GDR MAPYRO Symposium

Montpellier, Pôle Chimie Balard

Lundi 27 octobre 2025

De 9h00 à 17h00

Program & Book of Abstracts

Groupement de recherche
Mapyro Pyrrolic Macrocycles

Inscriptions/renseignements :
Claude P. Gros, ICMUB
claude.gros@u-bourgogne.fr
& Sébastien Richeter, ICGM
sebastien.richeter@umontpellier.fr

Pôle Chimie Balard
Amphithéâtre Balard
1919 route de Mende
CC 043
34293 Montpellier
Cedex 5

Institut Charles Gerhardt Montpellier

Sponsors

https://mapyro.chimie.unistra.fr

https://www.inc.cnrs.fr/fr

https://www.umontpellier.fr

https://www.icgm.fr

Many thanks to S. Clément for practical help.

Thanks to M. Lambert and A. Arnaud for administrative help.

Table of Contents

Program

8:30 - 9:00		**Welcome**
Chair: Sébastien Richeter & Stéphanie Durot		
ORAL #1 9:00 - 9:20 (15 min talk + 5 min questions)		**Emma El-Beaine, Sorbonne Université** Cobalt Phthalocyanine Integrated in Membrane Electrode Assembly for the Electrochemical Reduction of CO_2 to Methanol
ORAL #2 9:20 - 9:40 (15 min talk + 5 min questions)		**Prof. Charles Devillers, Université Bourgogne Europe** Synthesis of Porphyrin Material *via* Oxidative C-N Coupling of Porphyrin with Pyridinyl Functionalized Electrodes
ORAL #3 9:40 - 10:00 (15 min talk + 5 min questions)		**Dr. Philipp Gotico, CEA Saclay** Clear the Air! Redesigning Iron Porphyrin Catalysts to Tackle CO_2 Reduction Amid Oxygen
ORAL #4 10:00 - 10:20 (15 min talk + 5 min questions)		**Ashutosh Vishwakarma, Université Paris Saclay** Urea Functionalized Second Coordination Sphere on Iron Porphyrin Catalyst for CO_2 Reduction Under Aprotic and Protic Conditions
Flash 10:20 - 10:25 (5 min talk)		**Axel Eisenbeth, Université de Strasbourg** Synthesis of Bis-Acridinium-Zn(II) Porphyrin Tweezers for Chiral Substrate Recognition

10:30 - 11:00		**Coffee Break / Poster Session**

Chair: Jean Weiss		
Plenary Lecture #1 **11:00 - 11:50** (45 min talk + 5 min questions)		**Prof. Takashi HAYASHI, The University of Osaka** Metalloporphyrinoids as Artificial Cofactors for Preparation of Reconstituted Myoglobins
Prix de thèse 2025 **11:50 - 12:15** (20 min talk + 5 min questions)		**Dr. Morgane MOINARD, Université de Lorraine** Overcoming Folic Acid Instability for Potent Ovarian Cancer Photodynamic Therapy

12:30 - 13:45		**Lunch and Poster Session, Balard Hall**

Chair: Gabriel Canard		
ORAL #5 13:45 - 14:05 (15 min talk + 5 min questions)		**Dr. Cédric Colomban, Université Aix-Marseille** Corrole-based Cages : Getting Closer to Biological Receptors
Plenary Lecture #2 **14:05 - 14:55** (45 min talk + 5 min questions)		**Prof. Xavi RIBAS, Universitat de Girona** Multipurpose Porphyrin-Based Supramolecular Nanocapsules for Chemistry at the Confined Space
ORAL #6 14:55 - 15:15 (15 min talk + 5 min questions)		**Dr. Stéphanie Durot, Université de Strasbourg** Dynamic Porphyrin Cages: Supramolecular Catalysis, Allosteric Encapsulation of Guests and Application to [2]Rotaxanes

