalysts often lack selectivity.[4-6] In the work presented here, we explore the use of a novel protein scaffold, YfeX, to make these reactions more efficient and environmentally friendly for pharmaceutical and fine chemical synthesis. The product yields, stereochemistry of the products and the catalytic mechanism were analyzed using gas chromatography-mass spectroscopy (GCMS), supercritical fluid chromatography (SFC), UV-Visible spectroscopy, and density-functional theory (DFT) calculations. We compare wild-type (WT) YfeX to other heme-biocatalysts and artificial metalloenzymes. WT YfeX shows high levels of reactivity and stability in aqueous environments with a wide variety of substrates. Correspondingly, YfeX shows great potential to be an alternative to traditional industrial catalysts with the natural relative stereo- and enantioselectivity needed for the generation of pharmaceuticals and fine chemicals.

REFERENCES

1. Lim, X., The new breed of cutting-edge catalysts. *Nature News* **2016,** *537* (7619), 156.
2. JaneáWang, Z., P450-catalyzed asymmetric cyclopropanation of electron-deficient olefins under aerobic conditions. *Catal. Sci. Technol.* **2014,** *4* (10), 3640-3643.
3. Wang, Z. J.; Peck, N. E.; Renata, H.; Arnold, F. H., Cytochrome P450-catalyzed insertion of carbenoids into N–H bonds. *Chem. sci.* **2014,** *5* (2), 598-601.
4. Shanab, K.; Neudorfer, C.; Schirmer, E.; Spreitzer, H., Green solvents in organic synthesis: an overview. *Curr. Org. Chem.* **2013,** *17* (11), 1179-1187.
5. Sinou, D., Metal catalysis in water. *Modern Solvents in Organic Synthesis* **1999**, 41-59.
6. Horvath, I. T.; Anastas, P. T., Innovations and green chemistry. *Chem. rev.* **2007,** *107* (6), 2169-2173.

Synergistic Photodynamic and Photothermal Therapy of binaphthyl-Bridged AABB Phthalocyanines

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Theragnostic nanostructures for both, monitoring and therapeutic purposes, have a key role in the fight against cancer. Nanoassemblies of photophysically active molecules have furthered the efficacy of photodynamic (PDT) and photothermal therapies (PTT) [1].

The great advantage of nanomedicines based on self-assembly is their high potential to build smart photosensitisers (PS). By controlling non-covalent interactions between components, assembled nanoparticles (NP) can achieve precise targeting and enhanced therapy based on their reversible assembly/disassembly process. With intelligent monomer design, a partial disassembly of the nanostructures inside the cells results in the recovery of their photophysical activity (previously cancelled in the assembled state) [2], leading to a combination of photodynamic and photothermal therapy that can dramatically improve anti-tumour efficacy [3].

Phthalocyanines (Pcs) are frequently used as PS and, more recently, as promising photothermal agents due to their unique photochemical and structural characteristics. By tuning their structure, they can be programmed to self-assemble in aqueous media. Binaphthyl-bridged AABB Pcs previously reported in the group are representative examples of amphiphilic PS capable of forming highly stable NPs with PDT abilities [4].

We have designed and prepared different binaphthyl-bridged AABB Pcs with different hydrophilic substituents, programmed to spontaneously aggregate in aqueous media, forming stable spherical NP in the 10-50 nm scale. Biological assays indicate that the NP penetrate into cell, where remain partially assembled rendering: i) high temperature increase after laser irradiation (i.e. PTT), and ii) singlet-oxygen generation abilities (i.e. PDT).

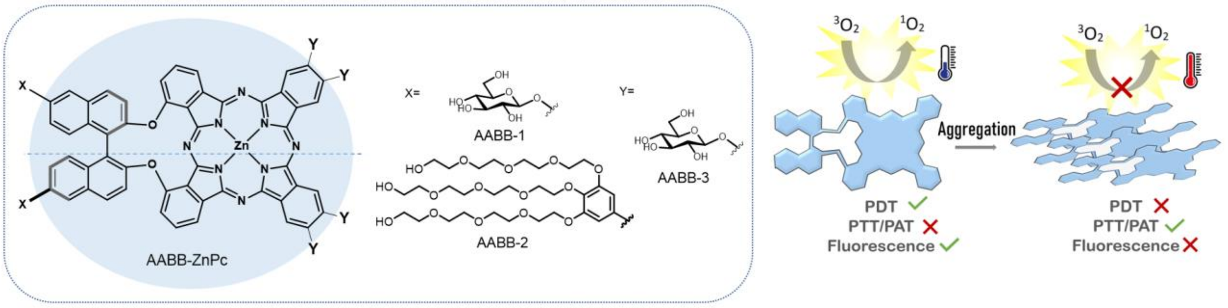

Figure 1: Binaphthyl-bridged AABB Pcs structure and schematic illustration of switchable photoactivity

REFERENCES

1. L. Zhao, Y. Xing, R. Wang, F. Yu, and F. Yu. ACS Applied Bio Materials. 2020, 3, 1, 86-106.
2. I. Paramio, T. Torres, G. De La Torre. ChemMedChem. 2021, 19, 2441-2451.
3. A. Ouyang, D. Zhao, X. Wang, W. Zhang, T. Jiang, A. Li, W. Liu. J. Mater. Chem. B. 2022, 10, 306-320.
4. M. A. Revuelta, E. De Las Heras, M. Agut, S. Nonell, T. Torres, G. De La Torre. Chem. Eur. J. 2021, 27, 15, 4955-4963.

Formation of zinc porphyrin network *via* non-covalent interaction

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Porphyrin derivatives are abundant in nature and are used as various functional building blocks such as chlorophyll, heme. In this study, a porphyrin tripod ($P_{Zn}T$) composed of three zinc porphyrin wings connected via triazole bridges was prepared as a monomeric building block for a supramolecular polymer. $P_{Zn}T$ formed long fibrous supramolecular polymers with a diameter of 7 nm through the axial coordination of triazole nitrogen atoms to zinc porphyrins. The molecular packing structure of a $P_{Zn}T$-based supramolecular polymer was assigned as a hexagonal columnar phase. $P_{Zn}T$ formed a stable 1:1 host–guest complex with 1,3,5-tris(4-pyridyl)benzene (Py3B) through axial coordination of pyridyl groups to zinc porphyrins. The host–guest complex between $P_{Zn}T$ and Py3B adopts a cone-shaped geometry. After the addition of Py3B, the host–guest complex exhibited a characteristic X-ray diffraction pattern of rectangular columnar ordering. Furthermore, the formation of supercoiled helical fibrous assemblies was observed by transmission electron microscopy (TEM).

REFERENCES

1. *Macromolecules* 2020, 53, 18, 8060–8067

Synthesis of hemihexaphyrazines

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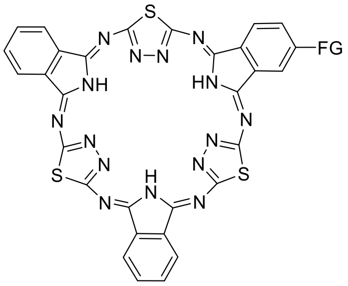
Expanded porphyrinoids display modified π-systems that alter the porphyrin aromatic character. In addition, their large, polydentate central cavities provide interesting coordination abilities, such as anion binding, or multimetallic complexation, which are virtually inaccessible within the corresponding tetramers [1,2,3]. Expanded porphyrinoids also show unusual optical, electrochemical and photophysical properties that render them promising building blocks for the construction of new molecular materials at different technological fields [4]. Contrasting with the great assortment of expanded porphyrins reported to date, examples of the corresponding expanded *meso*-aza-analogues are still very scarce. One prototypical example of the latter is the family of the hemihexaphyrazines, a kind of expanded hemiporphyrazine hexamer that has been developed in our group [5]. The aim of this work is to donate the periphery of the hemihexaphyrazine macrocycle with functional groups (FG= halogen, OH, CO_2H, etc.) that can supply different physicochemical properties and/or can function as linkers to assemble hemihexaphyrazines to other chromophores such as phthalocyanines. The latter should allow to generate new hybrid systems that combine the properties of both porphyrinoids, and study the electronic interactions between them.



REFERENCES

1. Tanaka T., Osuka A. *Chem. Rev.* **2017**, *117*, 4, p. 2584-2640.
2. Sung Y.M., Oh J., Cha W.-Y., Kim W., Lim J.M., Yoon M.-C., Kim D. *Chem. Rev.* **2017**, *117*, 4, p. 2257-2312.
3. Brewster J.T., Mangel D.N., Gaunt A.J., Saunders D.P., Zafar H., Lynch V.M., Boreen M.A., Garner M.E., Goodwin C.A.P., Settineri N.S., Arnold J., Sessler J.L. *J. Am. Chem. Soc.* **2019**, *141*, 44, p. 17867-17874.
4. Arambula J.F., Sessler J.L. *Chem.* **2020**, *6*, 7, p. 1634-1651.
5. Trukhina O.N., Rodríguez-Morgade M.S., Wolfrum S., Caballero E., Snejko N., Danilova E.A., Gutiérrez-Puebla E., Islyaikin M.K., Guldi D.M., Torres T. *J. Am. Chem. Soc.* **2010**, *132*, p. 12991-12999.

Photoinduced Energy and Electron Transfer in Cofacial Porphyrin Heterodimers

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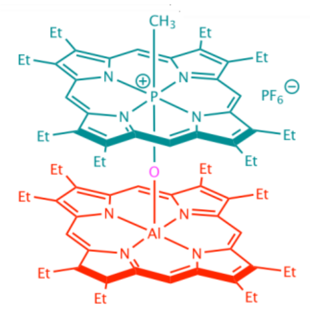
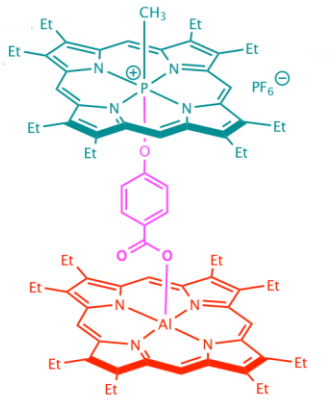
Cofacial 'aluminum(III) porphyrin – phosphorus(V) porphyrin' heterodimers have been synthesized to investigate the factors that govern the energy and electron transfer processes in a direction perpendicular to the porphyrin plane. The electron-rich aluminum(III) porphyrin acts as an electron and energy donor, whereas the electron-poor phosphorus(V) porphyrin performs the role of electron and energy acceptor. Steady-state absorption studies and DFT calculations performed to study the energy states and the orbital perturbation in the heterodimer compared to the corresponding monomers. Excitation of the AlPor unit in the heterodimer results in both energy and electron transfer from the ^{1}AlPor* to the PPor$^+$ unit. The relative yield of the energy and electron processes can be modulated by changing the solvent polarity or by changing the distance between two porphyrin rings. In contrast, excitation of the PPor$^+$ unit results exclusively in electron transfer from the AlPor unit to ^{1}(PPor$^+$)*. Regardless of the excitation wavelength, the resulting charge-separated state eventually decays to the triplet state of the PPor$^+$ unit.





REFERENCES

1. Zarrabi, N.; Bayard, B. J.; Seetharaman, S.; Holzer, N.; Paul, K. A.; Ciuti, S.; Barbon, A.; Valentin, M. D.; van der Est, A.; D'Souza, F.; Poddutoori, P. K. *Phys. Chem. Chem. Phys.*, **2021**, *23*, 960.
2. Bayard, B. J.; Zarrabi, N.; Seetharaman, S.; Paul, K. A.; van der Est, A.; D'Souza, F.; Poddutoori, P. K. *J. Photochem. Photobiol.*, **2021**, *8*, 100069.

Mesoporous Silica Nanoparticles with a Photo-cleavable Protein Corona for Drug Delivery

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During the last few years, our group has been developing drug delivery systems (DDSs) based on mesoporous silica nanoparticles (MSNs) for the co-release of multiple drugs for combination therapies of cancer [1]. The chemical versatility of MSNs allows the design of stimuli-responsive DDSs capable to release payloads selectively thanks to smart gates installed at their surface [2]. Despite the high potential of the use of nanoparticles, their clinical application is still far away. One of the main limitations is the short circulation time in the bloodstream. Once in the blood, nanoparticles are rapidly coated by plasma proteins forming the so-called protein corona. As a result, a considerable portion of nanoparticles (up to 95%) is eliminated by macrophages, hampering their accumulation in the target site [3]. Currently, our group is working on the preparation of MSNs coated by an artificial protein corona with the aim to prolong the half-life of nanoparticles in the bloodstream [4]. To take advantage of the capping, the proteins are attached to the surface of MSNs through stimuli-responsive linkers, cleavable at acidic conditions and in the presence of singlet oxygen. In this poster, we would like to report on our recent results in the development of novel photo-cleavable MSNs.

REFERENCES

1. Llinàs, M. C.; Martínez-Edo, G.; Cascante, A.; Porcar, I.; Borros, S.; Sánchez-García, D. Drug Deliv, **2018**, 25, 1137–1146.
2. Martínez-Edo, G.; Xue, E.Y.; Ha, S.S.Y.; Pontón, I.; González-Delgado, J.A.; Borrós, S.; Torres, T.; Ng, D.K.P.; Sánchez-García, D. *Chem. Eur. J.* **2021**, 27, 14610–14618.
3. Rezaei, G.; Daghighi, S. M.; Raoufi, M.; Esfandyari-Manesh, M.; Rahimifard, M.; Mobarakeh, V. I.; Kamalzare, S.; Ghahremani, M. H.; Atyabi, F.; Abdollahi, M. *Colloid Interface Sci*. **2019**, 556, 476–491.
4. Giulimondi, F.; Digiacomo, L.; Pozzi, D.; Palchetti, S.; Vulpis, E.; Capriotti, A. L.; Chiozzi, R. Z.; Laganà, A.; Amenitsch, H.; Masuelli, L. *Nat. Commun*. 2019, 10(1), 3686.

Catalytic Properties of Porphyrins Bearing Peripheral N-Heterocyclic Carbene Rhodium Complexes

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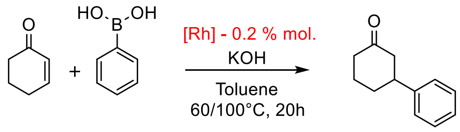
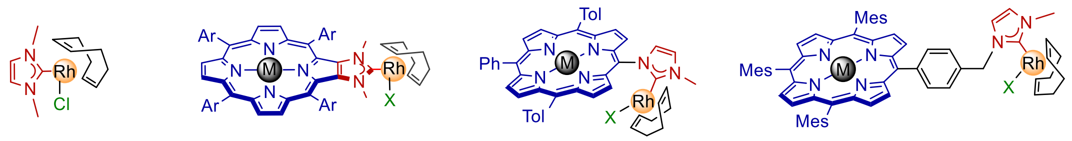
N-heterocyclic carbenes (NHCs) are both relevant ligands in the fields of coordination and organometallic chemistry.[1-2] During the last decade, several molecular systems combining porphyrins and NHC ligands were reported in the literature.[3] Merging metalloporphyrins and NHC-metal complexes within 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 notably show 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 centres. The results of these structure-function relationship study show a modulation of the catalytic properties of NHC-Rh(I) complexes by the porphyrin.





REFERENCES

1. W. A. Herrmann, *Angew. Chem. Int. Ed*. **2002**, *41*, 1290-1309.
2. E. Peris, *Chem. Rev.* **2018**, *118*, 9988-10031.
3. J.-F. Longevial, C. Rose, L. Poyac, S. Clément, S. Richeter, *Eur. J. Inorg. Chem.* **2021**, *9*, 776-791.
4. C. Mejuto, G. Guisado-Barrios, E. Peris, Organometallics, **2014**, *33*, 3205-3211.
5. S. Ruiz-Botella, E. Peris, *ChemCatChem* **2018**, *10*, 1874-1881.
6. H.Türkmen, T. Pape, B. Çetinkaya, *Organometallics* **2008**, *27*, 571-575.

21-Carbaporphyrin-2,3,21-trione – a Cyclopentane-1,2,4-trione Moiety Entrapped into the *meso*-Tetraarylporphyrin Framework

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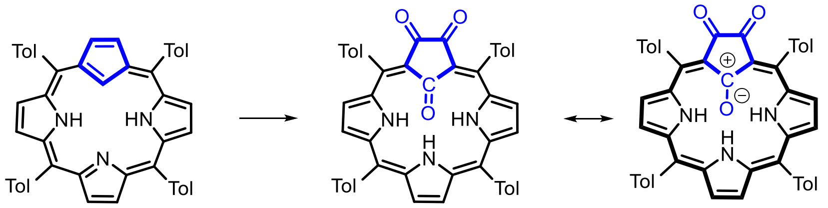
The incorporation of cyclopentadiene subunit into the porphyrinoid framework yielded carbaporphyrins, β-substituted 2-formyl-21-carbaporphyrin or 21-carba-23-thiaporphyrin [1-2]. The latter also shows an interesting reactivity by forming a dimer with a covalent bond between internal carbon atoms [3]. An interesting insight into 21-carbaporphyrin chemistry was provided by metal mediated contractions of *p*-benziporphyrin providing 21-carbaporphyrin complexes with gold and palladium [4-5]. The synthesis of *meso*-tetraaryl-21-carbaporphyrin **1**, the first macrocycle with a cyclopentadiene subunit entrapped in the *meso*-tetraarylporphyrin architecture provides significant motivation for further exploration of the chemistry of 21-carbaporphyrin and its derivatives [6].

A novel derivative of *meso*-tetraaryl-21-carbaporphyrin **1** with an embedded cyclopenta-1,2,4-trione motif formed from cyclopentadiene subunit, namely 21-carbaporphyrin-2,3,21-trione **2** has been identified. The route to obtain **2** relied either on modification of reported synthetic procedure for 21-carbaporphyrin **1** [6] or on the specific reactivity of silver(III) *meso*-tetraaryl-21-carbaporphyrin **1-Ag**. Due to its nontrivial structure, this compound possesses interesting chemical and physicochemical properties. The macrocyclic aromaticity of **2** was accounted for by the predominant participation of a charge-separated canonical structure **2'** with well-defined 18 π-electron delocalization route. In the solid state and in solution in lower temperature limits, 21-carbaporphyrin-2,3,21-trione **2** forms the chiral dimeric structure **[2]$_2$** with two subunits linked by network of hydrogen bonds. The kinetics of **[2]$_2$** enantiomerization was explored by ^{1}H NMR .



