

# Journée scientifique du GDR MAPYRO

## Conférence d'ouverture

du

**Dr. Bernard MEUNIER**

LCC Toulouse - France



**Vendredi 3 mai**

**9h00**

Amphi Grandjean  
Bât 10 B  
Campus de Beaulieu

Quand aurons-nous des médicaments  
pour traiter la maladie d'Alzheimer ?

**9h50 - 17h30**

Amphi Grandjean  
Bât 10 B  
Campus de Beaulieu

Contributions des partenaires du GDR



Contact : [bernard.boitre@univ-rennes1.fr](mailto:bernard.boitre@univ-rennes1.fr)

Tél : 02 23 23 58 56

[stephane.legac@univ-rennes1.fr](mailto:stephane.legac@univ-rennes1.fr)

Tél. 02 23 23 65 72

[www.scienceschimiques.univ-rennes1.fr](http://www.scienceschimiques.univ-rennes1.fr)

Institut des  
**Sciences Chimiques  
de Rennes**  
UMR CNRS  
6226

263 av. du Général Leclerc  
Campus de Beaulieu - Rennes



## Planning Vendredi 3 mai 2019

**8h45** : Introduction, B. Boitrel (Rennes)

**9h00 -9h50** : Conférence plénière par B. Meunier (Toulouse)

*Quand aurons-nous des médicaments pour traiter la maladie d'Alzheimer ?*

**9h50 - 10h10** : P. Arnoux (Nancy)

*Photosensitizer and multifunctional nanoparticles treatment of glioblastoma and ovarian metastases by PDT*

**10h10 - 10h30** : V. Heitz (Strasbourg)

*Multicomponent systems with porphyrins: switchable receptors, molecular photosensitizers and theranostic agents*

**10h30 - 10h50** : Pause-café

**10h50 - 11h10** : C. Bucher (Lyon)

*Porphyrins and expanded porphyrins in SUPRAMOLECULAR ELECTROCHEMISTRY: doing chemistry with electrodes*

**11h10 - 11h30** : W. Hosseini (Strasbourg)

*Variations on porphyrins*

**11h30 - 11h50** : S. Pascal (Marseille)

*Porphyrin Analogues at the CINaM: Corroles and Azacalixphyrins*

**11h50 - 12h10** : C. Gros (Dijon)

*Recent developments in the chemistry of polypyrroles and corrole derivatives*

**12h10 - 12h30** : V. Sol (Limoges)

*Vers des photosensibilisateurs tétrapyrroliques pour des applications biologiques*

**12h30 - 14h00** : Buffet déjeunatoire

**14h00 - 14h20** : S. Richeter (Montpellier)

*Molecular porphyrin derivatives and their inclusion into nanomaterials for biomedical applications*

**14h20 - 14h40** : A. Sorokin (Lyon)

*Catalytic applications of phthalocyanine metal complexes and single-atom bridged tetrapyrrole complexes*

**14h40 - 15h00** : B. Andrioletti (Lyon)

*Synthesis of Triazole-Appended Dipyrromethenes and their metallocomplexes*

**15h00 - 15h20** : C. Devillers (Dijon)

*Elaboration of Porphyrin/Phthalocyanine-based materials for analysis and chemosensing*

**15h20 - 15h40** : Z. Halime (Orsay)

*Rôle de la Seconde Sphère de Coordination dans la Réduction du CO<sub>2</sub> par la Porphyrine de Fer*

**15h40 - 16h00** : J.P. Mahy (Orsay)

*From antibodies to metal organic frameworks: a full set of envelops for metalloporphyrins to build up new artificial hemoproteins*

**16h00 - 16h20** : Pause-café

**16h20-16h40** : J. Weiss (Strasbourg)

*Porphyrin Based Supramolecular Scaffolds*

**16h40-17h00** : S. Le Gac (Rennes)

*Decorated porphyrin and hexaphyrin ligands*





# Photosensitizer and multifunctional nanoparticles treatment of glioblastoma and ovarian metastases by PDT

Philippe Arnoux<sup>a</sup>, Francis Baros<sup>a</sup>, Samir Acherar<sup>b</sup>, Mathilde Achard<sup>b</sup>, Valérie Jouan-Hureau<sup>c</sup>, Cédric Boura<sup>c</sup>,  
Noémie Thomas<sup>c</sup>, Muriel Barberi-Heyob<sup>c</sup>, Céline Frochot<sup>a</sup>

<sup>a</sup> LRGP, UMR 7274 CNRS-University of Lorraine, Nancy, France

<sup>b</sup> LCPM, UMR 7375 CNRS-University of Lorraine, Nancy, France

<sup>c</sup> CRAN, UMR 7039 CNRS-University of Lorraine, Nancy, France

Photodynamic therapy (PDT) is a therapeutic option for treating cancers and others diseases involving light, a photosensitizer and molecular oxygen leading to cell death. PDT has been used in clinics for years especially in dermatology and new clinical trials are underway in France and in all the world to treat for example glioblastoma (aggressive brain tumor) or mesothelioma (lung cancer due to asbestos) [1].

There are also some shortcomings of PDT: poor selectivity of photosensitizers for the tumor tissues, low penetration of light to treat deep-seated tumors.

For nearly 20 years, our strategy has been to design, to synthesize, to evaluate the photophysical properties as well as the *in vitro* and *in vivo* behavior of

- 1) targeted photosensitizers or multifunctional nanoparticles that are able to target
  - NRP-1 receptors over-expressed on neo-vessels to treat glioblastoma (coll. ILM UMR 5306 CNRS-Université de Lyon, Lyon, France). Different peptides have been tested such as ATWLPPR or KDKPPR [2,3]. AGuIX nanoparticles have been selected thanks to their small size (few nanometers) and easy chemical functionalization [4,5].
  - folic acid receptor over-expressed on peritoneal carcinosis of ovarian origin (coll. ONCOTHA1, U 1189, Lille, France) . Different photosensitizers have been synthesized [6,7] and the best one in term of solubility, photophysical properties and photostability has been patented.
- 2) multifunctional nanoparticles that can be excited by X-ray instead of light to allow the treatment of deep-seated tumors [8,9].

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4. Couleaud P; Bechet D; Vanderesse R; Barberi-Heyob M; et al. *Nanomedicine* **2011**, *6*, 995-1009.
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6. Stallivieri A; Colombeau L; Jetpisbayeva DG; Moussaron A; et al. *Bioorg. Med. Chem.* **2017**, *25*, 1-10.
7. Azais H; Schmitt C; Tardivel M; Kerdraon O; et al. *Photodiagnosis Photodyn. Ther.* **2016**, *13*, 130-138.
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# Multicomponent systems with porphyrins: switchable receptors, molecular photosensitizers and theranostic agents.