15:15 - 16:00		**Coffee Break & Poster Session**

Chairman: Sébastien Richeter		
ORAL #7 16:00 - 16:20 (15 min talk + 5 min questions)		**Fangbing Liu, Université Claude Bernard Lyon 1** Design and Synthesis of a Stable Porous Porphyrinic Zirconium MOF for Applications in Photocatalysis
ORAL #8 16:20 - 16:40 (15 min talk + 3 min questions)		**Dr. Nesrine Amiri, Université Bourgogne Europe** β-Bromination of 2,7,12,17-Tetrabromoporphyrins. Functionalization of the Dibrominated Derivative with Thiopyridine Substituents for Oxidative C-N Fusion in *meso* Positions
ORAL #9 16:40 - 17:00 (15 min talk + 3 min questions)		**Fatima Awada, Université Bourgogne Europe** Electrochemical Oxidation of *Meso*-substituted Monoaminophenylporphyrins
17:00		**End**

cnrs GDR Groupement de recherche
Mapyro Pyrrolic Macrocycles

Plenary Lectures

Metalloporphyrinoids as Artificial Cofactors for Preparation of Reconstituted Myoglobins

Takashi Hayashi

Department of Applied Chemistry, The University of Osaka, 2-1 Yamadaoka, Suita 565-0871, Japan.
E-mail: thayashi@chem.eng.osaka-u.ac.jp

Myoglobin is an oxygen-storage hemoprotein that generally exhibits no enzymatic activity. In contrast, apomyoglobin, obtained by removing a heme cofactor from the heme pocket, can serve as an attractive reaction scaffold because it allows artificially synthesized metalloporphyrinoids to be inserted into the apoprotein cavity. Our group has focused on generating artificial metalloproteins by replacing the native heme cofactor with a metalloporphyrinoid. Recently, our group has prepared three types of porphyrinoids; a constitutional porphyrin isomer such as porphycene, a cyclic tetrapyrrole compound lacking one meso-carbon such as corrole or corrin derivatives, and substituent-modified protoporphyrins (Figure 1). After the metalation of the porphyrinoids, myoglobins reconstituted with each complex were found to function as an artificial enzyme or serve as a model for unclear metalloenzymes.[1] For example, myoglobin reconstituted by manganese porphycene promoted the hydroxylation of inert alkane species to give the corresponding alcohol as a product.[2] Iron porphyrin with CF_3 groups at peripheral positions works as a catalyst for the cyclopropanation of olefins with ethyl diazoacetate in the myoglobin scaffold.[3] Furthermore, it is found that cobalt corrin derivatives are an excellent cofactor model for cobalamin in the myoglobin heme pocket.[4] This presentation describes several myoglobins reconstituted with metalloporphyrinoids, as well as their physicochemical properties and catalytic activities.

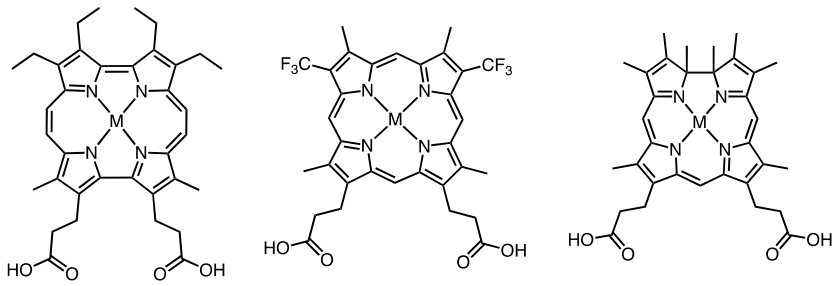


Figure 1. Three types of metalloporphyrinoids as a myoglobin cofactor

This work was supported by JSPS KAKENHI (particularly, 25H00887 and 22K21348).