1 **2** **2'**

REFERENCES

1. Berlin K., Angew. Chem. Int. Ed. Engl., **1996**; 35, 1820.
2. Berlicka A, Dutka P, Szterenberg L., Latos- Grażyński L., *Angew. Chem. Int. Ed.* **2014**; *53*, 4885.
3. Berlicka A, Białek M. J., Latos- Grażyński L., *Angew. Chem. Int. Ed.* **2016**; *55*, 11231.
4. Szyszko B, Kupietz K, Szterenberg L and Latos- Grażyński L., *Chem. Eur. J.,* **2014***; 20*, 1376.
5. Szyszko, B., Latos- Grażyński, L., Szterenberg, L., *Angew. Chem. Int. Ed*., **2011**, *50*, 6587.
6. Garbicz, M., Latos-Grażyński, L., *Angew. Chem. Int. Ed.,* **2019**, *58*, 6089.

A Novel Exchange Coupled *m-m* linked bis-Vanadyl 5, 10, 15-Triphenylporphyrin for Quantum Information Processing

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Qubits are the fundamental unit of the quantum computer and for the realization of universal quantum gates, it is necessary to have at least two interactive qubits in the quantum circuits. Therefore, molecular spin qubits are attractive because it is possible to combine two or more qubits in one molecule and tune their magnetic interactions by varying the ligand or spin-spin distance. Especially Porphyrins are well suited for the realization of multi-qubit systems since it is possible to link two or more Porphyrin units together in *m* or *β* position varying the distance and the interaction between the paramagnetic metal centers [1-2].

In this work, we synthesized a *m-m* linked bis-Vanadyltriphenylporphyrin ($[VO(TrPP)]_2$) and investigated its magnetic properties (Fig. 1). A detailed crystallographic study showed that the torsion angle between the two $[VO(TrPP)_2]$ planes varies depending on the pseudo-polymorph investigated. The angle goes from 64° for the monoclinic species to 72° for the orthorhombic species. Cw-EPR measurements on single crystals of $[VO(TrPP)]_2$ showed that the larger the torsion angle is, the larger is the exchange interaction. The results obtained are counterintuitive with respect to previously studied dimers where flat triply linked Cu^{II} Porphyrin dimers showed strong antiferromagnetic interactions, while the singly *m-m* linked Porphyrin dimer showed only weak interactions [2-3]. Additionally, the coherence times (T_m) of $[VO(TrPP)]_2$ molecules, measured with pulsed EPR measurements, are around 1 μs in the temperature range from 2 to 30 K making the $[VO(TrPP)]_2$ molecules interesting for quantum information processing. The tilting angle in both crystal structures makes the two spin centers in the $[VO(TrPP)]_2$ molecules distinguishable and individually addressable by microwave radiation, thus opening the possibility to build two-qubit quantum logic gates.

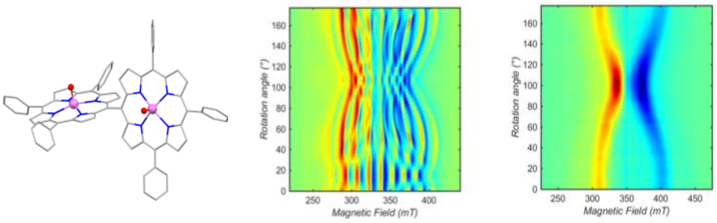

Fig 1: Molecular structure of $[VO(TrPP)]_2$ (left) and angle-resolved cw-EPR spectra of monoclinic (middle) and orthorhombic (right) crystals of $[VO(TrPP)]_2$ with different tilting angles of the porphyrin rings.

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REFERENCES

1. Hiroto, S. *et. al*. *Chem. Rev.* **117**(4), 2910-3043 (2017).
2. Ikeue, T. *et al. Angew. Chemie - Int. Ed.* **44**, 6899–6901 (2005).
3. Wili, N. *et al. Phys. Chem. Chem. Phys.* **21**, 11676–11688 (2019).

Synergistic effect between AgNWs and metallic phthalocyanines for electrochemical applications

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Phthalocyanines present the ability to act as electronic mediators in voltammetric sensors by improving the electronic transfer between the analyte and the sensor surface. It has been demonstrated that the modification of electrochemical sensors surfaces with electrocatalytic and/or conductive elements such as nanomaterials or phthalocyanines can improve the sensitivity of the sensor towards certain compounds [1-4]. For this reason, the design of hybrid systems combining different materials has become an interesting tool for the development of new and more efficient electrochemical sensors. In this work, we analyse the existence of a synergistic effect between silver nanowires (AgNWs) and phthalocyanines/bis-phthalocyanines along with its influence on the electrochemical effectiveness of the sensor. Thin films of silver nanowires together with cobalt phthalocyanines (CoPc) or gadolinium bis-phthalocyanines ($GdPC_2$) have been prepared by Langmuir-Blodgett (LB) technique. The nanostructured films were deposited at different pressures (45 mN/m and 25 mN/m) onto indium tin oxide (ITO) substrates to assess the alterations in the electrochemical behaviour due to conformational changes of the LB layer. These changes can be due to the phthalocyanines or the interaction between the phthalocyanines and the AgNWs. The characterization of the LB layers was carried out by π-A isotherms, Brewster angle microscopy (BAM) and atomic force microscopy (AFM). The deposited LB films were used as voltammetric sensors to test their electrochemical response towards different reference solutions. The increase in the intensity of the redox peaks and a reduction of the overpotential demonstrated a synergistic effect between the AgNWs with both phthalocyanines and bis-phthalocyanines. Furthermore, the surface pressure established for the preparation of the nanostructured films leaded to changes in the electrochemical activity of each sensor which indicates a different degree of interaction of the components within the monolayer.

REFERENCES

1. Alessio et al., “Structural and electrochemical properties of lutetium bis-octachloro-phthalocyaninate nanostructured films. Application as voltammetric sensors,” J. Nanosci. Nanotechnol., vol. 14, no. 9, pp. 6754–6763, 2014, doi: 10.1166/jnn.2014.9355
2. C. Medina-Plaza et al., “Analysis of organic acids and phenols of interest in the wine industry using Langmuir-Blodgett films based on functionalized nanoparticles,” Analytica Chimica Acta, vol. 853, no. 1. pp. 572–578, 2015, doi: 10.1016/j.aca.2014.10.046
3. C. Salvo-Comino, F. Martin-Pedrosa, C. Garcia-Cabezon, and M. L. Rodriguez-Mendez, “Silver Nanowires as Electron Transfer Mediators in Electrochemical Catechol Biosensors,” Sensors (Basel)., vol. 21, no. 3, pp. 1–13, Feb. 2021, doi: 10.3390/S21030899
4. C. Medina-Plaza, L. N. Furini, C. J. L. Constantino, J. A. De Saja, and M. L. Rodriguez-Mendez, “Synergistic electrocatalytic effect of nanostructured mixed films formed by functionalised gold nanoparticles and bisphthalocyanines,” Anal. Chim. Acta, vol. 851, no. C, pp. 95–102, 2014, doi: 10.1016/j.aca.2014.08.049

Theoretical electronic absorption spectrum of octachlorotetrapyrazinoporphyrazine complex with Ga

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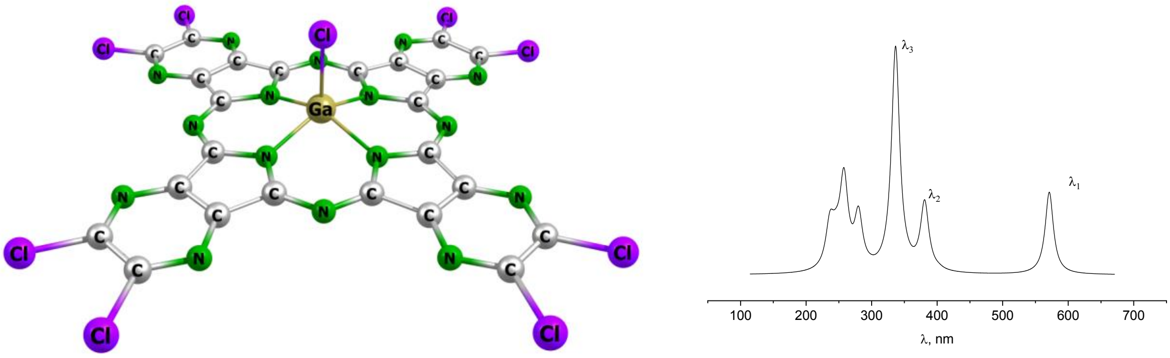
Tetrapyrrolic macrocycles have become attractive for researchers in the last century due to the many possibilities for their application. For example, these compounds can be applied as catalysts, photovoltaic cells, building blocks for new functional materials, in biomedicine. Therefore, a thorough study of their electronic structure and energy properties is important for explaining the chemical, biological and physical properties of this compounds.

Theoretical electronic spectrum of octachlorotetrapyrazinoporphyrazine complex with Ga(Cl) (Fig. 1) was obtained using TDDFT after geometry optimization with use of PBE0-D3/def2-TZVP. The number of the calculated excited states was set to 30.



a b

Figure 1. Equilibrium geometry (a) and electronic absorption spectrum (b) of octachlorotetrapyrazinoporphyrazine complex with Ga(Cl).

The presence of an intense Q-band (λ_1) and two Soret-bands (λ_2 and λ_3) in the spectrum (fig. 1b) is typical for macrocycles with a porphyrazine core.

The Q-band (571 nm) corresponds to the excited state 1^1E predominantly represented by an electron transition from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO).

Analysis of MOs shapes had demonstrated that HOMO localized on pyrrole rings along with pyrazine fragments. LUMOs are doubly-degenerated e^* molecular orbitals. The frontier orbitals are centered on the macrocycle framework and don’t include the AOs of the metal. The electron transition from HOMO-3 to LUMO strong contributes into the most intense band λ_3 (337 nm).

This work was supported by the Russian Science Foundation grant 21-73-10126.

Chirogenic Interaction of Chiral Cyclohexanohemicucurbit[*n*]urils with Bis(Zn Porphyrin)

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Porphyrins are suitable for chemical sensor development due to their chemical and optical properties [1]. Particularly, bis(zinc octaethylporphyrin) (**bis–ZnOEP**) has been thoroughly studied and proved to sense chirality of small monodentate and bidentate chiral molecules [2,3].

Previously, our group has shown that macrocyclic cyclohexanohemicucurbit[n]urils (**cycHC[*n*]**s, n = 6, 8) [4, 5, 6] induced chirality to achiral zinc(II) monoporphyrins through supramolecular interactions [7]. To continue further chirogenic studies we investigated the corresponding self-association of **bis–ZnOEP** with **cycHC[*n*]**s to enhance chirality induction of the complex and discovered that **bis–ZnOEP** is able to discriminate opposite enantiomers and sizes of chemically analogous **cycHC[*n*]**s (Figure 1) [8]. The binding of **cycHC[6]** showed fast equilibration and a tweezer-like conformation followed by subsequent transformation into *anti*-form of **bis–ZnOEP** upon further addition of **cycHC[6]**. Whereas, the interaction of **cycHC[8]** is more complicated and proceeds through the *syn*-to-*anti* conformational change of **bis–ZnOEP** and further intermolecular self-assembly via multiple noncovalent associations between **cycHC[8]** and **bis–ZnOEP**. Detailed spectroscopic studies and proposed supramolecular mechanisms are discussed.

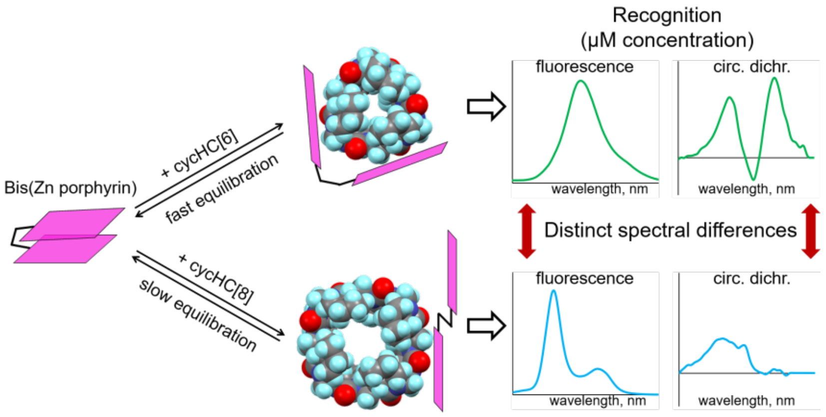

Figure 1: Schematic representation of **bis–ZnOEP** complexes with **cycHC[*n*]**s and respective fluorescence and CD spectra.

REFERENCES

1. Paolesse, R. *et al. Chem. Rev.* **2017**, *117*, 2517–2583
2. Borovkov, V.V. *et al. J. Am. Chem. Soc.* **2001**, *123*, 2979–2989
3. Borovkov, V.V. *et al. J. Org. Chem.* **2003**, *68*, 7176–7192
4. Aav, R. *et al. Org. Lett.* **2013**, *15*, 3786–3789
5. Prigorchenko E. *et al. Chem. Commun.* **2015**; 51: 10921-10924
6. Kaabel, S. *et al Angew. Chem. Int. Ed.* **2019**, 58 (19), 6230-6234
7. Ustrnul, L. *et al. Chem. Commun.* **2019**, *55*, 14434–14437
8. Šakarašvili M. *et al. Molecules* **2022**, 27(3), 937

Synthesis and Properties of Outer-Palladated Tetrapyridyldiazaporphyrin Complexes

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Although most of porphyrin metal complexes have metal ions in the inner cavity, outer-metallated porphyrins have been also investigated. Various outer-metallated porphyrins have been synthesized, of which properties are dependent on the inner metals. Among them, *meso*-metalated porphyrins with a carbon–metal σ-bond at the *meso*-positions have been actively explored [1]. There have beeen two synthetic strategies for the preparation of outer-metallated porphyrins, (i) oxidative addition of a C–X (X: halogen) bond with low valent metals [2] and (ii) metallation of a C–H bond with the aid of a directing group such as pyridyl groups [3].

5,15-Diazaporphyrins have imine-type nitrogen atoms at two *meso* positions, which provide the coordination ability. However, outer-metallated diazaporphyrins have remained rare because of the weak coordination ability of the *meso*-nitrogens [4]. Our group reported that pyridyldiazaporphyrin act as a bidentate ligand to form metal complexes with various metals [5].

Here, we have synthesized tetrapyridyldiazaporphyrin and its palladium complexes. We found that tetrapyridyldiazaporphyrin bispalladium complex underwent facile one- and two-electron reduction. In this presentation, we will disclose the detailed synthesis and properties of tetrapyridyldiazaporphyrin bispalladium complexes with various redox states.

REFERENCES

1. Hiroto, S.; Miyake, Y.; Shinokubo, H. *Chem. Rev.* **2017**, *117*, 2910.
2. a) Arnold, D. P.; Healy, P. C.; Hodgson, M. J.; Williams, M. L. *J. Organomet. Chem.* **2000**, *607*, 41; b) Hartnell, R. D.; Arnold, D. P. *Organometallics* **2004**, *23*, 391.
3. a) Yamaguchi, S.; Katoh, T.; Shinokubo, H.; Osuka, A. *J. Am. Chem. Soc.* **2007**, *129*, 6392; b) Song, J.; Aratani, N.; Heo, J. H.; Kim, D.; Shinokubo, H.; Osuka, A. *J. Am. Chem. Soc.* **2010**, *132*, 11868; c) Rao, Y.; Kim, T.; Park, K. H.; Peng, F.; Liu, L.; Liu, Y.; Wen, B.; Liu, S.; Kirk, S. R.; Wu, L.; Chen, B.; Ma, M.; Zhou, M.; Yin, B.; Zhang, Y.; Kim, D.; Song, J. *Angew. Chem. Int. Ed.* **2016**, *55*, 6438.
4. Longevial, J.-F.; Miyagawa, K.; Shinokubo, H. *Dalton Trans.* **2020**, *49*, 14786.
5. Yamaji, A.; Shin, J.-Y.; Miyake, Y.; Shinokubo, H. *Angew. Chem. Int. Ed.* **2014**, *53*, 13924.

Synthesis, Spectral, Electrochemical, and Nonlinear Optical Properties of *β*-Substituted "Push-Pull" Porphyrins

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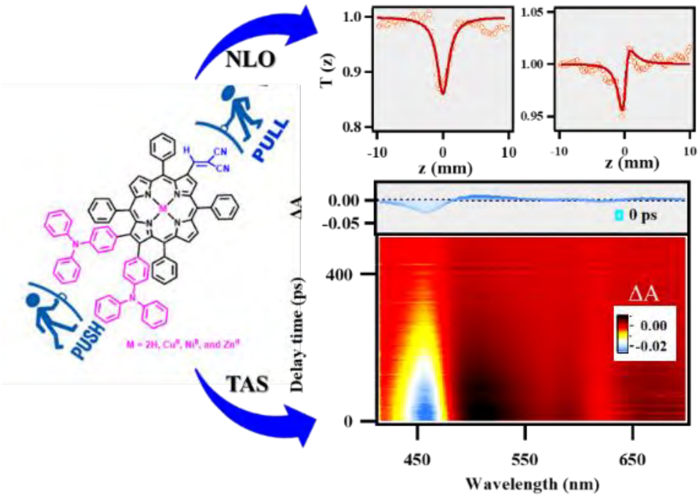
Materials with high nonlinear optical performance have always been of utmost importance due to their potential application in the area of photonics, such as telecommunications, optical switching, data storage, optical limiting, optical computing, optical fibre technology, optical information processing, and photodynamic therapy.[1,2] Due to the potential candidacy of 'push-pull' porphyrins towards nonlinear optics, a series of "push-pull" porphyrins, $MTPP(DCV)(TPA)_2$ (M = 2H, Cu^{II}, Ni^{II}, and Zn^{II}) having dicyanovinyl (DCV) and triphenylamine (TPA) at antipodal positions were synthesized and characterized by various spectroscopic techniques and electrochemical methods. These porphyrins were utilized for third-order NLO measurements. Remarkably, $MTPP(DCV)(TPA)_2$ (M = 2H, Cu^{II}, Ni^{II}, and Zn^{II}) exhibited 21-48 nm and 38-80 nm bathochromic shift in B and $Q_x(0,0)$ bands, respectively as referenced to corresponding MTPPs (M = 2H, Cu^{II}, Ni^{II}, and Zn^{II}); the results are in consistent push-pull effect of substituents and electron withdrawing effect of DCV moiety. The "push-pull" porphyrins exhibited cathodic shift (0.13-0.51 V) in their first oxidation potential as compared to the precursor owing to the presence of electron donating TPA groups. The third-order nonlinear optical responses were recorded using single beam femtosecond Z-scan technique to retrieve the information about the nonlinear absorption, and nonlinear refraction of the samples. The estimated two-photon absorption coefficients (β) are in the range of 0.87×10^{-13} to 4.28×10^{-13} mW^{-1} and nonlinear refractive index (n_2) in the range of 1.21×10^{-19} to 7.36×10^{-19} $m^2\ W^{-1}$. The ultrafast absorption dynamics of the ground state bleaching (GSB) and the photo-induced absorption (PIA) are monitored by femtosecond broadband transient absorption studies. The strong nonlinearity of these "push-pull" porphyrins endowing them as potential candidates for nonlinear optical and photonic devices applications.