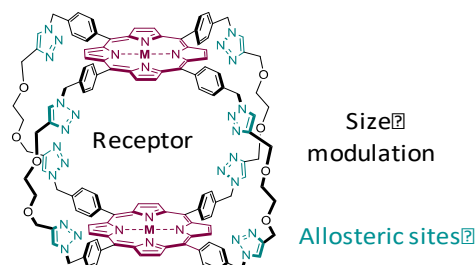
Valérie Heitz, Stéphanie Durot, Henri-Pierre Jacquot de Rouville

Laboratoire de Synthèse des Assemblages Moléculaires Multifonctionnels, Institut de Chimie de Strasbourg CNRS/UMR 7177, Université de Strasbourg

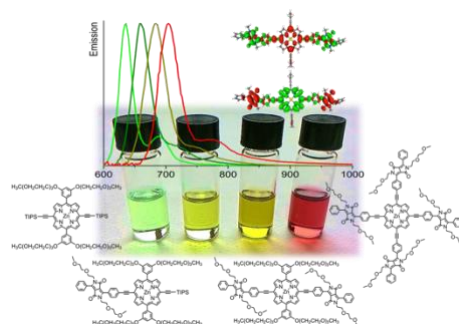
E-mail: [v.heitz@unistra.fr](mailto:v.heitz@unistra.fr)

Porphyrins have been incorporated in many systems due their appealing coordination, electronic and photophysical properties. Our group is involved in the development of multicomponent systems bearing porphyrins for different topics related to supramolecular chemistry (synthesis of receptors, tweezers, switchable systems, molecular machines) and also to biological chemistry (imaging agent, photosensitizer for PDT, theranostic molecule).

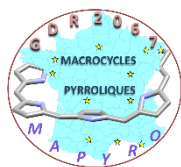
Molecular cages incorporating porphyrins as binding sites as well as regulation sites are appealing systems for an allosteric control of their properties as receptor, catalyst or drug carrier. Our group has developed coordination and covalent porphyrin cages porphyrins and an overview of their properties will be discussed.<sup>1,2</sup> In particular, flexible covalent cages with peripheral binding sites have shown to modulate to a large extent their cavity size with a chemical stimulus (pH change or metal binding) and to act as allosteric nanoreceptors.<sup>2</sup>



Due to their ability to generate cytotoxic singlet oxygen, porphyrins are also appealing photosensitizers for photodynamic therapy (PDT). Nevertheless, their excitation is not optimal and situated outside the optical therapeutic window. Our results on the development of new porphyrin photosensitizers for two-photon PDT in the near infrared will be presented.<sup>3</sup> Moreover, PDT photosensitizers combine with imaging agents for MRI will be discussed in the context of theranostics.<sup>4</sup>



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2. 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. d) R. Djemili, L. Kocher, S. Durot, A. Peuronen, K. Rissanen, V. Heitz, *Chem. Eur. J.* **2019**, *25*, 1481.
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. a) A. Sour, S. Jenni, A. Orti-Suarez, J. Schmitt, V. Heitz, F. Bolze, P. Loureiro de Sousa, C. Po, C. S. Bonnet, A. Pallier, E. Tóth, B. Ventura, *Inorg. Chem.* **2016**, *55*, 4545-4554. b) 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. c) J. Schmitt, S. Jenni, A. Sour, V. Heitz, F. Bolze, A. Pallier, C. S. Bonnet, É. Tóth, B. Ventura, *Bioconjugate Chem.*, **2018**, *29*, 3726.



## Porphyrins and expanded porphyrins in SUPRAMOLECULAR ELECTROCHEMISTRY: doing chemistry with electrodes

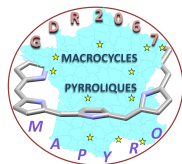
Christophe Bucher

Ecole Normale Supérieure de Lyon . Laboratoire de Chimie, *CNRS UMR 5182, F69342, Lyon, France.*  
[Christophe.bucher@ens-lyon.fr](mailto:Christophe.bucher@ens-lyon.fr)

The field of supramolecular electrochemistry focuses on the behavior of (supra)molecular systems submitted to electric stimulations. It encompasses the use of electrons either to activate/deactivate/monitor a given molecular recognition process or to trigger large-scale structural rearrangements within complex molecules and organized assemblies. The concepts of supramolecular chemistry are also relevant to the development of electrosynthetic processes towards valuable organic molecules and electrode materials.<sup>1-3</sup>

We will present in this lecture a selection of results obtained along these lines in our group involving pyrrole-containing macrocycles as key building/functional elements. Emphasis will be placed on the properties of a series of switchable molecular architectures allowing redox-controlled binding/release of guest molecules or to control the organization within self-assembled coordination polymers. It will also include selected examples of electrochemically driven syntheses of porphyrin analogs from simple pyrrole containing building blocks.

- 1) Bucher, C.; Buda, M. *Electrochemistry of Pyrroles and Oligopyrroles : Analytic and Synthetic Aspects*, in *Handbook of Porphyrin Science*. Kadish, K., Smith, K., Guillard, R., Eds.; World Scientific, 2012; Vol. 17; pp 239-375.
- 2) Kahlfuss, C.; Saint-Aman, E.; Bucher, C. *Redox-controlled intramolecular motions triggered by  $\pi$ -dimerization and  $\pi$ merization processes*. In *Organic Redox Systems: Synthesis, Properties, and Applications*; Nishinaga, T., Ed.; John Wiley and sons: New-York, 2016; pp 39-88.
- 3) Bucher, C.; Devillers, C. H.; Moutet, J.-C.; Royal, G.; Saint-Aman, E. Ferrocene appended porphyrins: syntheses and properties. *Coord. Chem. Rev.* **2009**, 253, 21-36.