References

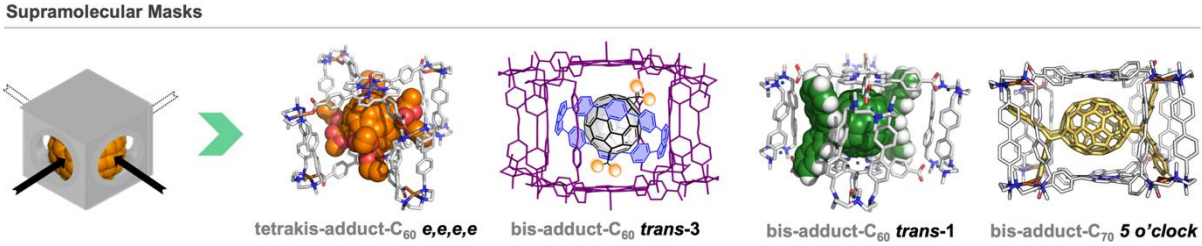
1. K. Oohora, A. Onoda, T. Hayashi, *Acc. Chem. Res.*, **2019**, *52*, 945–954.
2. K. Oohora, H. Meichin, Y. Kihira, H. Sugimoto, Y. Shiro, T. Hayashi, *J. Am. Chem. Soc.*, **2017**, *139*, 18460–18463.
3. Y. Kagawa, K. Oohora, T. Himiyama, A. Suzuki, T. Hayashi, *Angew. Chem. Int. Ed.*, **2024**, *63*, e202403485.
4. Y. Miyazaki, K. Oohora, T. Hayashi, *Chem. Soc. Rev.*, **2022**, *51*, 1629–1639.

Multipurpose Porphyrin-Based Supramolecular Nanocapsules for Chemistry at the Confined Space

Xavi Ribas*[1]

[1] *Institut de Química Computacional i Catàlisi (IQCC), Universitat de Girona, E17003 Girona, Catalonia-Spain*
E-mail: xavi.ribas@udg.edu

The design of a confined cavity dictates the type of guest to be encapsulated, and supramolecular cages are tunable scaffolds that allow the rational design of their cavities. Targeting fullerenes as guests, their regioselective functionalization and the control of the number of adducts are highly important to unlock 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 general, multi-adduct mixtures with uncontrolled regioselectivity (multi-isomers) are obtained, and chromatographic purification is too costly and time-consuming. Herein, porphyrin-based supramolecular nanocapsules[2,3] are used as supramolecular shadow masks to tame the over-reactivity of Bingel-Hirsch-type cyclopropanation reactions and, more importantly, to have full control over the equatorial regioselectivity and 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 synthesizing a single trans-3 bis-Bingel-C_{60} for the first time.[4] Also, the mask strategy is extended to Diels Alder reactions with full control of the regioselectivity in the synthesis of trans-1 bis-pentacene-C_{60}.[5] These results, recently extended to C_{70},[6,7] are fully attributed to the confinement control imposed by the capsule's cavity, and 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. We will also discuss the selective purification of fullertube mixtures and the encapsulation of photo-active guests.



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.
5. M. Pujals, X. Ribas, et al, *Cell Rep. Phys. Sci*. **2022**, 3, 100992.
6. V. Iannce, X. Ribas et al, *J. Am. Chem. Soc*. **2024**, 146, 5186−5194.
7. T. Pèlachs, X. Ribas et al, *CCS Chem*. **2025**, 7, 703–715

PhD award 2025

Overcoming Folic Acid Instability for Potent Ovarian Cancer Photodynamic Therapy

Moinard Morgane[a], Boidin Léa[b], Moussaron Albert[c], Stoup Nicolas[b], Grolez Guillaume[b], Morales Olivier[b,d], Arnoux Philippe[a], Acherar Samir[c], Bastogne Thierry[e], Delhem Nadira[b] and Frochot Céline[a]

[a] Université de Lorraine, CNRS, LRGP, F-54000 Nancy, France [b] Université de Lille, INSERM, CHU Lille, U1189-ONCO-THAI, F-59000 Lille, France [c] Université de Lorraine, CNRS, LCPM, F-54000 Nancy, France [d] Université de Lille, CNRS, UMR 9020, F-59000 Lille, France [e] Université de Lorraine, CNRS, CRAN, F-54000 Nancy, France
E-mail: morgane.moinard@univ-lorraine.fr