REFERENCES

1. (a) Williams, D. J. et al. Angew. Chem. Int. Ed. 1984, 23, 690. (b) J. D. Bhawalkar, et al. *J. Clin Laser Med Surg,* 1997, 15, 201.
2. (a) Rohal, R. K. et al. Inorg. Chem. 2022, 61, 1297. (b) Samal, M. et al. *Chem. Commun.* 2019, 55, 11025.

Synthesis, Spectral and Electrochemical Studies of *β*-Cyano Substituted Porphyrins

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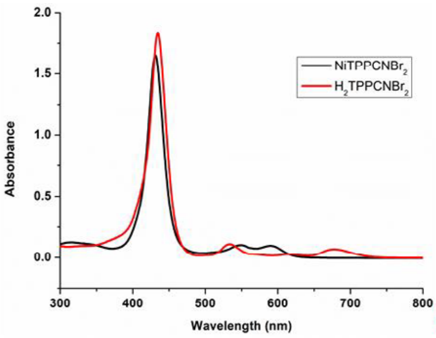
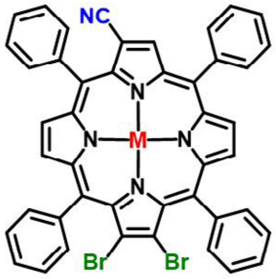
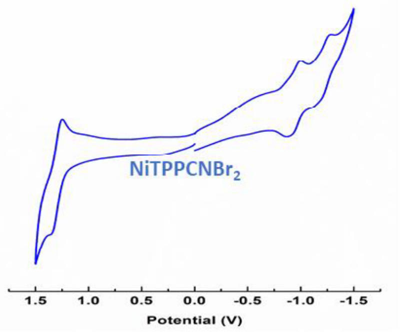
β-Substitution at the macrocyclic ring is an effective approach towards altering different properties of the porphyrin moiety. Cyano group is less sensitive towards steric factors and has the potential to create pronounced effect [1]. Nitrile-containing porphyrins are known to be utilized in various fields such as toxic ion sensing, nonlinear optics, solar cells and fabrication of nanostructures [2]. The presented work mainly emphasizes on the synthesis of *β*-cyano appended porphyrin derivatives.





M= 2H, Co(II), Ni(II), Cu(II), Zn(II)



Herein, *β*-cyanodibromoporphyrin and their metal complexes were synthesized *via* a facile synthetic pathway in excellent yield and characterized by various spectroscopic techniques such as UV-vis, fluorescence, NMR spectroscopy, MALDI mass spectrometry, cyclic voltammetry, and density functional theory (DFT) studies. The cyanation of the mono-bromo porphyrin was carried out using cuprous cyanide in the presence of quinoline as solvent. Further, bromination in the presence of the controlled amount of N-bromosuccinimide yielded dibromo monocyanoporphyrin. The absorption spectral features of the synthesized molecules are marginally shifted as compared to the precursor. They exhibited 6-9 nm and 8-16 nm red shift in the Soret and $Q_x(0,0)$ bands, respectively, as compared to monocyano substituted porphyrins due to inductive effect of *β*-bromo substituents on the macrocyclic ring. In this presentation, we will discuss about the synthesis, spectral and electrochemical properties of *β*-cyano appended porphyrins in detail.

REFERENCES

1. (a) Callot, H. J. *et al. Chem. Soc., Perkin Trans.* **1975**, *2,* 1321–1324. (b) Kumar, R. *et al. J. Porphyrins Phthalocyanines* **2016**; *20*, 1420–1425.
2. (a) Kumar, R.; Chaudhri, N.; Sankar, M. *Dalton Trans*., **2015**, *44*, 9147-57. (b) Kumar, R.; Sankar, M. *Inorg. Chem*., **2014**, *53*, 12706-19. (c) Rohal, R. K. *et al. Inorg. Chem*., **2022**, *61*, 1297-1307. (d) Lepper, M. *et al. Angew. Chem. Int. Ed.,* **2018**, *57*, 10074–10079. (b) Mitchell, R.*et al. Eur. J. Org. Chem.* **2017**, *17*, 5750–5762.

Hosting Fullerenes using Tetrabenzoporphyrin Dimers

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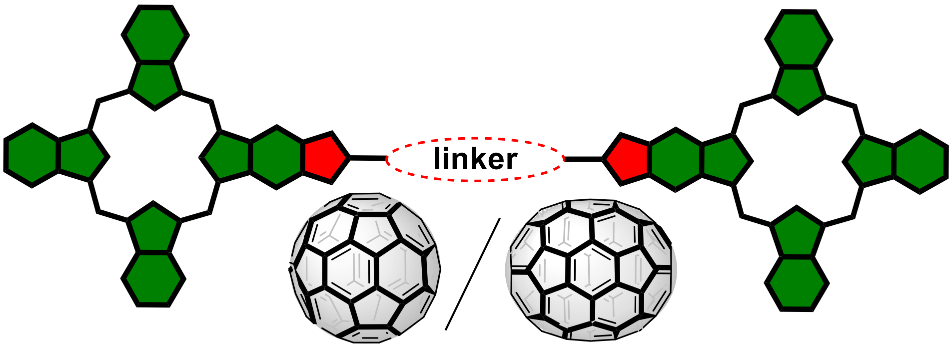
The use of porphyrin receptor systems in fullerene recognition is a well-established strategy based on their favourable donor-acceptor interactions. [1, 2] Other approaches exploit the shape complementarity between the spherical fullerene and bowl-shaped PAHs. [3,4] In general, high binding interactions are depending on a careful design of the host system to achieve a good alignment of the binding sites. We chose tetraaryltetrabenzoporphyrins as the host systems in our research to make use of the intrinsic saddle shaped curvature of those π-extended porphyrins. [5, 6] To this end several host systems were synthesized using rigid and flexible linkers to tune and compare shape and dimensions of their cavities. Their binding interactions with fullerenes C_{60} and C_{70} were analysed using different techniques from fluorescence and absorptions spectroscopies to mass spectrometry.



REFERENCES

1. E. M. Pérez, N. Martín, *Pure Appl. Chem.,* 2010, **82**, 523-533.
2. G. Gil-Ramírez, S. D. Karlen, A. Shundo, K. Porfyrakis, Y. Ito, G. A. D. Briggs, J. J. L. Morton, H. L. Anderson, *Org. Lett.*, 2010, **12**, 3544-3547.
3. K. Ikemoto, R. Kobayashi, S. Sato, H. Isobe, *Org. Lett.,* 2017, **19**, 2362-2365.
4. M. Takeda, S. Hiroto, H. Yokoi, S. Lee, D. Kim, H. Shinokubo, *J. Am. Chem. Soc.,* 2018, **140**, 6336-6342.
5. A. Y. Lebedev, M. A. Filatov, A. V. Cheprakov, S. A. Vinogradov, *J. Phys. Chem. A*, 2008, **112**, 7723-7733.
6. M. Ruppel, D. Lungerich, S. Sturm, R. Lippert, F. Hampel, N. Jux, *Chem. Eur. J.*, 2020, **26**, 3287-3296.

Manganese 10-Thiacorroles

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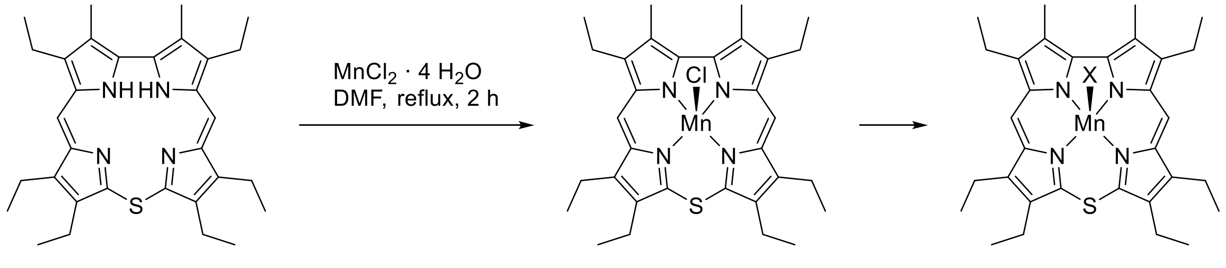
Manganese complexes of porphyrinoids have been studied in detail for a long time. They are used in biological studies because of their similarity to iron porphyrins such as heme [1]. Furthermore manganese corroles and manganese porphyrins show catalytic behaviour for example in C-H halogenation and polymerisation of epoxides [2, 3].

By synthesizing modified porphyrins with altered electronic properties, these processes can be investigated in more detail. 10-Thiacorroles can be considered as the intermediate between porphyrins and corroles. They are dianionic ligands and have a contracted cavity size.[4] Already known complexes of 10-heterocorroles show unusual electronic and magnetic properties[5], so the synthesis of novel manganese complexes of these ligands is of great interest.

The poster will give an overview of the manganese thiacorroles obtained so far and provide detailed insight into electronic and magnetic properties of such compounds.



X = N, NCS,NCO, ...

Figure 1: Synthesis of Chlorido manganese thiacorroles with a following substitution of the axial ligand.

REFERENCES

1. R. A. Baglia, J. P. T. Zaragoza D. P. Goldberg Chem. Rev. 2017, 117, 21, 13320-13352.
2. W. Liu, J. T. Groves, *J. Am. Chem. Soc.* **2010**, 132, 37, 12847-12849.
3. C. Robert, T. Ohkawara, K. Nozaki, *Chem. Eur. J.* **2014**, 20, 16, 4789-4795.
4. D. Sakow, B. Böker, K. Brandhorst, O. Burghaus, M. Bröring, *Angew. Chem. Int. Ed.* **2013**, 52, 4912-4915.
5. D. Sakow, D. Baabe, B. Böker, O. Burghaus, M. Funk, C. Kleeberg, D. Menzel, C. Pietzonka, M. Bröring, *Chem. Eur. J.* **2014**, 20, 2913-2924.

Thermally Activated Delayed Fluorescence in π-Extended Palladium(II) and Platinum(II) Porphyrins

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Luminescent porphyrins are a well-researched class of compounds with many applications in diverse fields such as diagnostics and therapeutics[1] or dye-sensitized solar cells[2]. Porphyrins are widely applied in sensor materials[3], where phosphorescent Pd(II) and Pt(II) porphyrins are especially important in oxygen sensing. Likewise, thermally activated delayed fluorescence (TADF) materials have attracted much interest lately which is mainly due to their application in OLEDs[4]. In 2009 Endo et al. introduced Sn(IV) porphyrins as the first TADF molecules in OLEDs[5]. Nonetheless, TADF in porphyrins remains a poorly researched phenomenon with most known examples suffering from low efficiency of TADF. Recently, Zach et al. showed that Pd(II) and Pt(II) tetraarylbenzoporphyrins with strongly electron withdrawing groups in beta position (most notably alkylsulfones) exhibit dual TADF and phosphorescence emission with remarkably efficient TADF at elevated temperatures. These unique properties were shown to be of high interest for simultaneous self-referenced sensing of temperature and oxygen[6]. Unfortunately, the optimal ratio of TADF and phosphorescence has only been achieved at relatively high temperatures (above 60 °C) which is not optimal for measurements at physiological conditions.

In this work, we aimed to further increase the TADF efficiency of π-extended Pd(II) and Pt(II) porphyrins by reducing the singlet-triplet energy gap. For this purpose, we screened the TADF/phosphorescence ratio of several π-extended Pd(II) porphyrins bearing various substituents in beta and meso positions. By far the highest ratio of TADF/phosphorescence of over 2/1 (at RT in deaerated toluene) is reached by the Pd(II) complex of tetranaphthoquinono meso-tetraarylporphyrin[7] that features a S_1-T_1 energy gap of 2045 cm^{-1}. Although the ratio of TADF/Phosphorescence is inverted to 1/4 for the corresponding Pt(II) complex, the overall TADF brightness is unprecedented for the Pt(II) complexes. Notable, the Pt(II) complex is better suited for sensing applications due to significantly shorter luminescence decay time. When embedded into gas blocking polymers this dye serves as ratiometric molecular thermometer with negligible oxygen cross-talk and immobilization in common polymers such as polystyrene provide unique (nano)sensors for self-referenced dual temperature (ratiometric) and oxygen sensing (lifetime based).

Acknowledgements: Financial support from Austrian Science Fund (Project [P32079-N37]) is gratefully acknowledged

REFERENCES

1. Josefsen LB and Boyle RW. *Theranostics* 2012; **2** (9): 916–966.
2. Li L-L and Diau EW-G. *Chem Soc Rev* 2013; **42** (1): 291–304.
3. Paolesse R, Nardis S, Monti D, Stefanelli M and Di Natale C. *Chem Rev* 2017; **117** (4): 2517–2583.
4. Yang Z, Mao Z, Xie Z, Zhang Y, Liu S, Zhao J, Xu J, Chi Z and Aldred MP. *Chem Soc Rev* 2017; **46** (3): 915–1016.
5. Endo A, Ogasawara M, Takahashi A, Yokoyama D, Kato Y and Adachi C. *Adv Mater* 2009; **21** (47): 4802–4806.
6. Zach PW, Freunberger SA, Klimant I and Borisov SM. *ACS Appl Mater Interfaces* 2017; **9** (43): 38008–38023.
7. Banala S, Rühl T, Sintic P, Wurst K and Kräutler B. *Angew Chem Int Ed Engl* 2009; **48** (3): 599–603.

Supramolecular porphyrin conjugates with pyridinic nanographenes

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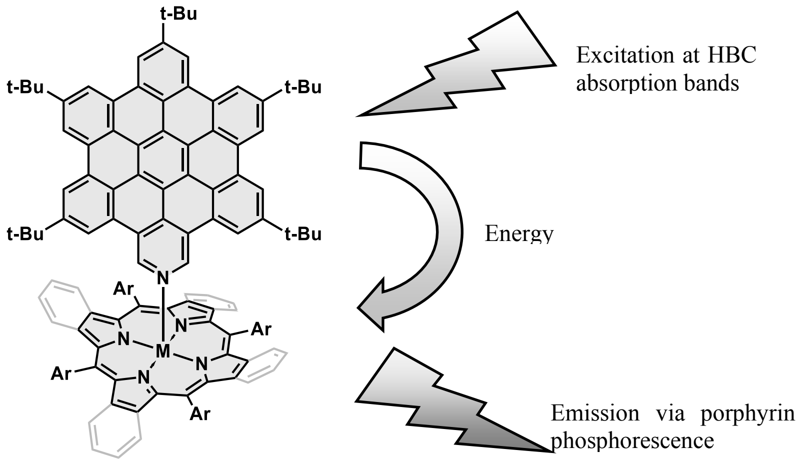
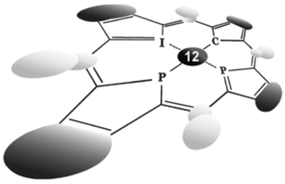
In recent years, covalently linked porphyrin-nanographene structures have moved into the focal point of attention, as they serve as models for porphyrin-graphene hybrids.[1] Herein, we introduce the first examples of a supramoleculary associated hexa-*peri*-hexabenzocoronene (HBC) featuring (metallo)tetra-arylporphyrins *via* coordination. Our concept was realized by the efficient synthesis of a pyridinic-HBC, which contains a nitrogen-atom at its periphery on an exposed position.[2] With this in hand, pyridinic-HBC supports the coordination of sterically demanding metal complexes such as (metallo)porphyrins, as sketched below. Here, we present examples of (metallo)porphyrins or tetrabenzoporphyrins featuring a variety of different metals ranging from Ru and Zn to Co and their photophysical investigations. In analogy to covalently bound porphyrin-HBC conjugates [3] an energy transfer from the pyridinic-HBC to the (metallo)porphyrin dictates their excited state deactivation.



Porphyrin or Benzoporphyrin
M = Ru(CO), Zn, Co
Ar = 3,5-di-*tert*-butylphenyl

REFERENCES

1. Borissov A, Maurya YK, Moshniaha L, Wong W-S, Żyła-Karwowska M and Stępień M. *Chem. Rev.* 2022; **122**: 565–788.
2. Reger D, Schöll K, Hampel F, Maid H, and Jux N. *Chem. Eur. J.* 2021; **27**: 1984–1989.
3. Englert JM, Malig J, Zamolo VA, Hirsch A and Jux N. *Chem. Commun.* 2013; **49**: 4827–4829.



Molecular mechanism of the last step of the heme *b* biosynthesis pathway in Gram-positive bacteria

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The coproporphyrin-dependent heme biosynthesis pathway, used by pathogenic Gram-positive bacteria to produce heme *b,* has been discovered in 2015 [1]. In the last step of this pathway, the coproheme decarboxylases (ChdCs) generate heme *b* via the H_2O_2-mediated stepwise decarboxylation of the two propionate groups of coproheme at positions 2 and 4 (p2 and p4, respectively), forming vinyl groups. After cleavage of p2, the transiently formed three-propionate intermediate, monovinyl monopropionyl deuteroheme (MMD), undergoes a reorientation to bring p4 in close proximity to the catalytic tyrosine [2, 3], to allow its decarboxylation for the formation of the heme *b* final product.