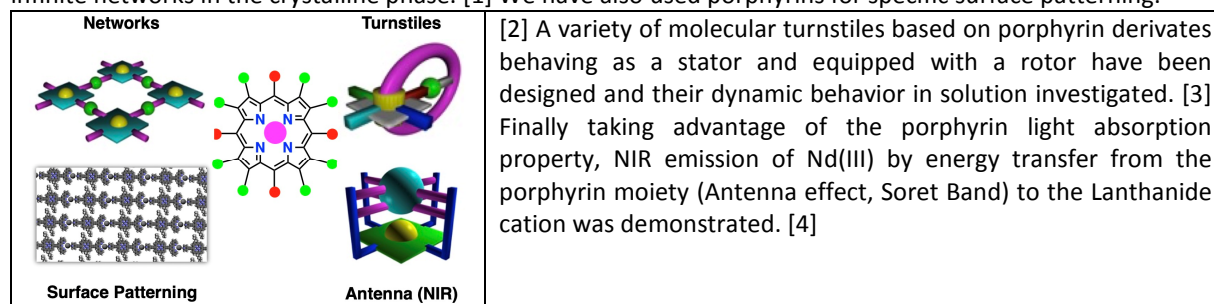


## Variations on porphyrins

**Mir Wais Hosseini**

Laboratoire de Tectonique Moléculaire, Université de Strasbourg, Institut Le Bel, 4, rue Blaise Pascal, 67000 Strasbourg

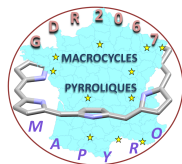
The porphyrin backbone is one of the most interesting platform for the design of a variety of molecules for many different applications ranging from small molecule activation to catalysis and devices. This unit, being conjugated, also offers specific properties such as redox, absorption and emission. Owing to possible functionalization of the porphyrin backbone at the *beta*-pyrrolic as well as *meso* positions, one may introduce up to 12 identical or different groups at the periphery of the macrocyclic entity. We have used the porphyrin platform in molecular tectonics for the design of porphyrin based tectons and their assembly into periodic infinite networks in the crystalline phase. [1] We have also used porphyrins for specific surface patterning.



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# Porphyrin Analogues at the CINaM: Corroles and Azacalixphyrins

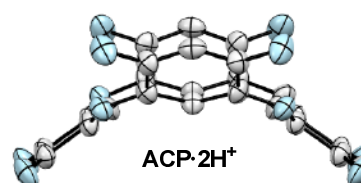
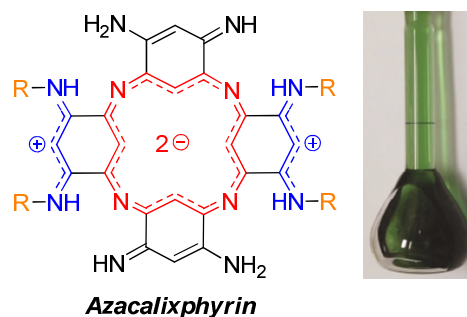
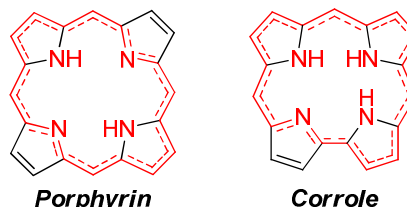
**Simon Pascal, Gabriel Canard, Olivier Siri**

Aix-Marseille Univ, CNRS UMR 7325, CINAM, Campus de Luminy, case 913, Marseille 13288 Cedex 09

This talk will focus on recent progress on two porphyrin analogues, corroles and azacalixphyrins (ACPs), which are still retaining the 18  $\pi$ -electrons aromatic system of the parent porphyrin macrocycle.

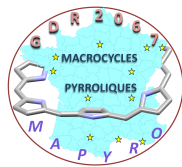
First, we have studied how the corrole's *per*-aryl substitution impacts the macrocycle conformation and tunes the electrochemical and hole-transport properties of the corresponding copper complexes.<sup>1-3</sup> We will also show how *meso*-ester groups are affecting the physico-chemical characteristics of corroles despite their low steric hindrance.<sup>4,5</sup>

Second, the azacalixphyrins (ACP) macrocycle was reported in 2013 as the only known porphyrin analogue introducing four oxidized tetraaminobenzene units that promote a stable bis-zwitterionic ground electronic state.<sup>6</sup> Its aromatic core confers to the ACP a strong absorption in the NIR *ca.* 900 nm that can be tuned by chemical substitution.<sup>7,8</sup> Recently, we designed ACPs bearing aryl substituents that strongly impact the physico-chemical properties of the macrocycles, enabling hyperchromic and bathochromic shifts of the absorption compared to the *N*-alkylated analogues.<sup>9</sup> Thus, since they are NIR absorbers and totally non-emissive chromophores, ACPs stand as prime candidates for photoacoustic imaging (PAI), an emerging non-invasive method that enables the high-contrast imaging of biological media due to the excellent penetration of ultrasounds within tissues.<sup>10</sup>



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## Recent developments in the chemistry of polypyrroles and corrole derivatives

**Claude P. Gros, Nicolas Desbois, Stéphane Brandès, Anthony Romieu, Léo Bucher, Sandrine Pacquelet, Yoann Rousselin, Valentin Quesneau, Jian Yang, Flavien Ponsot, Renaud Andrieux**

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

DPP, BODIPY, porphyrin and corrole derivatives are often-studied groups of dyes and macrocycles because of their unique spectral and electrochemical properties and their potential uses for a rich variety of applications. The chemical versatility of pyrrole allows one to build different fluorophores and macrocycles (Figure 1) starting from simple pyrrole units and aryl-aldehydes. We will present and discuss our recent works in the design and synthesis of new polypyrroles and porphyrin/corrole derivatives for *e.g.* small molecule binding, the synthesis of porous materials and the development of gas sensors (CO), the design of BHJ solar cells and the synthesis of new NIR dyes for biological applications.