On the basis of the protein crystal structure [4], the electronic absorption and resonant Raman spectroscopic study on the wild-type and relevant variants of ChdC of actinobacterial *Corynebacterium diphtheriae (Cd)* [5, 6] upon titration with hydrogen peroxide, strongly supports the rotation of MMD reaction intermediate within the active site rather than a release and rebinding mechanism, before the second decarboxylation takes place. [5]

Interestingly, *Cd*ChdC appeared highly reactive to hydrogen peroxide, as confirmed by the presence of side reactions in presence of an excess of H_2O_2, leading to the hydroxylation of a porphyrin ring, compatible with the formation of an iron chlorin-type heme *d* species [7]. Furthermore, we analyzed the behavior of this protein upon reduction studying the status of the proximal Fe-His bond strength during the hydrogen peroxide-mediated decarboxylation [6]. Finally, since actinobacterial *Cd*ChdC uses a distal histidine residue (H118) for deprotonation and subsequent heterolytic cleavage of hydrogen peroxide [4], we probed the distal cavity by the spectroscopic characterization of CO-adducts. Important information on the role of this key distal polar residue in ligand binding have been obtained. The results on *Corynebacterium diphtheriae* coproheme decarboxylase have been compared and discussed with respect to those obtained for ChdCs from other clades [3].

REFERENCES

1. Dailey HA, Gerdes S, Dailey TA, Burch JS & Phillips JD (2015) *Proc Natl Acad Sci USA* **112**, 2210– 2215.
2. Streit BR, Celis AI, Moraski GC, Shisler KA, Shepard EM, Rodgres, KR, Lukat-Rodgers GS, DuBois JL (2018) *J. Biol. Chem.* **293**, 3989–3999.
3. Milazzo L, Gabler T, Pühringer D, Jandova Z, Maresch D, Michlits H, Pfanzagl V, Djinović-Carugo K, Oostenbrink C, Furtmüller PG, Obinger C, Smulevich G, Hofbauer (2019) *ACS Catal.* **9**, 6766–6782.
4. Michlits H, Lier B, Pfanzagl V, Djinović-Carugo K, Furtmüller PG, Oostenbrink C, Christian Obinger C, Hofbauer S (2020) *ACS Catal.* **10**, 5405-5418.
5. Sebastiani F, Michlits H, Lier B, Furtmüller PG, Oostenbrink C, Obinger C, Hofbauer S, Smulevich G (2021) *Biophys J.* **120**, 3600–361.
6. Sebastiani F, Risorti R, Niccoli C, Michlits H, Becucci B, Hofbauer S, Smulevich G (2022) *J. Inorg. Biochem.* **229**, 111718.
7. Sebastiani F, Niccoli C, Michlits H, Risorti R, Becucci B, Hofbauer S, Smulevich G (2022) *J. Raman Spectrosc.* - Accepted.

POSTERS

Dimeric Corrole Analogs of Chlorophyll Special Pairs

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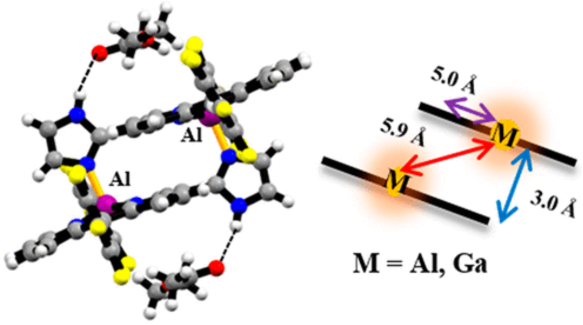
Chlorophyll special pairs in photosynthetic reaction centers function as both exciton acceptors and primary electron donors. Although the macrocyclic natural pigments contain Mg(II), the central metal in most synthetic analogs is Zn(II). Here we report that insertion of either Al(III) or Ga(III) into an imidazole-substituted corrole affords an exceptionally robust photoactive dimer. Electronic interactions between dimer subunits are relatively strong, as documented by signature changes in NMR and electronic absorption spectra, as well as by cyclic voltammetry, where two well-separated reversible redox couples were observed. EPR spectra of one-electron oxidized dimers closely mimic those of native special pairs, and strong through-space interactions between corrole subunits inferred from spectroscopic and electrochemical data are further supported by crystal structure analyses (3 Å interplanar distances, 5 Å lateral shifts, and 6 Å metal to metal distances).[1]



REFERENCES

1. V. K. Sharma, A. Mahammed, A. Mizrahi, M. Morales, N. Fridman, H. B. Gray, Z. Gross, J. Am. Chem. Soc. 2021, 15, jacs.1c02362.

Synthesis and Characterization of π Expanded Vitamin B12 Derivatives and Evaluation of the Catalytic Activities

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Vitamin B_{12} is one of unique metal complex which has the cobalt ion as a centered metal and the corrin as the ligand. The Co(I) state of the vitamin B_{12} reacts alkyl halide to form alkylated complex by the S_N2 type reaction and proceed the several catalytic reactions via alkyl radicals formed by homolysis of the cobalt-carbon bond.[1] Based on these characters of the vitamin B_{12}, many B_{12}-inspired reactions have been developed.[2] In general, the cobyrinate complex (**1**) was used as the B_{12} derivatives. In this work, we succeeded the synthesis and characterization of the Co(II) state of pyrocobseter (**2**) with π-expanded structure. Moreover, we clarified the catalytic reactivities of the complex.

The pyrocobester was synthesized by the pyrolysis of the cobyrinate.[3] The absorption of the pyrocobester showed red-shift compared to the cobyrinate because of the conjugated corrin ligand (**Figure 2.** (a)). Furthermore, Co(II)/Co(I) redox potentials were +0.3 V shifted (**Figure 2.** (b)). To investigate the reactivities of Co(I) species, Co(I) species and CH_3I was reacted. The spectrum of Co(I) species was changed after adding the CH_3I. It is suggested that Co(I) state of pyrocobester reacted with CH_3I and alkylated complex (CH_3-Co(III)) was formed.

We constructed the eco-friendly photocatalytic system composed of the pyrocobester as the active center and tungsten oxide (WO_3) as visible light responsive photocatalyst. In this system, Co(I) species was formed under visible light irradiation by using water (or methanol) as electron source. In this presentation, we will report experimental detail of pyrocobester chemistry.

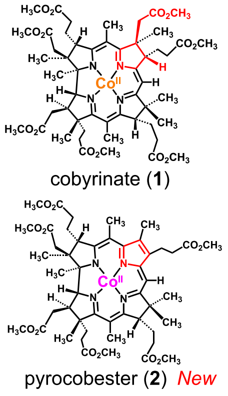

Figure 1. Structures of complex **1**and **2**.

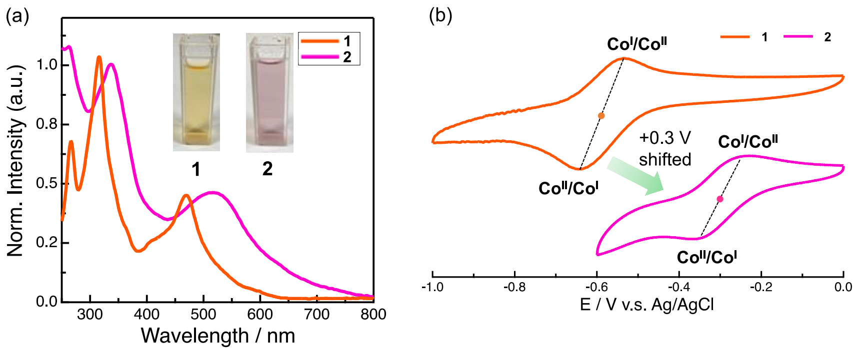

Figure 2. (a) UV-vis spectra of prepared sample, **1** and **2** in CH_3CN.
(b) CVs of complex **1** and **2** in CH_3CN under N_2. WE: Glassy carbon, CE: Pt wire, RE: Ag/AgCl electrode, supporting electrolyte: n-Bu_4NClO_4

REFERENCES

1. M. Giedyk, K. Goliszewska, D. Gryko, *Chem. Soc. Rev.*, **2015**, *44*, 3391.
2. H. Shimakoshi, Y. Hisaeda, *Chem. Rec.*, **2021**, *21*, 2080.
3. B. Kraütler, R. Stepanek, *Helv. Chim. Acta.*, **1983**, *66*, 1493.

Synthesis of Near-Infrared Absorbing Donor-Acceptor BODIPY Dyes as Two-Photon Photoacoustic Imaging Contrast Agents

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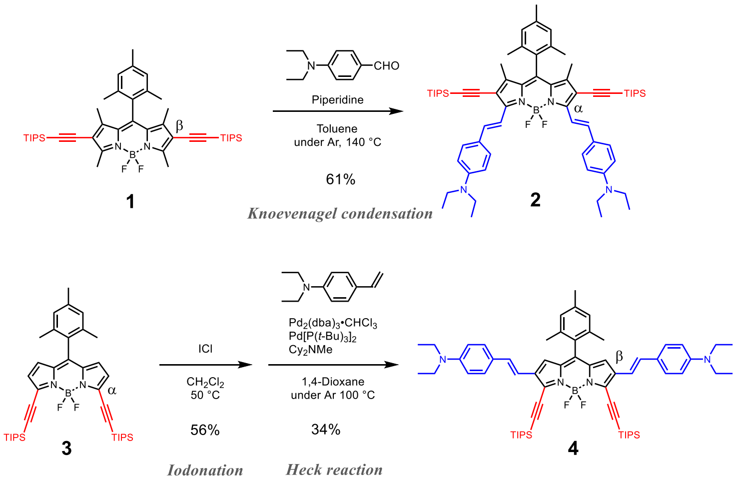
To date, various near-infrared (NIR) light-absorbing boron-dipyrromethenes, namely BODIPYs, have been reported for numerous applications such as bio-imaging, photosensitizers, sensory indicators, and so on. Along with these derivatives, the development of non-emissive BODIPY-based contrast agents has paid attention to photoacoustic imaging (PAI) of the deeper biological tissues in recent years. Especially, the two-photon-induced PAI strategy is advantageous in the high 3D-spatial resolved visualization at the local excitation area of tissues. For this purpose, donor-acceptor-donor structured BODIPY derivatives are expected to demonstrate intense PAI signals via large two-photon absorption cross-section values.

In this work, we have successfully synthesized *N,N*-diethyl-4-vinylaniline-substituted BODIPY derivatives (**2** and **4**) from ethynyl-substituted derivatives (**1** and **3**) by Knoevenagel condensation and Heck reaction, respectively [1]. The resulting dyes exhibit broad NIR absorption bands beyond 800 nm with relatively high molar coefficients, and photoacoustic signals induced by two-photon excitation at 1064 nm were observed under pulsed laser irradiation. In particular, the α-donor-substituted derivative **2** exhibited two-photon-induced PA signals with low energy pulsed laser excitation (3.0 μJ).



Scheme. Synthesis of ethynyl- and vinylaniline-substituted BOIDPY derivatives.

REFERENCES

1. T. Shimada, S. Mori, M. Ishida, H. Furuta, *Beilstein J. Org. Chem,* **2020**, *16*, 587.

The influence of combined azasubstitution and halogenation on properties of subphthalocyanine-type dyes

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Subphthalocyanine-type compounds possess unique properties that allow using them in various fields, including photovoltaics, organic electronics and medicine. Thereby, synthesis and characterization of such compounds is an important step in the development of mentioned fields. In this work unsymmetrical azaanalogues of perhalogenated subphthalocyanine were obtained for the first time (Fig.1). They were characterized by different methods, but in our report we want to focus mainly on redox, fluorescent and acid-base properties. Increasing the degree of azasubstitution in benzene rings of the macrocycle, when moving from F_{12}sPc to Cl_6N_6sPc (synthesized in our group earlier [1]), facilitates the reduction of the macrocycle due to electron-withdrawing character of pyrazine fragments. Along with hypsochromic shift of the Q band due to increase of the HOMO-LUMO gap fluorescence efficiency is reduced in a series: F_{12}sPc, $F_8Cl_2N_2$sPc, $F_4Cl_4N_4$sPc, Cl_6N_6sPc. The influence of acids and nucleophiles on spectral properties and stability of obtained macrocycles in solution has been studied as well [2] and will be discussed.

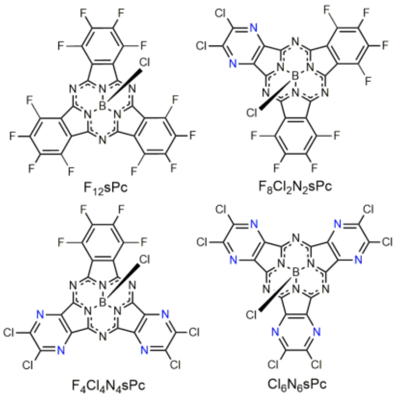

Figure 1. Perhalogenated azaanalogues of subphthalocyanine

Figure 2. Electronic absorption spectra for perhalogenated azaanalogues of subphthalocyanine

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REFERENCES

1. Skvortsov, I. A. *et al.* Subphthalocyanine-type dye with enhanced electron affinity: Effect of combined azasubstitution and peripheral chlorination. *Dye. Pigment.* **185**, 108944 (2021).
2. Skvortsov, I. A., Kovkova, U. P. & Stuzhin, P. A. Effect of protonation on the spectral properties of subphthalocyanine and tripyrazinosubporphyrazine. *J. Phys. Conf. Ser.* **1822**, (2021).

1,3-Dipolar Cycloaddition of Polycyclic Azomethine Ylide to Norcorroles: Towards Dibenzoullazine-fused Derivatives

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Aromaticity is one of the most important and most thoroughly explored concepts. In contrast, antiaromaticity is in the process of becoming more and more significant field of organic chemistry. The main reason of its lower popularity is the instability of the antiaromatic compounds. The traces of norcorrole were discovered in 2008 [1] and 4 years later a gram-scale synthesis of norcorrolatonickel(II) was developed [2]. Metal-templated synthesis of the contracted porphyrin without two meso atoms afforded to the smallest, antiaromatic, stable and reactive porphyrinoid. Despite of their structural similarities, the reactivity of norcorroles is distinct from the reactivity of aromatic compounds. These macrocycles readily undergo regioselective substitution [3], 1,3-dipolar cycloaddition [4], insertion [5], amination [5] and nitration [6]. In comparison to aromatic and non-aromatic materials, antiaromatic systems often have higher molecular conductivity because of the narrow HOMO-LUMO energy gaps and relevant electron-donating and accepting abilities.

A 1,3-cycloaddition reaction of 2-(tert-butyl)-8H-isoquinolino[4,3,2-de]phenanthridin-9-ium chloride to Ni(II) norcorrole in the presence of base was carried out. As a result, we obtained a group of a chiral mono- and diadducts with polycyclic system(s) fused with pyrrole subunits(s) of the macrocycle. One of the goals was to find out if the dehydrogenation has the influence on the conformation. The analysis of the results showed that it strongly depends on the number and position of hydrogen atoms in the linking part.

REFERENCES

1. M. Bröring, S. Köhler, C. Kleeberg, *Angew. Chem., Int. Ed.*, 2008, **47**, 5658.
2. T. Ito, Y. Hayashi, S. Shimizu, J.-Y. Shin, N. Kobayashi, H. Shinokubo, *Angew. Chem., Int. Ed.*, 2012, **51**, 8542.
3. R. Nozawa, K. Yamamoto, J.-Y. Shin, S. Hiroto, H. Shinokubo, *Angew. Chem., Int. Ed.*, 2015, **54**, 8454.
4. X. Fu, Y. Meng, X. Li, M. Stępień, P. J. Chmielewski, *Chem. Commun.*, 2018, **54**, 2510.
5. B. Liu, T. Yoshida, X. Li, M. Stępień, H. Shinokubo, P. J. Chmielewski, *Angew. Chem., Int. Ed.*, 2016, **55**, 13142.
6. Z. Deng, X. Li, M. Stępień and P. J. Chmielewski, *Chem. Eur. J.*, 2016, **22**, 4231.

CO_2 Electrochemical Reduction and Phthalocyanines: linkers on Metal-Organic Framework Catalysts

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Reducing the amount of atmospheric CO_2 to mitigate the effects of climate change is an ambitious goal that can be achieved in several ways. One of them is the electrochemical reduction of this gas, converting into highly useful chemical products. To carry out this reduction reaction, a series of catalyst have been used, including those of inorganic complexes of copper, gold, silver and tin. as well as organic-type structures such as metallophthalocyanines (MPcs) that have been reported as highly selective towards CO production.[1]

Another approach is the use of metal-organic frameworks (MOFs). MOFs are materials with a repetitive structural units of inorganic metal ions and organic linkers to form an ordered porous network. The large surface area, tunable porosity, design flexibility and adaptable nature of MOFs make them ideal candidates for use as catalysts in electrochemical reactions.[2] Thus, combination of phthalocyanines and inorganic ions can result in a great advance in the catalytic field to obtain a highly valuable chemical products from CO_2.

In this communication, we will present the synthesis of new SiPcs compounds axially functionalized and MPc peripherally substituted (Figure 1), to generate, in combinations with inorganic ions, MOFs structures which will be used as catalysts in CO_2 reduction.

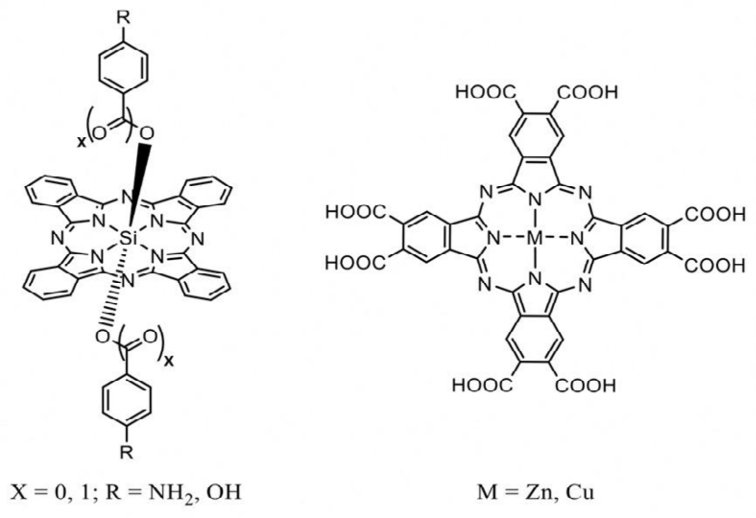

Figure 1. SiPcs and MPcs compounds used as organic linkers in MOFs.

REFERENCES

1. G. F. Manbeck, E. Fujita, *J. Porphyrins Phthalocyanines*, **2015**, *19*, 45-64.
2. a) D. Narváez-Celada, A. Sofia-Varela, *J. Mater. Chem. A*, **2022**, *Advanced article,* 10.1039/D1TA10440C; b) T. Zhan, Y. Zou, Y. Yang, X. Ma, Z. Zhang, S. Xiang, *ChemCatChem* **2022**, *14*, e202101453.
3. V Sobrino-Bastán, J. Follana-Berná, F. E. Oropeza, L. Martín-Gomis, Y. Pérez, P. Horcajada, Á. Sastre-Santos, *in preparation*.