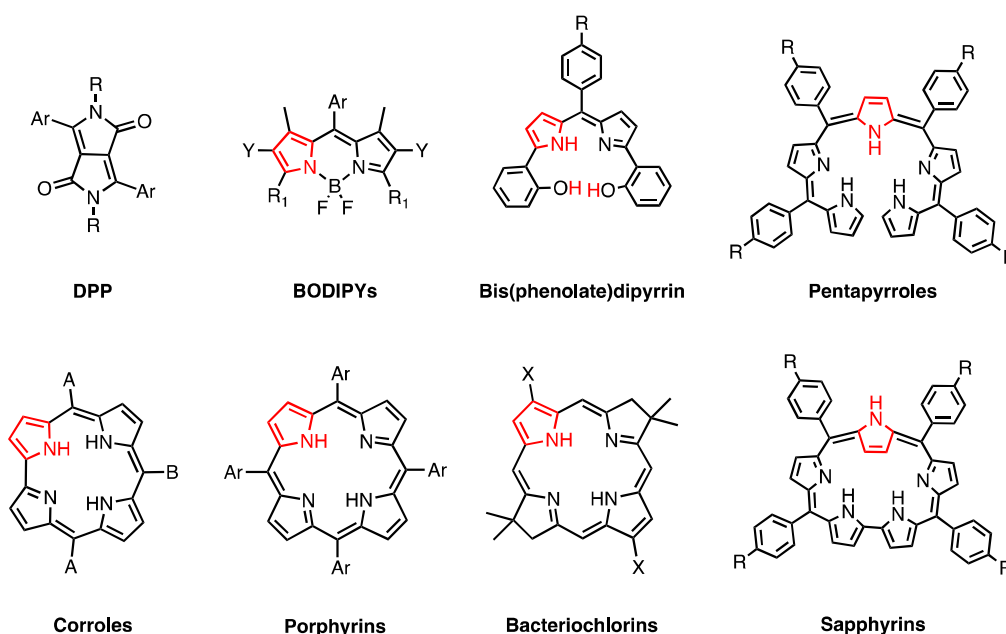


Figure 1

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# Vers des photosensibilisateurs tétrapyrroliques pour des applications biologiques

Vincent SOL

Laboratoire PEIRENE, EA 7500 Université de Limoges 87000 Limoges France

Notre laboratoire développe l'extraction, l'hémisynthèse et la synthèse de nouveaux photosensibilisateurs tétrapyrroliques pour des applications biologiques en PhotoThérapie Dynamique (PDT). Ainsi le laboratoire a mis au point des PS pour des applications dans le domaine de la PDT anticancéreuse,<sup>a,e</sup> antimicrobienne<sup>c,d</sup> et également pour le traitement de plante.<sup>b</sup> L'une des spécificités du laboratoire est d'associer des polymères d'origines naturelles (biomacromolécules) à des PS afin de développer des nanoparticules d'origine naturelles, d'utiliser des polysaccharides pour favoriser la biocompatibilité et le ciblage cellulaires des PS ou des nano-objets portant des PS pour des applications anticancéreuses. Le laboratoire développe également des biomatériaux constitués de polysaccharides et sur lesquels sont greffés de manière covalente des PS pour des applications antimicrobiennes.<sup>c,d</sup>

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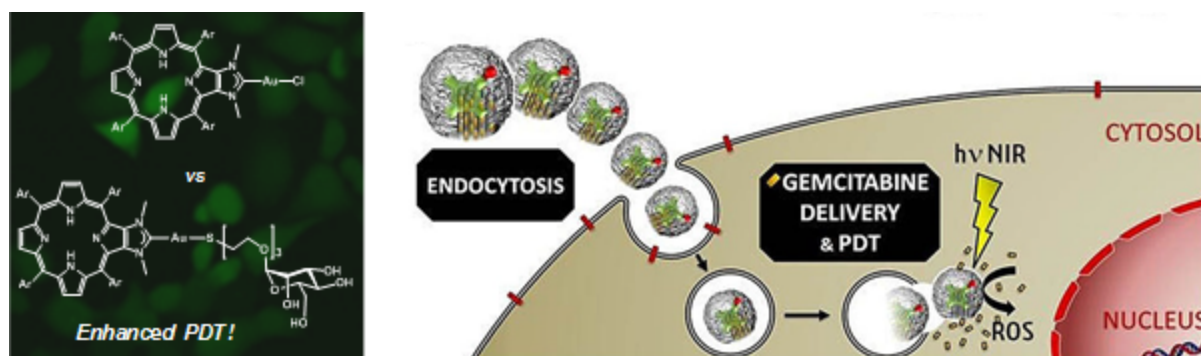
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# Molecular porphyrin derivatives and their inclusion into nanomaterials for biomedical applications

Sébastien Richeter, Sébastien Clément, Jean-Olivier-Durand

Institut Charles Gerhardt Montpellier, UMR-5253 CNRS-UM-ENSCM, CC 1701, Place E. Bataillon, 34095, Montpellier Cedex 05  
sebastien.richeter@umontpellier.fr

Porphyrin have attracted tremendous interest due to their unique photophysical properties, notably for photodynamic therapy (PDT) applications. PDT relies on the use of light-susceptible photosensitizers like porphyrins to generate reactive oxygen species and singlet oxygen ( $^1\text{O}_2$ ), which lead to the death of cancer cells by necrotic and apoptotic mechanisms. Our research activity in the *Institut Charles Gerhardt* is mainly focused on developing the synthesis of original porphyrin derivatives and to include such molecular building blocks in nanomaterials in view of applications in PDT (Figure 1). Among molecular species we have developed in the group, porphyrins equipped with imidazolium rings are promising candidates for biomedical applications. They are notably excellent N-heterocyclic carbene precursors to anchor metal complexes at the periphery of the macrocycle bringing additional properties<sup>[1]</sup> (cytotoxicity, heavy atom effect boosting  $^1\text{O}_2$  generation) and structural diversity.<sup>[2]</sup> Inclusion of porphyrins into nanomaterials is also actively investigated for biomedical applications, since these systems offer unique opportunities to combine PDT with other therapeutic approaches (drug delivery, gene delivery) and imaging modes.<sup>[3,4]</sup>



**Figure 1.** Left. Porphyrins conjugated with peripheral thiolato gold(I) complexes for enhanced photodynamic therapy.<sup>[1]</sup> Right. Gemcitabine delivery and photodynamic therapy in cancer cells via porphyrin-ethylene-based periodic mesoporous organosilica nanoparticles.<sup>[3]</sup>

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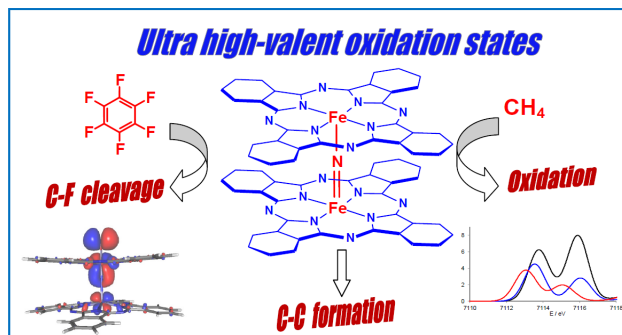
# Catalytic applications of phthalocyanine metal complexes and single-atom bridged tetrapyrrole complexes

Alexander B. Sorokin<sup>a</sup>

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

Porphyrin catalytic chemistry relevant to cytochrome P-450 is well-documented and synthetic porphyrin complexes have been largely used for a variety of catalytic transformations. Until recently, application of MPC in catalysis was still limited compared to that of their porphyrin counterparts. MPC are attractive as practical catalysts because of structural analogy with porphyrin complexes, their accessibility in terms of the cost and preparation on a large scale and due to their chemical and thermal stability. The efforts of our group have been focused on the development of novel catalytic methods using MPC complexes including mechanistic studies and characterization of active catalytic species. This field shows a rapid development in terms of number and scope of catalytic applications during recent years.<sup>1</sup>

We have recently proposed a novel bio-inspired approach to the development of powerful catalysts for oxidation based on using of N-bridged diiron phthalocyanine and porphyrin complexes.<sup>2</sup> This scaffold is particularly suited for the stabilization of Fe<sup>IV</sup>Fe<sup>IV</sup> entities and can therefore be useful for the preparation of oxidizing active species using peroxides including H<sub>2</sub>O<sub>2</sub>. The ultra high-valent diiron oxo species (L)Fe<sup>IV</sup>-N-Fe<sup>IV</sup>(L<sup>+</sup>)=O (L = phthalocyanine, porphyrin) have been detected at low temperatures and characterized by cryospray MS, UV-vis, EPR, X-ray absorption spectroscopy and Mössbauer techniques.<sup>3</sup> These highly electrophilic (L)Fe<sup>IV</sup>-N-Fe<sup>IV</sup>(L<sup>+</sup>)=O species show outstanding reactivity. The catalytic applications of  $\mu$ -nitrido diiron complexes include oxidation of methane and benzene, transformation of aromatic C-F bonds in oxidative conditions, oxidative dechlorination, formation of C-C bonds.<sup>4</sup> Importantly, all these reactions can be carried out in clean and mild conditions with high conversions and turnover numbers.  $\mu$ -Nitrido diiron species demonstrate similar mechanistic features (<sup>18</sup>O labelling, formation of benzene epoxide and NIH shift in the aromatic oxidation) as enzymes operating *via* high-valent iron oxo species.

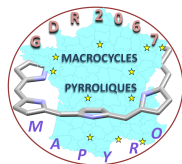


This approach has a great potential for further development. Different macrocyclic ligands (porphyrins, phthalocyanines, porphyrazines, corroles, etc.) can be used to support homometallic or heterometallic M-X-M units with various metals and bridging groups. Moreover, a variety of homoleptic and heteroleptic complexes is potentially available. The structural variation should considerably affect the electronic structure and can therefore be used to tune catalytic properties to access to the improved and tailored catalysts for many reactions. These studies are in progress in our group to open new possibilities in biomimetic catalysis.

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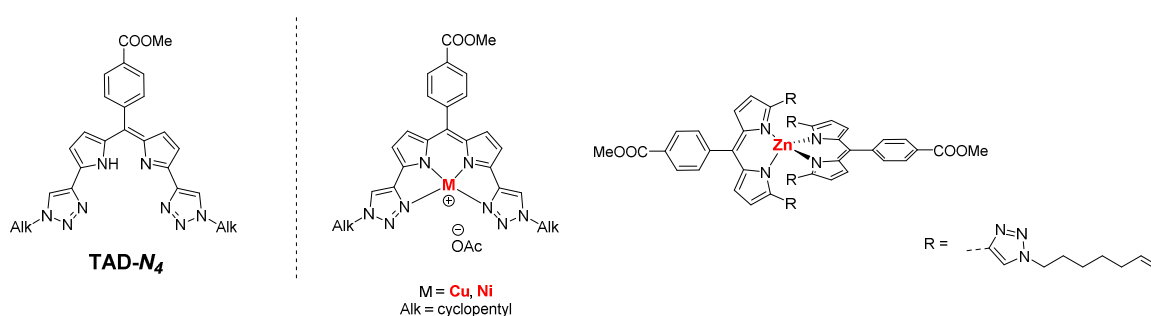


# Synthesis of Triazole-Appended Dipyrromethenes and their metallocomplexes

**Rago, A.<sup>a</sup>, Guerin, C.<sup>a</sup>, Framery, E.<sup>a</sup>, Jean-Gerard, L.<sup>a</sup>, Andrioletti, B.<sup>a</sup>**

<sup>a</sup> Univ. Lyon, Université Claude Bernard Lyon1, ICBMS (UMR 5246); Campus Lyon-Tech La Doua, 1, Rue Victor Grignard, 69622-Villeurbanne Cedex.

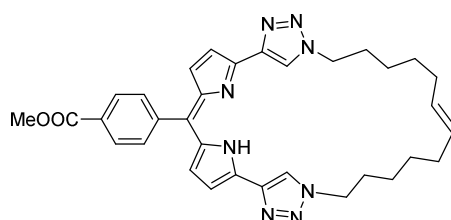
Our group has recently designed a new family of dipyrromethene-based ligands called triazole-appended dipyrromethenes, **TAD**. [1, 2] This L3X donor exhibits a rigid structure that can promote the coordination of metals displaying square planar or octahedral geometry (**Figure 1**). These geometries were observed for copper and nickel. For the zinc complex, a dimer ML<sub>2</sub> was observed in a tetrahedral environment.



**Figure 1.** TAD- $N_4$  and corresponding complexes

Interestingly, a simple quaternarization of the **TAD- $N_4$**  ligand followed by the *in-situ* deprotonation of the acidic CH triazole protons allowed for the formation of the TAD- $N_3C$  carbene ligand in excellent yield.

In addition, in order to develop a new family of macromolecules, the alkene-substituted **TAD- $N_4$**  was submitted to RCM-conditions to afford the macrocyclic molecule in high yield (**Scheme 1**).



**Scheme 1.** Structure of a Macrocyclic TAD-structure.

Efforts are on-going in our group in order to explore further the fascinating coordination properties of the **TAD- $N_4$**  and **TAD- $N_3C$**  families as well as their use in the construction of catenane structures.