Fusion of porphyrins within a strained nanoring: porphyrin tape - cycloparaphenylene hybrids

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and Harry L. Anderson[a*]**

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[b]*National Crystallography Service, School of Chemistry, University of Southampton, SO17 1BJ, U.K.*

Porphyrin nanorings have attracted attention recently due to their unique properties [1-2]. However, synthesis of such large cyclic molecules remains challenging, especially when a substantial ring strain is introduced.
Fusion of two and more porphyrins via a *meso* and two β positions leads to formation of the porphyrin tapes; highly π-conjugated species with absorption in the NIR region [3] and with remarkably 'wire-like' charge transfer behavior [4].
Although several nanorings bearing a *meso*-*meso* linked porphyrin motif have been reported [5-6], involvement of a triply fused, highly π-delocalised porphyrin tape into a three-dimensional, strained nanoring-like structure has been scarcely explored [7-8].
In this work, we describe an efficient synthesis of strained *para*-phenylene linked porphyrin nanorings bearing a *meso*-*meso* linked motif and their postsynthetic modification by fusion of porphyrins (see: Figure).

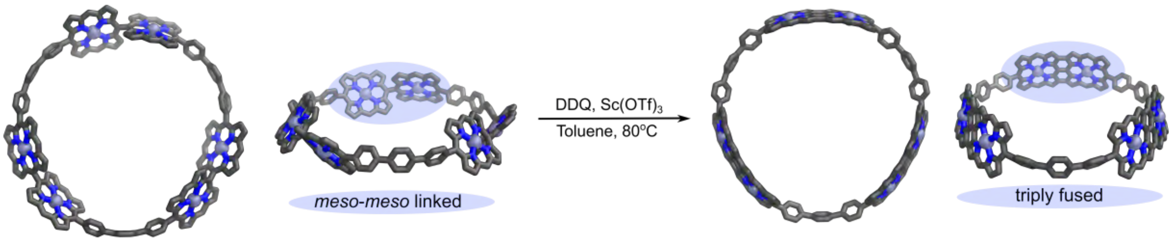

Figure. DFT-optimized structures of synthesised nanorings before and after fusion of porphyrin units.

REFERENCES

1. Bolls, P.T. *et al*., *Acc. Chem. Res.* 2018, **51**, 2083.
2. Jirasek, M. *et al*., *Acc. Chem. Res.* 2021, **54**, 3241.
3. Tsuda, A. *et al*., *Science*, 2001, **293**, 79.
4. Leary, E. *et al*., *J. Am. Chem. Soc.* 2018, **140**, 12877.
5. Peng, X. *et al*., *J. Am. Chem. Soc.* 2004, **126**, 4468.
6. Nakamura, Y. *et al., J. Am. Chem. Soc.* 2005, **127**, 236.
7. Yoon, M.-C. *et al., J. Phys. Chem. A* 2007, **111**, 9233.
8. Kopp, S., Gotfredsen, H. *et al. J. Am. Chem. Soc.* 2020, **142**, 19393.

Synthesis and comparative study of Si(IV) complexes with octaphenyl substituted porphyrazine and corrolazine

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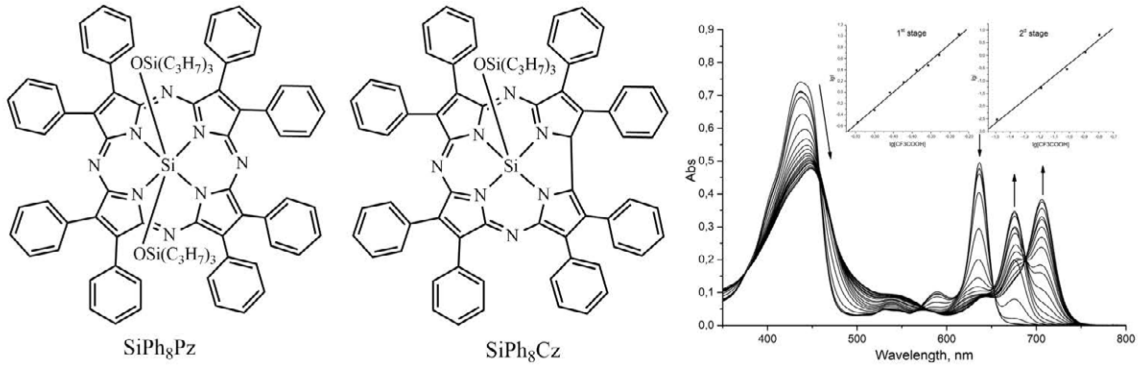
Corrolazines are ring π-contracted analogs of porphyrazines in which one *meso*-nitrogen is missed. They show very strong light absorption in both the blue and the red regions and have photophysical and photochemical properties which are easily tunable by chemical modification. Consequently, corrolazines can find important applications in such fields as photovoltaics and photodynamic therapy (PDT) [1].

In this work, the Si(IV) complex of octaphenylcorrolazine ($SiPh_8Cz$) was obtained by the interaction of dihydroxysilicon(IV) complex of octaphenylporphyrazine with chlorotripropylsilane in pyridine. In addition to the contraction of the macrocycle, the HO ligands in the initial porphyrazine are substituted by the tripropylsiloxy groups ($SiPh_8Pz$).

The compounds obtained were characterized using spectral methods of analysis (UV-Vis, IR, ^{1}H NMR). The effect of contraction of the macrocyclic ligand on the photophysical, photochemical, and acid-base properties of Si(IV) complexes is discussed. The spectrophotometric titration data of $SiPh_8Cz$ in the presence of CF_3COOH reveal two consecutive stages of protonation of *meso*-nitrogen atoms, allowing to determine the corresponding constants ($pK_{s1} = 0.93\pm0.2$, $pK_{s2} = 0.45\pm0.07$). Having a high ability to generate singlet oxygen (Φ_Δ=0.76), $SiPh_8Cz$ can be considered as a promising photosensitizer for PDT.



$SiPh_8Pz$ $SiPh_8Cz$

Figure 1. The structures of $SiPh_8Pz$ and $SiPh_8Cz$ and UV-vis spectral changes observed for $SiPh_8Cz$ in CH_2Cl_2 upon titration by CF_3COOH

This study was supported by the RFBR (grant No. 20-53-26004 Czech_a).

REFERENCES

1. Zhang X.-F. Tetrabenzotriazacorrole: Its synthesis, reactivity, physical properties, and applications // *Coord. Chem. Rev.* 2015. Vol. **285**. P. 52-64.

Friedel-Crafts alkylation of arenes with a 3-hydroxymethyl-chlorophyll-*a* derivative

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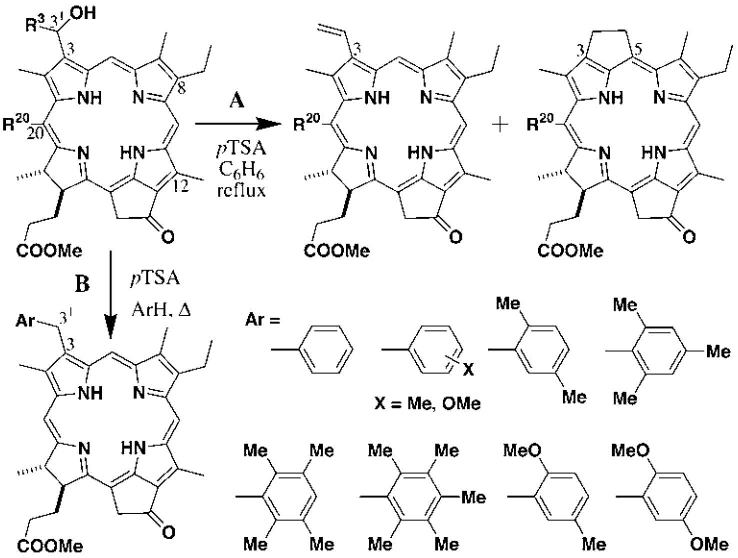
One of the bacteriochlorophyll(BChl)-*d* analogs, methyl bacteriopheophorbide-*d* possessing the 8-ethyl and 12-methyl groups, was dehydrated by refluxing in a benzene solution of *p*-toluenesulfonic acid (*p*TSA) to give the corresponding 3-vinyl-chlorin, methyl pyropheophorbide-*a* (R^3 = Me, R^{20} = H in the step A of Scheme 1) [1,2]. Its 20-methyl derivative, methyl bacteriopheophorbide-*c* as a BChl-*c* analog, was treated with the same conditions to give the other type of dehydrated product, cyclized 3,5-ethano-chlorin with one more fused, 5-membered ring (R^3 = R^{20} = Me in the step A) [1,3]. Recently we found that the 20-substitution affected the acidic dehydration pathways to give these two different products [3,4]. As the control experiment for the above intramolecular reactions, refluxing a benzene solution of a 3-hydroxymethyl-chlorin lacking the 3^1-methyl group, methyl 3-hydroxymethyl-pyropheophorbide-*a*, with *p*TSA was examined (R^3 = R^{20} = H in the step B). The starting material was unexpectedly consumed during the acidic treatment to afford a new product, 3-benzyl-chlorin (Ar = C_6H_5) by the Friedel-Crafts alkylation of benzene as the reaction solvent. Herein, we report the synthesis of 3-arylmethyl-chlorins by the acidic intermolecular dehydra-tion of 3-hydroxy-methyl-chlorin with various arenes and their photophysical proper-ties in a solution. Their electronic absorption and fluorescence emis-sion properties were independent of the substituents on the 3^1-phenyl group.



Scheme 1. Acidic de-hydration of 3-(1-hydroxyethyl)chlorins (R^3 = Me) in a molecule (A) and a 3-hydroxy-methyl-chlorin (R^3 = H) with arenes ArH (B).

REFERENCES

1. Kenner GW, Rimmer J, Smith KM, Unsworth JF. *J Chem Soc Perkin Trans 1* 1978: 845–852.
2. Tamiaki H, Ariki N, Sugiyama H, Taira Y, Kinoshita Y, Miyatake T. *Tetrahedron* 2013; **69**: 8412–8421.
3. Takarada Y, Doi M, Ogasawara S, Tamiaki H. *Tetrahedron* 2021; **93**: 132260.
4. Doi M, Tamiaki H. *Tetrahedron Lett* 2019; **60**: 150934.

Diastereoselective coordination of pyridyl terminal to zinc center in 13^2-epimeric chlorophyll-*a* derivatives

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In the primary step of photosynthesis, chlorophyll(Chl)-*a* works in light-harvesting, energy-migrating, and charge-separating systems. Chl-*a* molecules are usually surrounded by protein supports and primarily coordinated by the imidazolyl moiety of histidine residues. Since there are two coordination directions of the imidazolyl nitrogen atom against the central magnesium atom of Chl-*a*, Oba *et al*. categorized them as *α*- and *β*-coordination based on IUPAC rules [1]. It is noteworthy that the *α*-coordination of the imidazolyl moieties is favorable over the *β*-coordination in photosynthetic organisms [1,2]. Although the intermolecular *α*/*β*-coordinated species in solution cannot be separated due to rapidly reaching its equilibrium state, the coordination-dependent diastereomers of asymmetric Chl-*a* were expected to be isolated under specific conditions. To achieve stereoselective *α*/*β*-coordination of Chl-*a*, we here designed intramolecular coordination systems using the C13^2-stereochemistry, the (13^2*R*/*S*)-epimers.

Chl-*a* derivatives possessing the zinc center and the C13^2-alkanoate residue with a terminal pyridyl group were synthesized. Their C13^2-epimerically pure products were isolated by preparative reverse phase HPLC. The C13^2-stereochemistry gave two directional terminal pyridinyl groups to coordinate the central zinc atom in each stereoisomeric molecule; *α*/*β*-intramolecular axial coordination (Fig. 1). The diastereomerically dependent conformers in solution were characterized by 1D/2D NMR, visible absorption, and fluorescence emission as well as circular dichroism (CD) spectroscopy. The ^{1}H NMR and DOSY spectra revealed that the stereoselectively intramolecular coordination occurred in less coordinative deuterated chloroform, whereas a deuterated pyridine molecule as a highly coordinative solvent replaced the terminal pyridine moiety as the axial ligand to form a mixture of *α*/*β*-coordinated species. Their optical spectra in pyridine were nearly independent of the C13^2-stereochemistry and the linkers in the C13^2-substituents. The CD bands of *β*-coordinated species in chloroform were more intense than those of the corresponding *α*-coordinated stereoisomers, indicating that the distortion of the chlorin π-plane in the former was larger than that in the latter. Therefore, the *α*-coordinated Chl complex would be more conformationally stable than the *β*-complex.

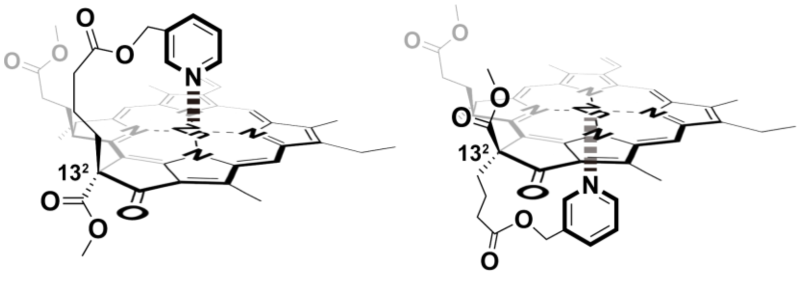

Figure. Intramolecularly *β*-coordinated conformer of zinc methyl 13^2-[3-{(3-pyridyl)methyloxycarbonyl}-propyl] pheophorbide-*a* (left) and the *α*-coordinated one of its 13^2-epimer (right).

REFERENCES

1. T. Oba, H. Tamiaki, *Bioorg. Med. Chem.* **2005**, *13*, 5733–5739.
2. T. Oba, H. Tamiaki, *Photosynth. Res.* **2002**, *74*, 1–10; T. S. Balaban, P. Fromme, A. R. Holzwarth, N. Krauß, V. I. Prokhorenko, *Biochim. Biophys. Acta Bioenerg.* **2002**, *1556*, 197–207; T. Oba, H. Tamiaki, *J. Porphyr. Phthalocyanines* **2014**, *18*, 919–932.

Antimicrobial photodynamic therapy of Gram-negative and Gram-positive bacteria through the action of cationic Si(IV) phthalocyanines

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Photodynamic inactivation of microorganisms (PDI) has emerged as an alternative to conventional antibiotics [1]. Lately, Si(IV) phthalocyanines (SiPcs) have been used as photosensitizers (PSs) in PDI approach due to their excellent absorption and emission features [2]. To increase the knowledge about the potential of cationic SiPcs as PSs, one novel (**1a**) and two previously described (**2a** and **3a**) axially substituted compounds with di-, tetra-, and hexa-ammonium units, respectively, were synthesized and characterized [3]. Their PDI effect was evaluated under white-light irradiation against *Escherichia coli* and *Staphylococcus aureus*, a Gram-negative and a Gram-positive bacterium, respectively. The photodynamic treatments were conducted with PS concentrations of 3.0 and 6.0 µM under white light irradiation (150 mW.cm^{-2}, 60 min).

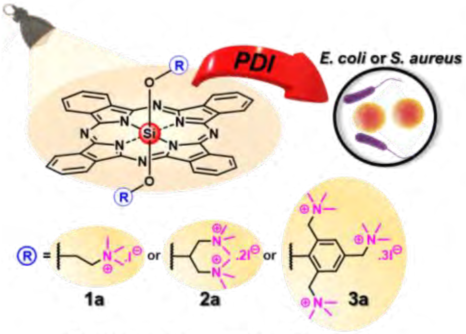

Figure 1. PSs used in this work

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REFERENCES

1. a) Santos, I.; Gamelas, S.R.D.; Vieira, C.; Faustino, M.A.F.; Tomé, J.P.C.; Almeida, A.; Gomes, A.T.P.C.; Lourenço, L.M.O. *Dyes Pigm*., **2021**, 193, 109557. b) Gamelas, S.R.D.; Gomes, A.T.P.C.; Faustino, M.A.F.; Tomé, A.C.; Tomé, J.P.C.; Almeida, A.; Lourenço, L.M.O. *ACS App. Bio Materials*. **2020**, 3, 4044–4051.
2. Ribeiro, C.P.S.; Lourenço, L.M.O. *J. Photochem. Photobiol. C*. **2021**, 48, 100422.
3. a) Lo, P.C.; Huang, J.D.; Cheng, D.Y.Y.; Chan, E.Y.M.; Fong, W.P.; Ko, W.H.; Ng, D.K.P. *Chemistry-A Eur. J*. **2004**, 10, 4831–4838. b) Uslan, C.; Şebnem Sesalan, B. *Inorg. Chim. Acta* **2013**, 394, 353–362.

Preliminary Study on Metal and Substituent Effects of Aqueous Porphyrin-based Redox Flow Batteries Systems

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Redox flow batteries (RFBs) are one amongst promising energy storage technologies for large-scale applications. Both energy and power can be easily adjusted from a few hours to days for storage depending on the application, which is an important advantage for renewable integration of energy management [1,2].

Aqueous RFBs exhibit faster dynamics and higher ionic conductivity compared with non-aqueous RBFs. For large-scale energy storage applications, the comparatively low cost of aqueous electrolyte compared to non-aqueous electrolyte adds additional competitiveness [3].

In a recent paper, the results have shown that the porphyrin based RFB in a non-aqueous system can work in as low as -40°C. Such a low working temperature has been a problem for commercialized type RFB systems due to the freezing point of the electrolyte, resulting in damages to the battery system [4].

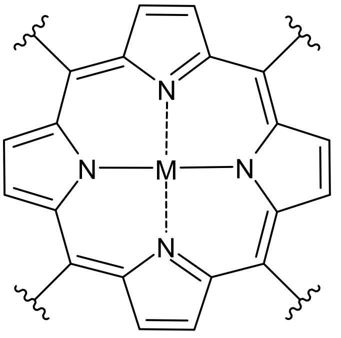

Figure 1. The basic structure of water-soluble (metallo)porphyrins

In this work, we studied a few water-soluble porphyrins and their metal derivatives (*Figure 1*). The synthesized porphyrins and metalloporphyrins were characterized by different analytical techniques and electrochemically investigated in different pHs in aqueous media. Also, we studied the metal and substituent effect on the redox potentials to accomplish a better candidate for water-soluble porphyrin based RFBs.