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# Elaboration of Porphyrin/Phthalocyanine-based materials for analysis and chemosensing

**Charles H. Devillers, Rita Meunier-Prest, Dominique Lucas, Marcel Bouvet**

*Electrochemistry, Molecular Materials and Devices team (EMMD), Institut de Chimie Moléculaire de l'Université de Bourgogne, 9 av. Alain Savary, 21078 Dijon Cedex*

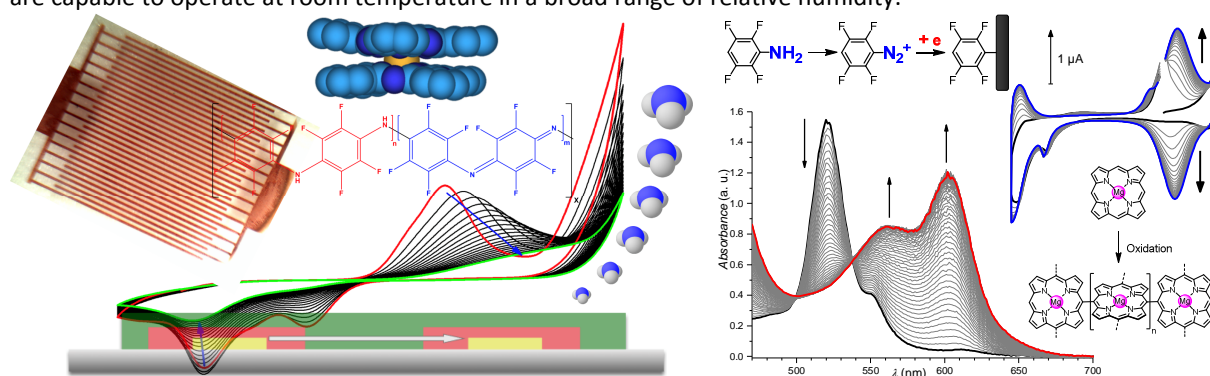
**EMMD** (Electrochemistry, **M**olecular **M**aterials and **D**eVICES) research activities are devoted to molecular materials, from molecules to materials and from materials to devices. Electrochemical techniques are used to synthesize, to immobilize and to detect chemical or biological species. The synthetic aspect relates to the synthesis and functionalization of macrocycles (porphyrins, phthalocyanines...) and polymers. The analytical aspect 1) exploits the redox properties of compounds or sensitive layers (biomaterials, conducting polymers, charge-transfer complexes,...) for the characterization and the detection of biomolecules or chemical pollutants in sensor devices; 2) aims to apprehend reaction mechanism of molecular processes. More particularly, porphyrin/phthalocyanine topics are focused on:

**-(Electro)functionalization:** the redox reactivity of porphyrins upon (electro)chemical oxidation or reduction is scrutinized in the absence (dimerization/polymerization processes) or in the presence of nucleophiles (such as pyridine, phosphines, nitrites, halides...). These electrochemical transformations lead to new functional molecules/materials. Currently, our efforts are mainly focused on the intramolecular electrochemically-driven pi-extension of porphyrins.<sup>1</sup>

**-Electropolymerization:** oxidation of different types of monomers (aniline and pyrrole-based derivatives, porphyrins) leads to original functional materials. Optimization of the experimental electrodeposition conditions (concentration of the monomer, solvent, temperature, potentiostatic/potentiodynamic modes, potential values, additives such as bases...) is essential to obtain a better control of the electropolymerization process.<sup>2</sup>

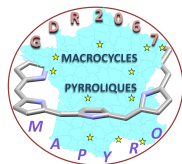
**-Electroreduction of aryl-diazonium:** it lies on the electroreduction of the diazonium function grafted on aromatic compounds (phenyl-based, porphyrins...). The electrogenerated aryl-radicals react with the electrode surface and formed covalently-bonded monolayers. As for electropolymerization, numerous experimental parameters have to be controlled to insure the good reproducibility of the modified electrodes.<sup>3</sup>

**-Organic electronic devices:** we also develop new organic electronic devices based on a combination of single and double decker phthalocyanines. Used as ammonia sensors, they exhibit a sub-ppm limit of detection and are capable to operate at room temperature in a broad range of relative humidity.<sup>4</sup>



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# Rôle de la Seconde Sphère de Coordination dans la Réduction du CO<sub>2</sub> par la Porphyrine de Fer

Asma Khadhraoui<sup>a</sup>, Philipp Gotico<sup>b</sup>, Bernard Boitrel<sup>c</sup>, Marie Sircoglou<sup>a</sup>, Winfried Leibel<sup>b</sup>, Zakaria Halime<sup>a</sup>, Ally Aukauloo<sup>ab</sup>

<sup>a</sup> Laboratoire de Chimie Inorganique, Institut de Chimie Moléculaire et des Matériaux d'Orsay, Université Paris Sud, 91405 Orsay, France

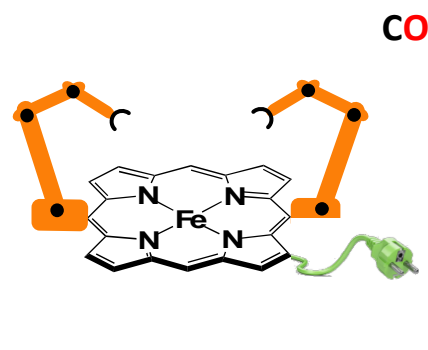
<sup>b</sup> Laboratoire des Mécanismes Fondamentaux de la Bioénergétique, Institut de Biologie Intégrative de la Cellule, CEA Saclay, 91191, Gif-sur-Yvette, France

<sup>c</sup> Université de Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes), UMR 6226, Rennes F-35000, France

Pour maintenir la vie oxygénique, la Nature a développé une multitude de stratégies pour activer et transformer des petites molécules comme l'H<sub>2</sub>O, O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub> ...etc. Lors de la photosynthèse, seule l'énergie solaire est utilisée afin d'extraire des électrons et protons de l'eau pour la transformation du CO<sub>2</sub> en molécules riches en énergie. Prenant l'inspiration de ces processus naturels, les scientifiques visent à développer des systèmes synthétiques pour reproduire ces réactions chimiques de manière efficace et à grande échelle. Cette tâche s'avère extrêmement ardue à la vue de la sophistication de l'architecture chimique des sites catalytiques. En effet, la sélectivité et spécificité des enzymes sont orchestrés au travers d'un fin réglage à la fois de la première et de la seconde sphère de coordination des centres métalliques. Parmi les fonctionnalités apportées par cette seconde sphère de coordination, on peut citer la capture et l'orientation du substrat, le relais de transfert d'électrons et/ou de protons et l'abaissement de l'énergie d'activation *via* la stabilisation des intermédiaires réactionnels.

Inspiré par le site actif de la Monoxyde de Carbone Déshydrogénase (CODH), qui réduit réversiblement le CO<sub>2</sub> en CO, nous avons développé des catalyseurs de type porphyrine de fer modifiée qui comportent différents groupements fonctionnels dans la deuxième sphère de coordination du centre métallique (Figure 1). [1 et 2] A l'aide de nos nouveaux catalyseurs nous avons démontré que l'introduction pré-organisée en 3D de ces groupements fonctionnels permet non seulement de baisser le coût énergétique de la réduction électrocatalytique du CO<sub>2</sub> en CO mais aussi d'améliorer la fréquence du cycle catalytique (TOF) tout en maintenant une excellente sélectivité.

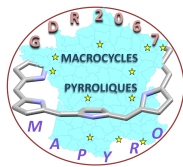
**Figure 1** : Représentation schématique de notre stratégie de manipulation de la deuxième sphère de coordination afin d'améliorer les performances catalytiques des porphyrines de fer vis-à-vis de la réduction du CO<sub>2</sub>.



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# From antibodies to metal organic frameworks: a full set of envelopes for metalloporphyrins to build up new artificial hemoproteins

Jean-Pierre MAHY<sup>a</sup>, Wadih GHATTAS<sup>a</sup>, Frédéric AVENIER<sup>a</sup> and Rémy RICOUX<sup>a</sup>

<sup>a</sup> Institut de Chimie Moléculaire et des Matériaux d'Orsay, UMR 8182 CNRS, Laboratoire de Chimie Bioorganique et Bioinorganique, Bât. 420, Université Paris-sud/Paris-Saclay 91405 Orsay Cedex (France)

Considering current economic and ecological contexts, there is a crucial need to develop reactions that would address the problem of the selective transformation of chemicals under eco-compatible conditions. This urges industries to develop "green chemistry" procedures that have not only to include catalytic processes to limit waste, but also to use harmless solvents, the ideal of which would be water, with low temperatures and pressures to limit energy consumption. Enzymes, and in particular metalloenzymes, are biocatalysts that already fulfill such conditions. Because their properties are complementary to those of chemical catalysts, it is conceivable to design catalysts that would combine their ability to work under mild conditions in aqueous medium and with high selectivity with the robustness and wide range of reactions of chemical catalysts. These properties can thus be obtained through the design of new artificial metalloenzymes or "Artzymes" by associating a metal complex, that would be responsible for the catalytic activity, with a protein that would induce chemo and/or stereo-selectivity thanks to its chiral environment around the substrate and also would protect the metal cofactor from degradation.

In previous work, that has been extensively reviewed,<sup>1-3</sup> a first generation of artificial hemoproteins was prepared by the non-covalently insertion (Trojan-Horse and Host-Guest strategies) of Fe- and Mn- complexes of water-soluble tetra-arylporphyrins, into various proteins such as monoclonal antibodies (generation of catalytic antibodies or HemoAbZyMes), Xylanase A or a Neocarzinostatin variant, NCS 3-24 (HemoZyMes). The obtained hybrid biocatalysts were found to be able to catalyze the stereo-selective oxidation of organic compounds such as sulfides and alkenes by H<sub>2</sub>O<sub>2</sub> or KHSO<sub>5</sub>.

The most recent developments of our research that are turning towards four directions will be presented:

- The production of new artificial Mn-porphyrin-BSA- or -Xylanase A HemoZyMes that are able to perform the photooxidation of H<sub>2</sub>O in the presence of Ru-biPy complexes and the stereoselective oxidation of sulfides,<sup>4,5</sup>
- The association of a Mn-porphyrin with an artificial polyethyleneimine polymer-based reductase to afford the first entirely synthetic hemoprotein that was able to perform the reductive activation of O<sub>2</sub> and catalyze the subsequent oxidation of organic substrates in water.<sup>6</sup>
- The insertion of microperoxidase 8 (MP8), a minienzyme with peroxidase and monooxygenase activity, into Metal Organic Frameworks in order to get new artificial metalloenzymes that are able to catalyze in water the selective oxidation of dyes by H<sub>2</sub>O<sub>2</sub> (coll. C. Serre, N. Steunou, C. Sicard, ILV, versailles, Paris-Saclay),<sup>7,8</sup>
- **The synthesis of new artificial hemoproteins by covalent attachment of Mn-porphyrins into a new family of artificial proteins based on a thermostable alpha-helical repeated motif (αRepeat proteins or αRep, coll. Ph. Minard and A. Urvoas, I2BC, Paris-Saclay).**

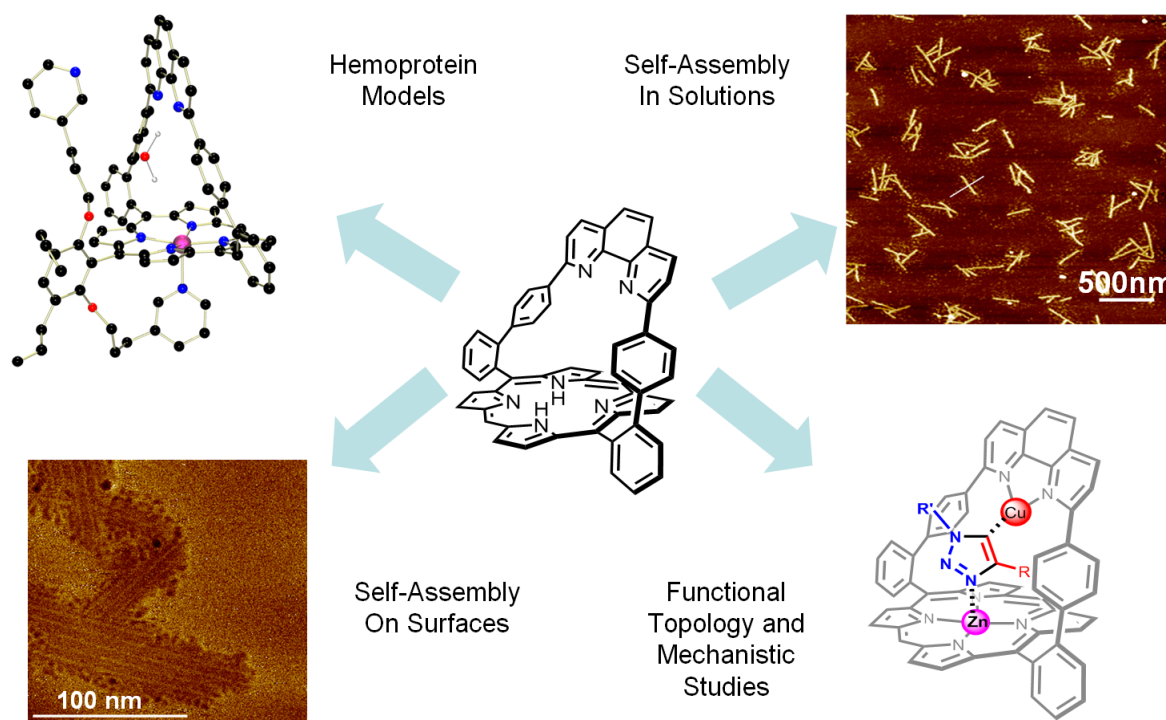
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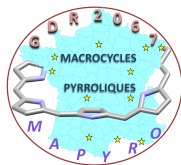
## Porphyrin Based Supramolecular Scaffolds