Acknowledgement: This work is partially sponsored by *Frontier Speciality Chemicals* and the *Finnish Foundation for Technology Promotion*.

REFERENCES

1. V. Singh *et al. Nano Research* **2019**, 12, 1988.
2. R. G. Gordon and M. J. Aziz, *Nature* **2014**, 505, 195.
3. A. Z. Weber *et al.*, *J. Appl. Electrochem.* **2011**, 41, 113.
4. T. Ma *et al.*, *Ang. Chem. Int. Ed.* **2018**, 57, 3158.

UPGRADED TO AN ORAL PRESENTATION

Synthesis, Spectroscopy and Electrochemistry of 5,10,15-Tris(pentafluorophenyl)corrolatoindium(III)

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Corroles are tetrapyrrole containing aromatic molecules which are often categorized as contracted porphyrin derivatives. Many metallocorroles have been successfully synthesized, and both their molecular and electrochemical properties have been investigated. Although the group 13 elements (B, Al and Ga) metallocorroles are very well characterized, attempts to investigate the corresponding corrole complexes of the heavier elements of this main group are still quite rare. It has been tried many times to synthesize a stable indium corrole derivatives [1-3], but as a first time an indium corrole molecule has been recently synthesized and characterized by different analytical techniques [4].

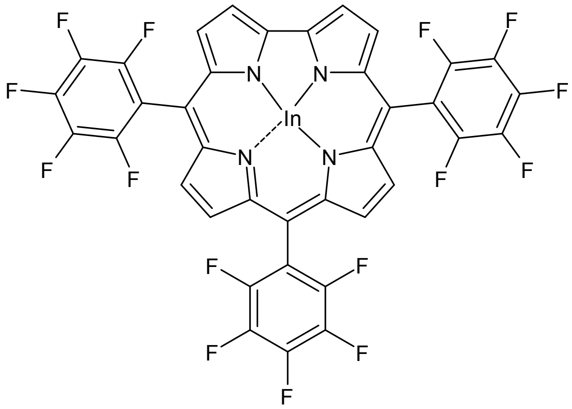

Figure 1. The structure of 5,10,15-Tris(pentafluorophenyl)corrolatoindium(III)

In this study, a new indium corrole compound was synthesized and characterized by UV-vis, HR-MS, CV, and 1D- and 2D-NMR techniques.

REFERENCES

1. Y. Fang, Z. Ou, and K. M. Kadish, Chemical Reviews 2017, 117, 3377-3419.
2. R. Paolesse, S. Licoccia and T. Boschi, Inorganica Chimica Acta 1990, 178, 9-12.
3. J. J. Weaver, Corroles, Doctoral Thesis 2005, California Institute of Technology, California, USA.
4. A. Tuna and G. Knör, Synthesis and Electrochemistry of a Stable Indium A3-Corrole, International Conference on Porphyrin and Phthalocyanine Conference (ICPP-11), 28 June - 3 July 2021, New York, USA.

Multi-Chromophore Ensembles with Subphthalocyanines and BODIPYs as Energy Transfer Systems for DSSCs

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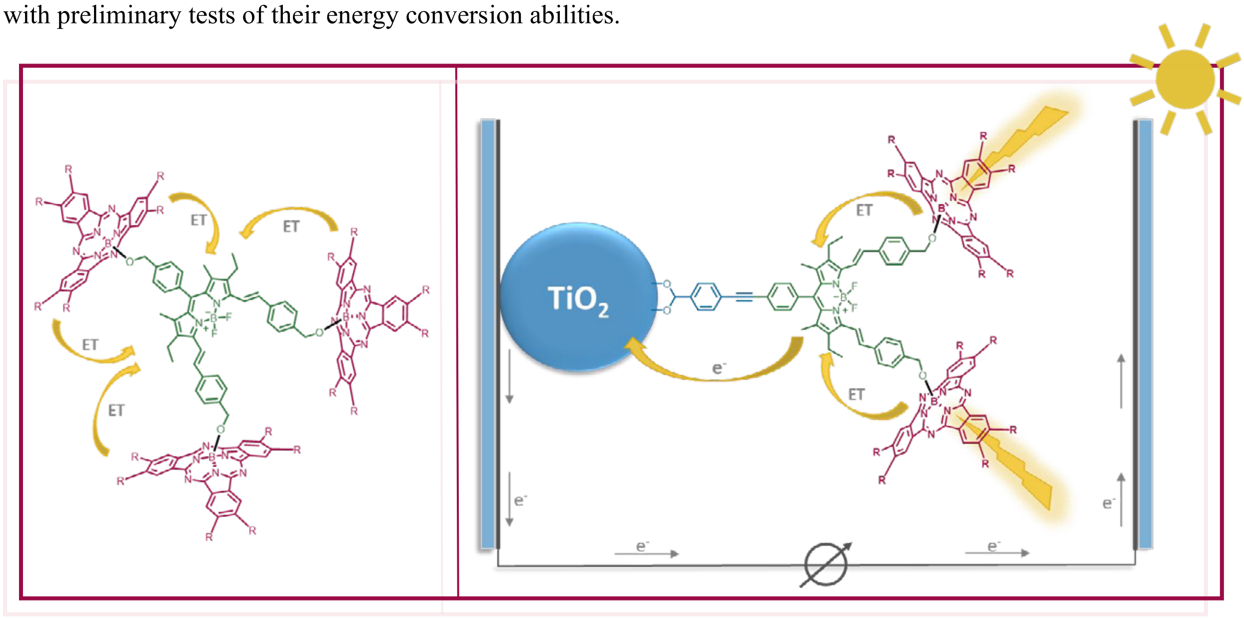
Already in 1991 GRÄTZEL and O'REGAN published the development of the first Dye Sensitive Solar Cell (DSSC).[1] Optimization of DSSCs, especially in terms of improving efficiencies, will currently become more and more important in tackling energy and environmental problems. Inspired by photosynthetic processes the demand of innovative energy transfer systems in particular for DSSCs increases.[2-3]

The aim of our current work is to assemble energy and electron transfer systems into one molecular ensemble. By combining multiple chromophores in a single confined space, the efficiency of their interaction with light will be maximized. As a prototype, we attached three cone-shaped subphthalocyanines (SubPcs) as antenna dyes to a BODIPY core (Figure left). Initial photophysical measurements confirm an energy transfer from the SubPc entities to the central BODIPY. In a further development, we modified the BODIPY/SubPc-ensemble by implementing a carboxylate-anchoring group to facilitate the binding of the multi-chromophore ensemble to the TiO_2 electrode of a DSSC (Figure right). We will report the syntheses of the multi-chromophore ensembles along with preliminary tests of their energy conversion abilities.



REFERENCES

1. B. O'Regan, M. Grätzel, Nature 1991, 353, 737-740. 2. D. González-Rodríguez, G. Bottari, J. Porphyrins Phthalocyanines 2009, 13, 624-636. 3. B. Balli, B. Demirkan, B. Sen, F. Sen, in Nanophotocatalysis and Environmental Applications: Energy Conversion and Chemical Transformations (Eds.: Inamuddin, M. I.Ahamed, A. M. Asiri, E. Lichtfouse), *Springer, Cham,* 2019, pp. 103-123.

Small Phospholipid Bicelles as Drug Delivery Vehicles for Porphyrinic Compounds

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Phospholipid (PL) bicelles are small disk-shaped particles typically consisting of long chain PLs forming a closed bilayer and short chain PLs forming the edges [1]. With size-ranges between 5 nm and 50 nm [1], bicelles provide potential nano platforms for topical applications of photosensitizers in the treatment of skin diseases. Similar to PL liposomes, the closed bilayer of bicelles offers a hydrophobic environment to accommodate lipophilic guest molecules. Moreover, the PL-based systems benefit from their good biocompatibility and availability.

The current presentation focuses on the encapsulation of porphyrinic compounds into bicelles and the characterization of the resulting systems with respect to their physicochemical properties. Different porphyrinic compounds covering the groups of chlorin e6 derivatives, tetra-phenyl-porphyrins and phthalocyanines were incorporated into PL-bicelles. The structure, size and substitution pattern of the porphyrinic guest molecule required specific adjustments for achieving the desired drug loading. This could be achieved by systematic variation of PL chain lengths and different combinations and molar ratios of long and short chain PLs (q-values) of the bicellar vehicles. ^{1}H-, ^{13}C- and ^{31}P NMR spectroscopy was applied as main tool to monitor encapsulation (Fig. 1), monomerization and localisation of the porphyrinic molecule at the bicellar interface [2]. Dynamic light scattering (DLS) and NMR diffusion ordered spectroscopy (DOSY, Fig. 1) allowed to determine the average size, size distribution and stability against dilution. In ongoing studies, in vitro skin permeation tests are performed for assessing the capability of the delivery systems to enhance porphyrin skin penetration.

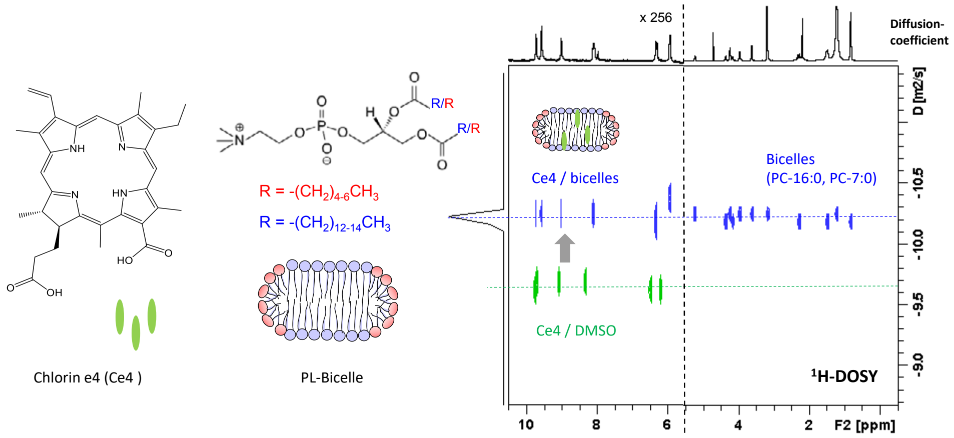

Figure 1: Structure of Chlorin e4 and sketch of a bicelle. Overlay of ^{1}H DOSY spectra of chlorin e4 encapsulated into bicelles (shown in blue) and dissolved in DMSO (shown in green).

REFERENCES

1. Dufourc, E.J. *BBA-Biomembranes*, *1863* (2021), 183478. doi.org/10.1016/j.bbamem.2020.183478.
2. Gjuroski I., Furrer J., Vermathen M. *Molecules* 26 (2021) 1942. doi.org/10.3390/molecules26071942.

Controlled Storage and Release of Singlet Oxygen *via* Pyridone-Subphthalocyanine-Dyads

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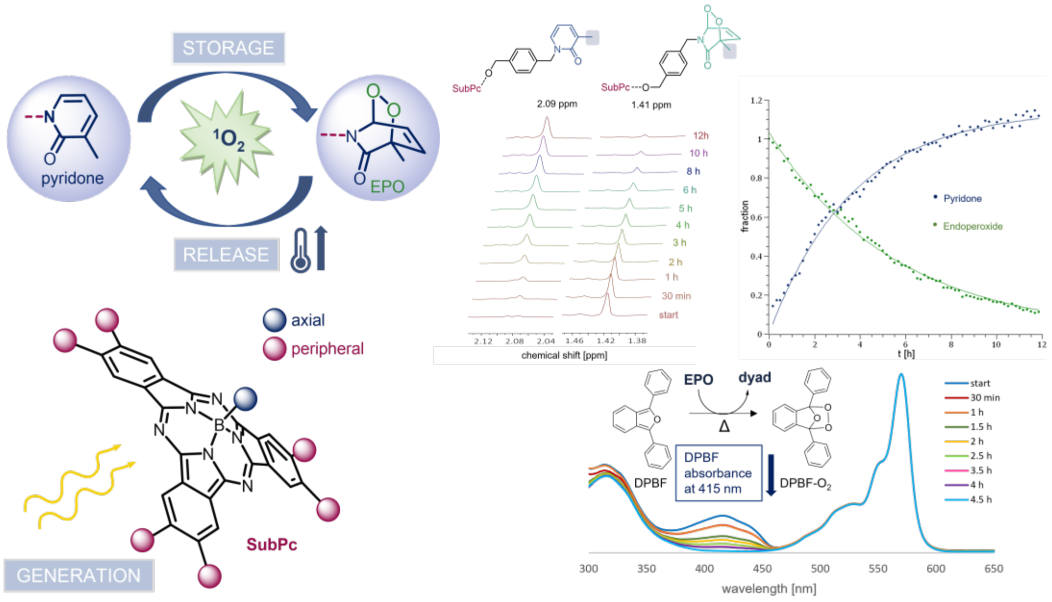
Instead of generating singlet oxygen ($^1O_2$) in situ at the intended site of action by the interaction of light, oxygen and an appropriate photosensitizer, we use the delayed provision of reactive oxygen through the thermal decomposition of an endoperoxide (EPO).[1] For this purpose, we synthesize and explore diverse dyadic systems of subphthalocyanines (SubPc) as photosensitizers and pyridones as EPO-forming units.[2][3] We realize these self-sensitized EPO-forming dyads by axial or peripheral functionalization of SubPcs. We show that the dyads are active as photosensitizers and still generate $^1O_2$ efficiently in the wavelength range of their absorption maxima. The dyads are able to store the SubPc-sensitized singlet oxygen, resulting in pyridone-centered endoperoxide formation. We are investigating the reversibility of this process by photophysical, photochemical and NMR-spectroscopic means. To verify that the released oxygen is in its singlet state, we use the selective $^1O_2$ trap 1,3-diphenyliso-benzofuran (DPBF).[4] These results will be presented along with the latest synthetic developments aimed at different ways of linking the dyads and trying to increase the pyridone units per SubPc and thus the amount of $^1O_2$ to be stored and released.



REFERENCES

1. M.A. Filatov, M.O. Senge, *Mol. Syst. Des. Eng.*, 2016, *1*, 258-272. 2.C. Claessens, D. González-Rodriguez, T. Torres, *Chem. Rev.,* 2002, *102*, 835-853. 3.M. Matsumoto, M. Yamada, N. Watanabe, *Chem. Commun.,* 2005, *4*, 483-485. 4. Y.-Q. He, W. Fudickar, J.-H. Tang, H. Wang, X. Li, J. Han, Z. Wang, M. Liu, Y.-W. Zhong, T. Linker, *J. Am. Chem. Soc*, 2020, *142*, 2601.

Supramolecular assemblies of Ru(II) and Zn(II) porphyrins and octahedral Mo(II) iodide cluster

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The modular construction of supramolecular assemblies from molecular components with specific properties is a current strategy for the preparation of functional materials. In this work we have demonstrated the strategy toward hybrid materials that combine two photoactive components from different classes of compounds: octahedral iodide Mo(II) cluster ($Mo_6I_8(Py)_6$) and zinc(II) or ruthenium(II) ditolyl-substituted A_2-type porphyrinates ((ZnPor) and (Ru(CO)Por), correspondingly). Axial ligation of cluster pendant pyridyl ligands to metalloporphyrins leads to formation of N_{py}...M bonds (M = Zn(II), Ru(II)) and to assembling of unique organic-inorganic architectures. The structure and composition of the obtained cluster-porphyrin hybrids in solutions (CH_2Cl_2 or $CHCl_3$) were investigated by ^1H NMR including COSY and DOSY as well as UV-Vis spectroscopies. It was demonstrated that in the case of ZnPor molecules, the components participate in the rapid exchange due to the lability of N_{py}...Zn bonds [1], in contrast to solutions of RuPor(CO) where hybrid structures with different cluster/porphyrin ratio have been detected even in polar acetone.

Indeed mixture of hybrid compounds with compositions $[Mo_6I_8(Py)_6](Ru(CO)Por)_n$, where n=1-6 were observed in ^1H NMR as well as COSY and DOSY experiments due to slow ligand-exchange on the NMR timescale. It was also demonstrated that at a large excess of porphyrin in acetone-d6 solution (cluster/porphyrin ratio is 1:14) the main particle was $[Mo_6I_8(Py)_6](Ru(CO)Por)_6$. The structure of such species has been confirmed by means of the single crystal X-ray analysis (Fig.1). It should be noted that this X-ray structure is similar to previously obtained hybrid material containing ZnPor [1]. Interestingly, the two uncoordinated metalloporphyrins are also present inside the crystal structure of both hybrids linked with cluster-porphyrin assembly by hydrogen bonds. The photophysical properties of obtained hybrid materials are under investigation.

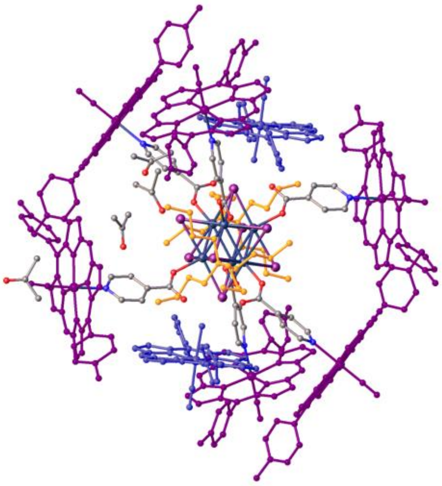

Fig. 1

Acknowledgements: This work is supported by Russian Science Foundation (grant 21-73-00284).

REFERENCES

1. M.V. Volostnykh, M.A. Mikhaylov, A.A. Sinelshchikova, G.A. Kirakosyan, A.G. Martynov, M.S. Grigoriev, D.A. Piryazev, A.Y. Tsivadze, M.N. Sokolov, Y.G. Gorbunova. Dalton Trans. 2019, 48, 1835-1842.

Synthesis and Optical Properties of Donor-Acceptor-Donor Pyrrolopyrrole aza-BODIPYs

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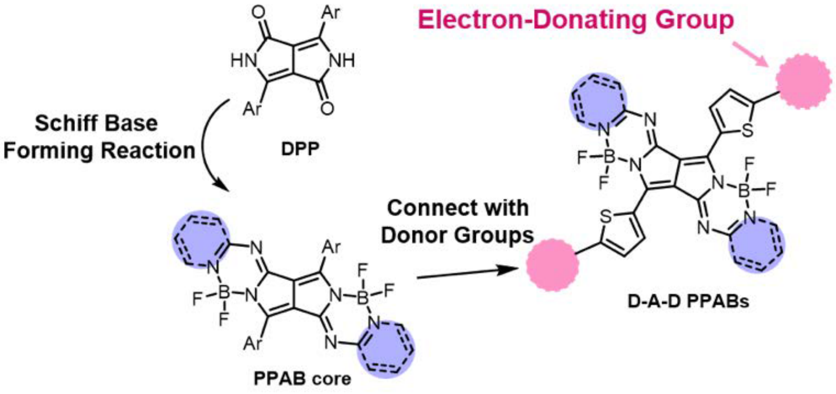
Diketopyrrolopyrrole (DPP)-based donor-acceptor small molecules and polymers have been investigated as functional materials in organic electronics.[1] To enhance the optical properties of DPP in the far-red and near-infrared (NIR) regions, we attempted to expand the π-conjugation of DPP using an aza-BODIPY structure and synthesized a dimeric aza-BODIPY analog called pyrrolopyrrole aza-BODIPYs (PPABs).[2]

In our previous study, we developed donor-acceptor-donor (D-A-D) structures using PPAB as an acceptor unit to shift the absorption and fluorescence emission of PPABs into the NIR region. Among them, D-A-D PPAB bearing diphenylamine as a donor and a phenylene linker exhibited the intense fluorescence and high fluorescence brightness ($\varepsilon_{\mathrm{Abs}} \times \Phi_{\mathrm{Fl}}$) value owing to the moderately large dihedral angle between the phenylene linker and the PPAB core. In this study, to give the detailed insight into the role of the linker, D-A-D PPABs with a thienyl linker were synthesized by a Buchwald-Hartwig amination reaction using carbazole, diphenylamine, and phenothiazine as a donor unit. Despite the possible fluorescence quenching due to the energy-gap law, they still exhibited significant red-shifts of fluorescence emission peaked at around 827 nm with a quantum yield of 0.3. The fluorescence brightness up to 2~3 × 10^4 L M^{-1} cm^{-1} was relatively high in this region. The photophysical properties of a series of D-A-D PPABs were investigated and discussed based on the theoretical calculations.



REFERENCES

1. Grzybowski, M.; Gryko, D. T. *Adv. Opt. Mater*. **2015**, *3*, 280.
2. Shimizu, S.; Iino, T.; Araki, Y.; Kobayashi, N. *Chem. Commun*. **2013**, *49*, 1621.

Structure and biological activity in BODIPYs designed for PDT and antimicrobial phototherapy

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Photodynamic techniques use non-toxic dyes - photosensitizers - that can be activated by absorption of visible light to form reactive oxygen species (prominently singlet oxygen) which in turn oxidize biomolecules and thus are capable of destroying eukaryotic as well as bacterial cells. Today, apart from the well-known application in tumour therapy (PDT) another rapidly developing field for photodynamic techniques is antimicrobial phototherapy as the increasing drug and multi-drug resistance of bacteria and microorganisms against standard antibiotics is a serious problem for public health systems around the world [1,2].

In view of a combined application in PDT and antimicrobial phototherapy a synthetic strategy for specifically functionalized BODIPY (boron dipyrromethene) dyes is presented. BODIPYs with the 8-(4-fluoro-3-nitrophenyl) and the 8-pentafluorophenyl substituent were used for the synthesis of new mono- and dibrominated BODIPYs. The *para*-fluorine atoms in these electron-withdrawing groups facilitate functional modification via nucleophilic aromatic substitution (S_NAr) with a number of amines and especially thio-carbohydrates.

Subsequently, the PDT activity of these BODIPYs has been investigated in tests in several (tumour) cell lines. The antibacterial phototoxic activity of these BODIPYs has been assessed in bacterial assays against the Gram-positive bacterium *S. aureus* and the Gram-negative bacterium *P. aeruginosa* [3]. Antibacterial testing was performed not only in phosphate-buffered saline (PBS) but also in the presence of serum, thereby more realistically modelling the complex biological environment that is present in clinical applications. In both series of tests specifically the brominated, carbohydrate-substituted BODIPYs exhibited a pronounced activity against tumour cells and bacteria. In addition, the non-brominated, carbohydrate-substituted BODIPYs could be of interest for tumour tissue detection due to their cell-uptake behaviour and intense fluorescence.

REFERENCES

1. A. Anas, J. Sobhanan, K. M. Sulfiya, C. Jasmin, P. K.Sreelakshmi, V. Biju, *J. Photochem. Photobiol. C: Photochem. Rev.* **2021**, *49*, 100452.
2. M. R. Hamblin, *Curr. Opin. Microbiol.* **2016**, *33*, 67–73.
3. B. F. Hohlfeld, B. Gitter, K. J. Flanagan, C. J. Kingsbury, N. Kulak, M. O. Senge, A. Wiehe, *Org. Biomol. Chem.* **2020**, *18*, 2416–2431.

Vitamin B_{12}-catalyzed difunctionalizations of olefins

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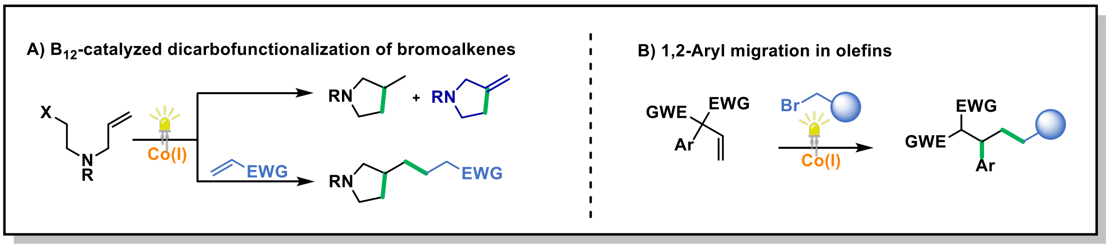
Vitamin B_{12} plays a crucial role in enzymatic transformations. This natural compound proved also useful as a catalyst in numerous organic reactions.[1] Commercial availability and lower cost than precious metal complexes, make cobalamin an attractive candidate for a broader use as a benign Co-catalyst and is in line with the *green chemistry* trends.[2]

Catalytic properties of vitamin B_{12} stem from the central Co(III) ion, which upon reduction generates either radical Co(II) or 'supernucleophilic' Co(I)-species. As such, they react, respectively, with radicals and electrophiles furnishing alkyl cobalamins. Subsequent photolytic or thermal homolytic cleavage of the C–Co bond leads to C-centered radicals, which with suitable partners forge new C–C bonds.[3] These are represented by the vitamin B_{12}-catalyzed dicarbofunctionalization of bromoalkenes with electrophilic olefins that leads to substituted pyrrolidines and piperidines in decent yields after only 15 minutes under light irradiation.[3] Cobalamine as a natural Co-complex can also catalyse 1,2-phenyl group migration reaction in various derivatives of 2-phenyl-2-vinylic acid. Radical aryl migration reactions are a useful source for the formation of new bonds in aromatic compounds, and the resulting free radical intermediates are often more stable than their ionic analogs, making them an excellent alternative to the ionic counterparts of these reactions.[4]



REFERENCES

1. S. M. Clardy, D. G. Allis, T. J. Fairchild, R. P. Doyle, *Expert Opin. Drug Deliv*. **2011**, 8, 127–140.
2. M. Giedyk, K. Goliszewska, D. Gryko, *Chem. Soc. Rev.* **2015**, 44, 3391–3404.
3. S. Smoleń, A. Wincenciuk, O. Drapała, D. Gryko, *Synthesis*, **2021**, 53, 1645-1653.
4. A. R. Allen, E. A. Noten, C. R. J. Stephenson, *Chem. Rev.* **2021**, DOI 10.1021/acs.chemrev.1c00388.

From Saddles to Sheets: Synthesis and Properties of Carpyridines

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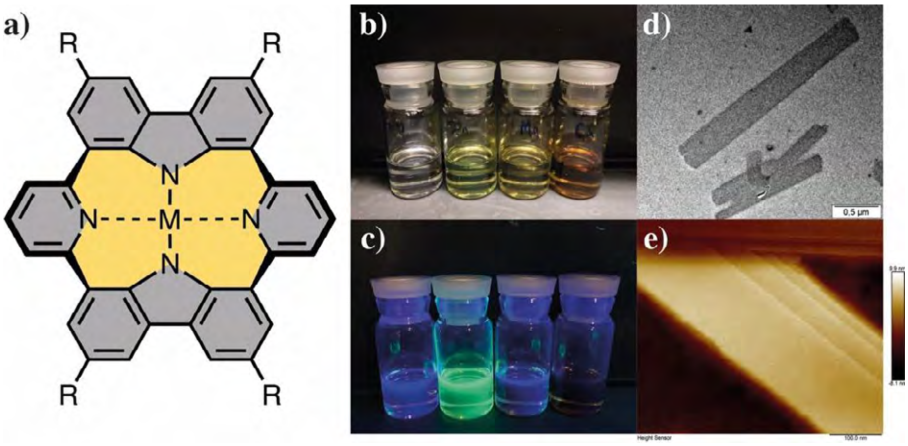
Questioning how molecular topography can govern supramolecular ordering is a relatively unexplored avenue of thought and one which poses great synthetic challenge that could lead towards new functional materials. “Carpyridines” — macrocycles fused from carbazoles and pyridines — are an underdeveloped example of a simple system bearing negative Gaussian curvature that could hold such promise [1].

Derivatisation of these non-planar systems through peripheral functionalisation of the aromatic core and metal coordination into the internal cavity has provided intriguing results in terms of optical findings as well as unusual supramolecular assemblies [2-3].



a) Structure of Carpyridine (Car) functionalised with R groups and metalated with M, vials of M-Car-R under b) visible light and c) 365 nm, d) TEM image of 2H-Car-C6 and e) AFM image of stacked sheets of 2H-Car-C6.

REFERENCES

1. L. Arnold, H. Norouzi-Arasi, M. Wagner, V. Enkelmann, K. Müllen, Chem. Commun., 2011, 47, 970.
2. J. F. Woods, L. Gallego, P. Pfister, M. Maaloum, A. Vargas Jentzsch, M. Rickhaus, DOI: 10.26434/chemrxiv-2022-7f103, submitted.
3. Unpublished results.

Synthesis of Fluorene Embedded Porphyrinoids

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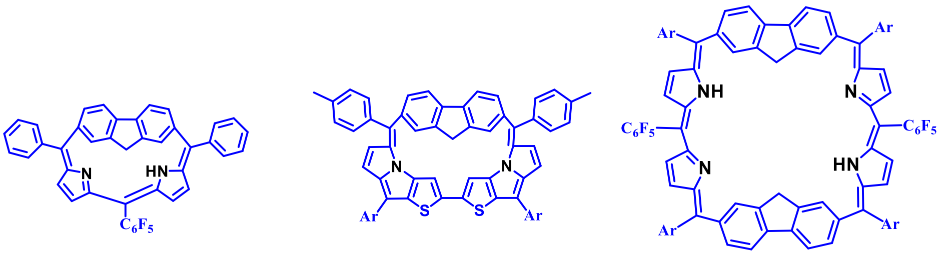
Polyaromatic hydrocarbons/heterocycles (PAHs) embedded porphyrinoids have drawn significant attention in the recent past in the light of their tremendous applications as fluorescent sensors and NIR dyes [1]. The altered π-conjugation in the macrocyclic framework of PAH embedded porphyrinoids leads to interesting coordination and physico-chemical properties. PAH embedded porphyrinoids are relatively new ligands in the literature where the polyaromatic hydrocarbon moiety may or may not participate in the macrocyclic ring π-delocalization. The fused expanded porphyrinoids have been explored for cation/anion sensing and as photosensitizers in photodynamic therapy but the reports on fused expanded PAH embedded porphyrinoids are very few. Our group has recently reported the synthesis of fluorene embedded porphyrins named as fluorenophyrin **I** [1] (Chart). In this poster, we describe the synthesis and characterization of the first examples of doubly fused fluorene embedded heterosapphyrin **II** [2] and *bis*-(fluorene) embedded hexaphyrin **III** [3] (Chart) using fluorene as a starting precursor. The structural, spectral, electrochemical and computational studies of these macrocycles also will be discussed in the poster.



I II III

Chart

REFERENCES

1. Laxman, K.; Kumar, A.; Ravikanth, M. *Asian J. Org. Chem*. **2020**, 9, 162–180.
2. Yadav, B.; Isar, P.; Ravikanth, M. *Org. Chem. Front*. **2021**, 8, 3059–3068.
3. Yadav, B.; Ravikanth, M. (Manuscript submitted).

Synthesis and Studies of Tetracyanobutadiene and Dicyanoquinodicyanomethane appended π-Extended Metallocorroles

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Tetracyanoethene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) are one of the most strongest cyano-based organic acceptors known in literature exhibiting fascinating material properties like magnetic and electrical conductivity [1]. Recently, tetracyanobutadiene (TCBD) appended porphyrins have been synthesized *via* [2+2] cycloaddition-reteroelectrocyclisation (CA-RE) click reaction of arylethynyl-substituted porphyrin with TCNE exhibiting excellent optical limiting and strong charge transfer properties [2]. Corrole based donor-π-acceptor (D-π-A) conjugates are potential candidates for optoelectronic applications. In this work, we report the facile synthesis of three new 3,17-bis(TCBD) and -bis(DCNQDCM) appended metallocorroles *via* [2+2] CA-RE reaction of diphenyethynyl-substituted corroles with TCNE or TCNQ (Figure 1a) in excellent yields. These π-extended metallocorroles contain strong acceptor arms on both sides which lead to shouldering in Soret band and broadening of Q-bands to NIR region which is the consequence of extensive charge transfer (Figure 1b). All these corroles exhibited push-pull effect and high ground state dipole moment which could be useful in nonlinear optical (NLO) applications.

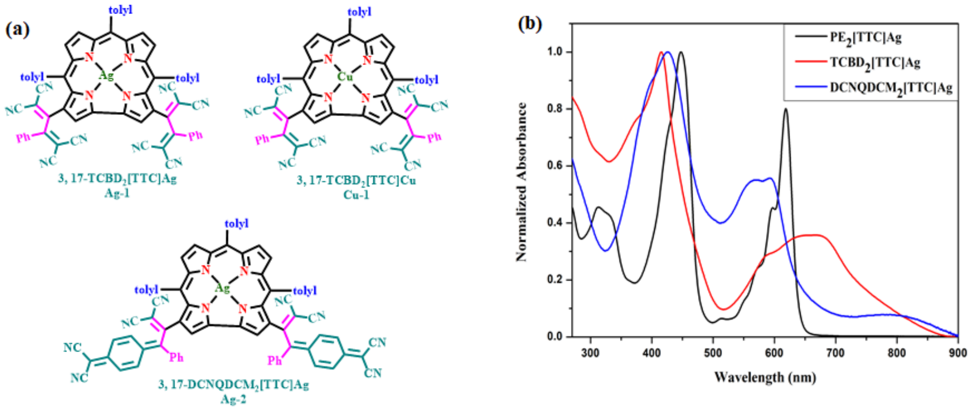

Figure 1. (a) Molecular structures of symmetrically *β*-disubstituted corroles; (b) Comparative UV-Vis spectra of PE_2[TTC]Ag, $TCBD_2$[TTC]Ag and $DCNQDCM_2$[TTC]Ag in CH_2Cl_2 at 298 K.

REFERENCES

1. (a) Her, J. H.; Stephens, P. W.; Davidson, R. A.; Min, K. S.; Bagnato, J. D.; Van Schooten, K.; Boehme, C.; Miller, J. S. *J. Am. Chem. Soc.* **2013**, *135*, 18060-18063. (b) Michinobu, T.; Diederich, F. *Angew. Chem. Int. Ed.* **2018**, *57*, 3552–3577. (c) Yadav, I. S.; Alsaleh, A. Z.; Misra, R.; D'Souza, F. *Chem. Sci.* **2021**, *12*, 1109-1120.
2. (a) Koszelewski, D.; Nowak-Król, A.; Gryko, D. T. *Chem. Asian J.* **2012**, *7*, 1887-1894. (b) Sekaran, B.; Dawson, A.; Jang, Y.; Mohansingh, K. V.; Misra, R.; D'Souza, F. *Chem. Eur. J.* **2021**, *27*, 14335-14344. (c) Rohal, R. K.; Acharyya, J. N.; Shanu, M.; Prakash, G. V.; Sankar, M. *Inorg. Chem.* **2022**, *61*, 1297-1307.

Molecular structure of perfluorinated subphthalocyanine F_{12}-SubPcBCl

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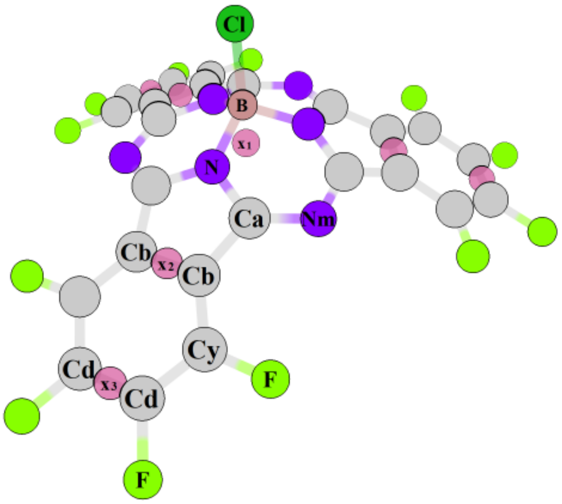

Figure 1. Molecular structure of F_{12}-SubPcBCl.