Jean Weiss, Institut de Chimie de Strasbourg, France

The presentation will discuss the use of photo and redox active structures in functional molecules ranging from elaborated bioinorganic models to supramolecular scaffolds and self-assemblies. A large part of our contribution to the field of porphyrin chemistry is based on a phenanthroline strapped porphyrin which can be prepared on large scale and functionalized to yield efficient cytochrome c oxidase models or photo-active rotaxanes as well as iterative motifs which can self-assemble in a highly controlled way on surfaces and in solution. Recent advances will be illustrated with our most significant results.



- 1) "From models of hemoproteins to self-assembled molecular wires" C. Kahlfuss, J. A. Wytko, J. Weiss *ChemPlusChem* **2017**, *4*, 584-594.
- 2) "Flexible viologen cyclophanes: odd/even effects on  $\pi$ -radical interactions" M. Berville, C. Boudon, L. Ruhlmann, S. Choua, C. Gourlaouen, C. Bailly, J. Wytko, S. Cobo, E. Saint-Aman, J. Weiss, *ChemPhysChem* **2017**, *18*, 796-803.
- 3) "CuAAC in a Distal Pocket: Metal Active-Template Synthesis of Strapped-Porphyrin [2] Rotaxanes" Y. Miyazaki, C. Kahlfuss, A. Ogawa, T. Matsumoto, J. A. Wytko, K. Oohora, T. Hayashi, J. Weiss *Chem. Eur. J.* **2017**, *23*, 13579-13582.
- 4) "Metal-mediated linear self-assembly of porphyrins" J. A. Wytko, R. Ruppert, C. Jeandon and J. Weiss, *Chem. Commun.*, **2018**, *54*, 1550-1558.
- 5) "Efficient fluorescence modulation and photopatterning with porphyrin tetra-dithienylethene switches" T. Biellmann, A. Galanti, J. Boixel, J. Wytko, V. Guerchais, P. Samori, J. Weiss, *Chem. Eur. J.* **2018**, *24*, 1631-1639.
- 6) "Light Triggers Molecular Shuttling in Rotaxanes: Control over Proximity and Charge Recombination" M. Wolf, A. Ogawa, M. Bechtold, M. Vonesch, J. A. Wytko, K. Oohora, S. Campidelli, T. Hayashi, D. M. Guldi, and Jean Weiss *Chem. Sci.* **2019**, doi: DOI: 10.1039/C8SC05328F

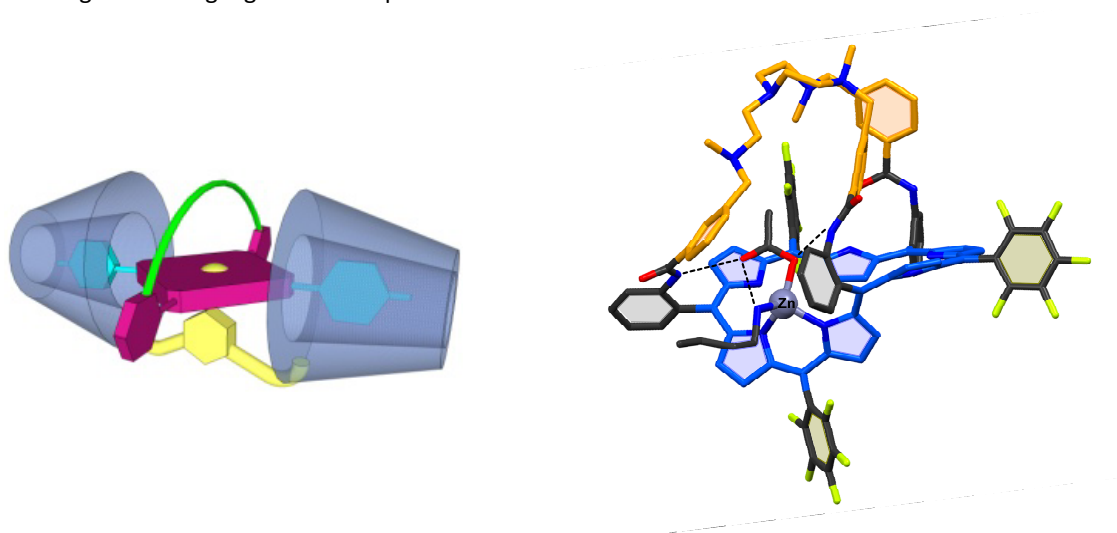


## Decorated porphyrin and hexaphyrin ligands

**Stéphane Le Gac<sup>a</sup> and Bernard Boitrel<sup>a</sup>**

<sup>a</sup> *Institut des Sciences Chimiques de Rennes (UMR CNRS 6226), Equipe Organométalliques : Matériaux et Catalyse, Université de Rennes 1, Campus de Beaulieu, Bâtiment 10C, 263 avenue du Général Leclerc, 35042 Rennes cedex (France). stephane.legac@univ-rennes1.fr, bernard.boitrel@univ-rennes1.fr*

The regular porphyrin skeleton is one of the most popular ligand, affording monometallic complexes with a wide range of elements. Over the last decade, our group has developed a family of polypyrrolic macrocycles “strapped” or “capped” by various functional groups (coordinating functions, cavities...) for different purposes, spanning from biomimetic processes to fundamental exotic coordinations: oxygen reduction and transport (Figure 1, left),<sup>[1]</sup> cancer therapy,<sup>[2]</sup> catalysis,<sup>[3]</sup> bimetallic molecular switches...<sup>[4]</sup> More recently, chiroptical switches and adaptative molecular receptors have been investigated with capped hexaphyrins (Figure 1, right),<sup>[5]</sup> and current work focuses on asymmetric preparation of inherently chiral Möbius molecular rings. Recent findings will be highlighted in this presentation.



**Figure 1.** Left: Illustration of a 1:1 bis-cyclodextrin/iron porphyrin host-guest complex for oxygen transport. Right: Möbius conformation (in blue) of a tren-capped hexaphyrin Zn(II) complex.

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