The structure of perfluorinated subphthalocyanine F_{12}-SubPcBCl determined by gas-phase electron diffraction and DFT calculations. The diffraction patterns were obtained in a synchronous gas-phase electron diffraction and mass spectrometric experiment carried out using the EMR-100/APDM-1 unit. Vapor composition was monitored by mass spectrometry during the GED/MS experiment. The mass spectra of the saturated vapor over the samples show a stable relative abundance of ions, indicating the presence of the only molecular species in the vapor at the temperature of the experiment. The starting model of the molecule used in the refinement of the data of the electron diffraction experiment was built on the base of the optimized geometry in the B3LYP/pcseg-2 approximation. The structural parameters of the F_{12}-SubPcBCl molecule obtained from the GED are in good agreement with the parameters obtained by quantum chemical calculations. Main geometric parameters: r_e(Cl-B)=1.850(10) Å, r_e(B-N)=1.487(3) Å, r_e(N-C_a)=1.362(3) Å, r_e(C-N_m)=1.331(3) Å, r_e(C_a-C_b)=1.449(3) Å, r_e(C_b-C_y)=1.385(3) Å, r_e(C_y-C_d)=1.384(3) Å, r_e(C_b-C_b)=1.425(4) Å, r_e(C_d-C_d)=1.394(3) Å, r_e(C-F)$_{ave}$=1.328(3) Å, r_e(N-X_2)=2.116(5) Å, r_e(X_2-X_3)=2.388(5) Å. Like subphthalocyanine, perfluorinated subphthalocyanine F12-SubPcBCl has a "bowl-shaped" geometry of the subporphyrazine macrocycle. The perfluorinated subphthalocyanine F_{12}-SubPcBCl has a "bowl-shaped" geometry of the subporphyrazine macrocycle, as does subphthalocyanine. This distortion is described using three bond angles a(X_1-B-N)=65.4(1)^0, a(X_2-N-B)=178.0(17)^0,a(X_3-X_2-B)=179.5(17)^0, which also varied in GED structural analysis. The disagreement factor between theory and experiment was $R_f = 4.1\%$.

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Molecular structure and conformational composition of substituted complexes of phthalocyanine with aluminum and zinc

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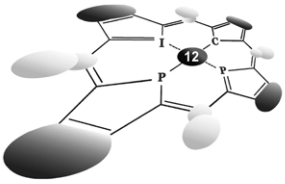
A unique aromatic π-system of phthalocyanines provides their high optical activity, chemical and thermal stability. In addition, the development of synthetic chemistry of the described compounds makes it possible to obtain phthalocyanines with structural substituents in peripheral and nonperipheral positions, which reveals practically inexhaustible possibilities of macromolecules [1]. It is known [2] that tetrasubstituted phthalocyanines are formed as a mixture of four position isomers – randommers in various ratios. In this regard, determination the most preferable structure of the complexes is an important task. Quantum chemical calculations of the geometric and electronic structures of aluminum and zinc phthalocyanine complexes substituted by 4-cyclohexylphenoxy group in the 3 or 4 position were carried out using the density functional theory method (DFT, B3LYP functional) in combination with the dgdzvp basis set. The gfn2 method implemented in the CREST software package was used to determine the conformational composition of the compounds under consideration. In the case of phthalocyanines with zinc, the existence of 56-132 conformers was found and 60 ones for aluminum complex. It should also be noted that, for considered phthalocyanine derivatives with aluminum, the plane of the macrocycle is distorted, the radicals are "attracted" to the axial substituent (chlorine) and the structure becomes similar to a "spiral". In the case of phthalocyanines with zinc, this effect was not observed. It should be noted that a "spiral" structure was obtained by the optimization of phthalocyanines complex with aluminum taking into account dispersion interactions by the Grimme method [3] (B3LYP-D3), and the using of the CAM–B3LYP functional does not lead to such an effect. We also calculated electronic absorption spectra modeled by the TDDFT method for the structures of phthalocyanines with aluminum obtained using the Grimme correction for long-range interactions (B3LYP-D3) and the CAM–B3LYP functional. Comparing the theoretical and experimental absorption spectra, we noted a great similarity between them in case the Grimme correction applied. Thus, we can conclude that the realization of the “spiral” structure of phthalocyanines with aluminum is more probable.

Quantum-chemical calculations were performed with the support of the Russian Science Foundation grant 21-73-10126.

REFERENCES

1. Nemykin V.N., Lukyanets E.A. Synthesis of substituted phthalocyanines // Arkivoc. 2010. Vol. 2010. P. 136–207.
2. Rager C., Schmid G., Hanack M. // Chem. Eur. J. 1999, Vol. 5, P. 280-288.
3. Grimme S., Antony J., Ehrlich S., Krieg H. A consistent and accurate *ab initio* parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu // J. Chem. Phys. 2010. V. 132. N.15. P. 154104–154119.



A universal free-energy landscape for near-reversible electron bifurcation

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Many electron transfer reactions in biology involve the motion of multiple electrons and protons, creating novel opportunities for novel electron correlation and spin effects to influence the reaction kinetics and dynamics. Electron bifurcation is a biological energy conversion process that oxidizes a two-electron donor at medium potential, coupled to the reduction of a high-and a low-potential acceptor species. This process is often fully reversible (can occur close to zero driving force), allowing the creation of strong reductants with minimal free energy cost, derived from compounds with higher reduction potentials. For many years, the internal workings of electron bifurcating enzymes were poorly understood, especially regarding how short-circuit reactions are prevented. Recently, we described an energy landscape that naturally insulates near-reversible electron bifurcation reactions from short-circuiting, thus enabling efficient and reversible electron bifurcation. I will describe the physical principles that underpin the EB scheme, describe how the reversible EB scheme is distinct from previous views, and outline open challenges and opportunities surrounding multi-electron transport processes.
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Synthesis, characterization and reactivity of borylated Subphthalocyanines

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Subphthalocyanines (SubPc) hold a privileged position among the most employed organic semiconductors.1 This unique non-planar aromatic macrocycle, which is composed of three N-fused 1,3-diiminoisondoline units around a central tetrahedral boron atom and a fourth substituent that occupies the axial position, exhibits multiple exciting properties easily tailored by functionalization. Whereas the replacement of the axial ligand (typically a chlorine atom) mainly affects physical properties such as solubility, stability, or tendency towards aggregation, the chemical modification of the substituents at the periphery leads to remarkable changes in the electronic properties of SubPcs. Thus, the preparation of novel, versatile SubPc-based building blocks is crucial for the further development of these macrocycles.

Herein we report the synthesis, characterization, and reactivity of borylated SubPcs. These derivatives are characterized by means of UV/Vis and fluorescence spectroscopy, as well as electrochemistry. Moreover, density functional theory (DFT) calculations are carried out to shed light into the experimental results. Then, we explored the reactivity and stability of these particular derivatives.

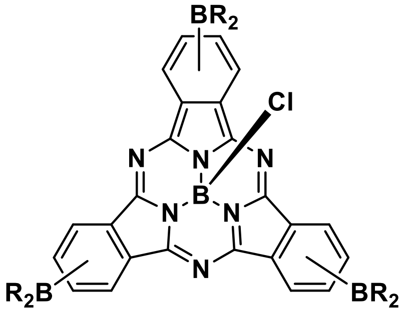

Figure 1. a) Molecular structure of borylated SubPcs.

REFERENCES

1. Claessens, C. G.; Gonzalez-Rodriguez, D.; Rodriguez-Morgade, M. S.; Medina, A.; Torres, T. *Chem. Rev.* **2014**, *114*, 2192-2277.

Binuclear Rhodium(III) Complex of N-Fused Porphyrin: A π-Extended NIR Absorbing Analogue of Cyclopentadienyl Rhodium(III) Dichloride Dimer

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N-fused porphyrin (NFP) is a unique class of photostable near-infrared (NIR) dye with an 18π aromatic tetrapyrrolic macrocyclic skeleton containing a fused tri-pentacyclic moiety. NFP is an ideal ligand platform for metal complexation by the monoanionic, tridentate N3 donor organized in a *fac* manner. Unlike porphyrin, NFP is isoelectronic to well-known ligands like cyclopentadienyl (Cp) and tris(pyrazolyl)borate (Tp). Hence, NFP can serve as a π-extended Cp analogue and can be exploited to investigate the broad array of metallocene and related chemistry.[1]

In this study, we have established a facile approach to expand the π-system in functional complexes like $[Cp^*RhCl_2]_2$. The π-extension was met with rhodium coordination at the NFP core supported by terminal and bridging chloride ligands providing the cofacial di-μ-chloro-bridged rhodium(III) complex **Rh-2** and the bromo derivative **Rh-2-Br**. Although N-fusion largely incites modification in the electronic and chemical properties of porphyrinoids, the bimetallic NFP scaffold is designed by minimizing the orbital interaction between ligand orbitals through bonds. **Rh-2** and **Rh-2-Br** illustrate typical NFP-like absorption with an intense visible band and NIR Q-like bands, signifying the typical π–π^* transitions of the NFP ligand. We also report the molecular characterization and DFT calculations of the NFP-rhodium complexes and their distinctness with the organo-rhodium reagent $[Cp^*RhCl_2]_2$.

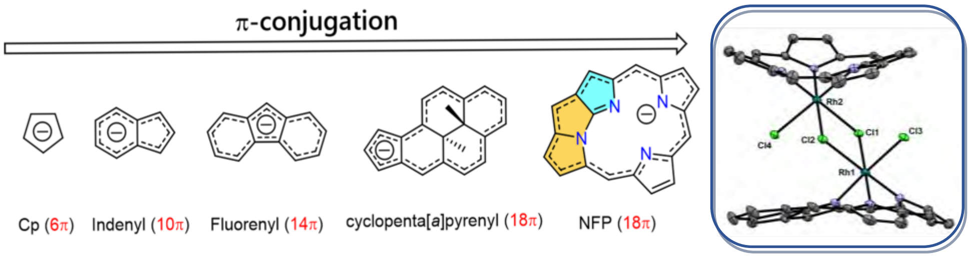

Figure 1. Extension of π-conjugated systems and crystal structure of **Rh-2**.

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REFERENCES

1. M. Toganoh, H. Furuta, *Chem. Lett.* **2019**, *48*, 615.

Synthesis of zinc 20-substituted 3-hydroxymethyl-chlorophyll-*a* derivatives and their self-aggregation in an aqueous micelle solution

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Chlorosomes are the main light-harvesting antenna systems of photosynthetic green bacteria. They are constructed by *J*-type self-aggregation of several chlorophyllous pigments including bacteriochlorophyll(BChl)s-*c*/*d* (Fig. 1, left). BChls-*c*/*d* have a similar chlorin π-system as in chlorophyll(Chl)-*a* and possess the 3^1-hydroxy group, a magnesium atom at the central position, and the 13-keto carbonyl group along their molecular *y*-axis. The self-aggregates are composed of a variety of intermolecular interactions, hydrogen bond of 3^1-OH···O=C-13, coordination bond of 3^1-OH···Mg, and π-π interaction of chlorin moieties [1]. It was reported that zinc 20-(un)substituted Chl-*a* derivatives were synthesized to be good models of natural BChls-*c*/*d* [2,3].

In this study, some zinc 3-hydroxymethyl-13^1-oxo-chlorins bearing an electron-withdrawing group at the 20-position (R = NO_2, $COCH_3$, and OCOX in Fig. 1, right) were prepared by chemically modifying Chl-*a* and their self-aggregation in an aqueous micelle solution to give chlorosomal models [3,4]. Their self-aggregates were compared with that of the corresponding 20-unsubstitute (R = H), and the 20-substitution effects including their electronegativity and steric size will be discussed.

Figure 1. *J*-type self-aggregates of BChls-*c*/*d* (left) and their synthetic models (right).

REFERENCES

1. S. Matsubara, H Tamiaki. *J. Photochem. Photobiol. C: Photochem. Rev.* 2020; **45**: 100385.
2. M. Shiozaki, T. Miyanishi, H. Tamiaki. *Chem. Lett.* 2021; **50**: 1539–1542.
3. K. Sakaguchi, M. Kishi, Y. Kinoshita, H. Tamiaki. *J. Porphyrins Phthalocyanines* 2021; **25**: 1104–1110.
4. K. Sakaguchi, M. Kishi, H. Tamiaki. *Chem. Lett.* 2021; **50**: 1416–1418.

Intramolecular asymmetric coordination of synthetic zinc chlorophyll-*a* derivatives

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Chlorophyll-*a* (Chl-*a*) is one of the most important natural pigments in the light-harvesting antennas and reaction centers of oxygenic phototrophs. The central magnesium atom of Chl-*a* is often coordinated by the imidazolyl group of a histidine residue in such photosynthetic proteins. The imidazolyl ligand can axially coordinate to the Mg atom either from the back (denoting as the α-coordination, L) or face side (the β-coordination, L') to give 5-coordinated species (Fig. 1, left). While the α-coordinated Chl-*a* has been found more frequently than the β-coordinated one in photosynthetic proteins [1], the functional differences between their stereoisomers have not been revealed yet. In order to address the issue, we prepared both intramolecularly α- and β-coordinated models by utilizing the 13^2-stereochemistry of a Chl-*a* derivative and examined their physical properties.

To construct the intramolecular coordination model complexes, we synthesized complexes with different positions of ester groups (Fig. 1, center). Their intramolecular coordination behaviors will be discussed based on spectroscopic analyses. Furthermore, stereoisomers of complexes having different linker distances at the 13^2-position were obtained by transesterification reaction of the 13^2-$COOCH_3$ moiety (Fig. 1, right). The major complexes (α-coordination) were separated by HPLC to give the stereochemically pure samples. Their coordination behaviors will be discussed.

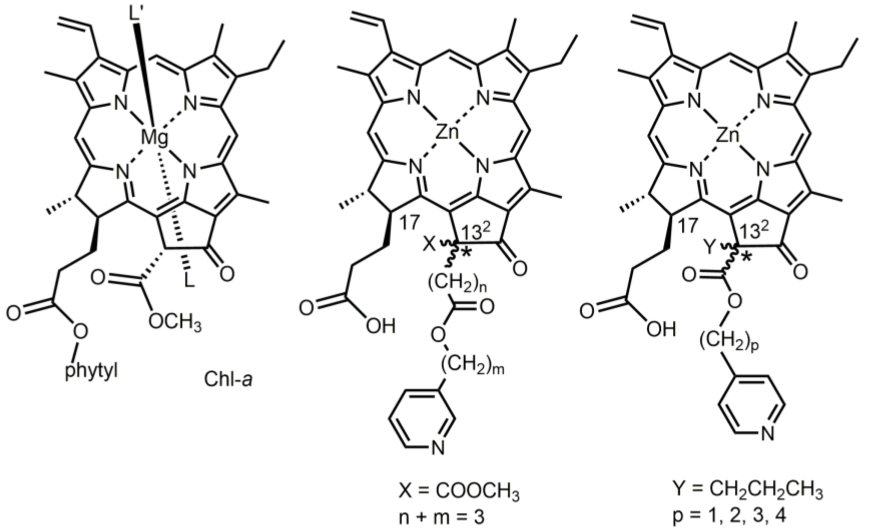

Fig. 1. Molecular structures of axially coordinated Chl-*a* (left) and zinc Chl-*a* derivatives bearing a pyridyl group at the 13^2-substituent terminal (center, right).

REFERENCES

1. T. Oba, H. Tamiaki, *Photosynth. Res.* **2002**, *74*, 1–10; *Bioorg. Med. Chem.* **2005**, *13,* 5733–5739; *J. Porphyrins Phthalocyanines* **2014**, 18, 919–932.

Metallophthalocyanine-based nanoparticles for photodynamic therapy (PDT)

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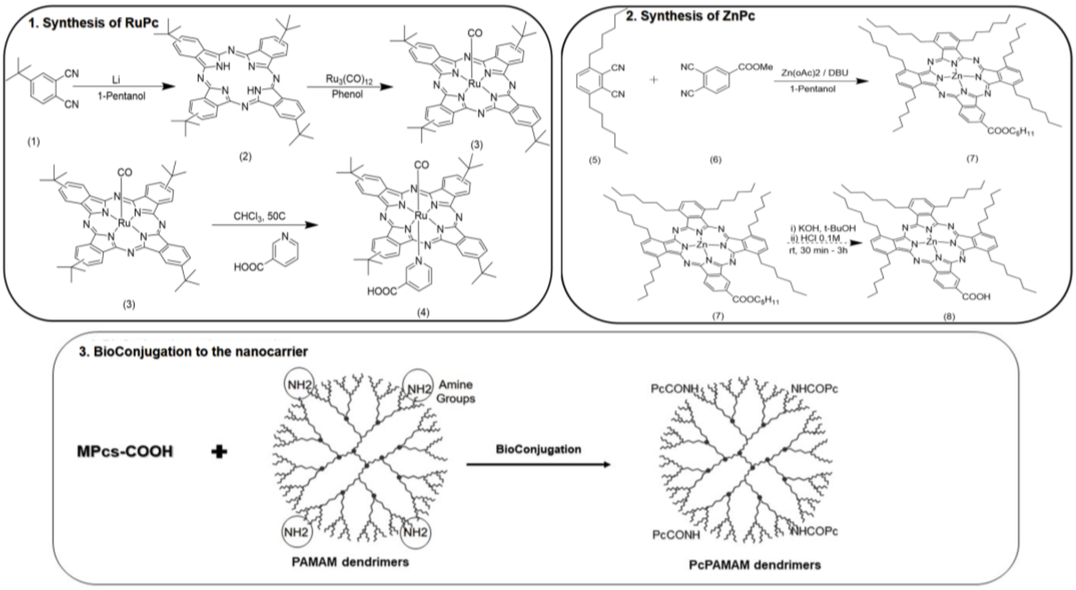
Photodynamic therapy (PDT) is a non-invasive, clinically approved, therapeutic procedure, which has been used to treat malignancies of different types and regions, as well as non-oncological diseases [1]. Phthalocyanines (Pcs) are artificial tetrapyrrolic macrocycles [2] that constitute optimal organic photosensitizing chromophores to be used as therapeutic agents for PDT. Their utility for PDT mainly arises from their ability to produce singlet oxygen, their non-toxicity and their strong absorption in the phototherapeutic window [3].

This work describes the synthesis and characterization of Metallophthalocyanine based photosensitizers (MPcs), bearing Zinc(II) and Ruthenium(II) ions within their central cavity. The chromophores have been functionalized at their peripheral or axial positions with a carboxylic acid group for their covalent linkage to a hyperbranched PAMAM dendrimer nanocarrier.



REFERENCES

1. Kwiatkowski S., Knap B., Przystupski D., Saczko J., Kędzierska E., Knap-Czop K., Kotlińska J., Michel O., Kotowski K., Kulbacka J. *Biomedicine and Pharmacotherapy*. **2018**, 106, p. 1098-1107.
2. Singh S., Aggarwal A., Bhupathiraju N.V.S.D.K., Arianna G., Tiwari K., Drain C.M., *Chem. Rev*. **2015**, 115, 18, p. 10261-10306.
3. Lo P.C., Rodríguez-Morgade M.S., Pandey R.K., Ng D.K.P., Torres T., Dumoulin F. *Chem. Soc. Rev*. **2020**, 49, p. 1041-1056.

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