Ovarian cancer is the deadliest gynecological malignancy due to late diagnosis and frequent recurrence. Folate receptor alpha (FRα), highly expressed in ovarian tumors but scarce in healthy tissues, is an attractive target, yet folic acid (FA)-based strategies suffer from poor stability[1-2]. We designed a novel folic acid analogue (FAA1) with improved stability and high FRα affinity. Conjugation to pyropheophorbide-a via a PEG linker yielded PS^{FAA1}, after 10 synthesis steps, showing excellent photophysical properties (Φ_F=0.32 and Φ_Δ=0.42 in ethanol), selective FRα-mediated uptake, and potent light-induced cytotoxicity with minimal dark toxicity[3]. Comparative stability studies highlighted the superior resistance of FAA1 and PS^{FAA1} compared to native FA and Pyro-PEG-FA (PS2). Furthermore, regioisomeric analysis revealed that the α-conjugated isomer of PS^{FAA1} exhibited enhanced photodynamic efficacy over its γ-counterpart, identifying positional conjugation as a critical factor in therapeutic performance. Finally, this strategy was extended to the development of third-generation photosensitizers targeting neuropilin-1 (NRP-1) for non-small cell lung cancer, demonstrating the broader applicability of this targeted PDT approach.

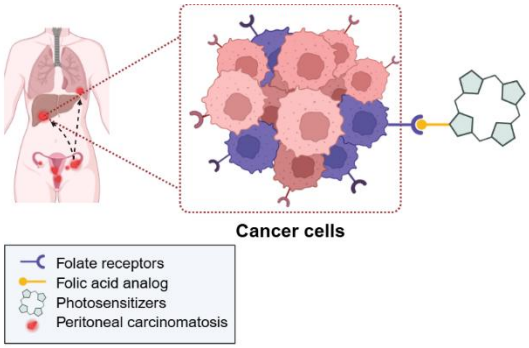


Figure 1. *Active targeting of folate receptors with folic acid analog-conjugated photosensitizers.*

This work was supported by INSERM through the interdisciplinary program "Approches interdisciplinaires des processus oncogéniques et perspectives thérapeutiques : Apports de la physique, de la chimie et des sciences de l'ingénieur à l'oncologie (PCSI)."

References

1. N. Parker, M. J. Turk, E. Westrick, J. D. Lewis, P. S. Low, C. P. Leamon, *Analytical Biochemistry*, **2005**, 338, 284–293.
2. M. Gazzali, A. Lobry, N. Colombeau, M. Acherar, C. André, L. Arnoux, O. Frochot, *European Journal of Pharmaceutical Sciences*, **2016**, 93, 419–430.
3. M. Moinard, L. Boidin, A. Moussaron, M. Merlier, O. Moralès, G. P. Grolez, M. Baydoun, A. Mohd-Gazzali, M. H. D. M. Tazizi, H. H. A. Allah, Y. Kerbage, P. Arnoux, S. Acherar, C. Frochot, N. Delhem, *Journal of Controlled Release*, **2024**, 371, 351–370.

Oral Communications

Cobalt Phthalocyanine Integrated in Membrane Electrode Assembly for the Electrochemical Reduction of CO_2 to Methanol

Emma El-Beaine,[1] Marc Robert[1,2]

[1]*Sorbonne Université, Institut Parisien de Chimie moléculaire*
4 Pl Jussieu, 75005 Paris, France
[2]*Institut Universitaire de France, IUF, 75005 Paris, France*
emma.el_beaine@sorbonne-universite.fr

The electrochemical reduction of CO_2 offers a sustainable route to fuels and chemical feedstocks, with methanol (CH_3OH) being particularly attractive.[1] Achieving high selectivity and current density remains challenging. In fact, very few catalysts have shown appreciable activity. A rare molecular catalyst able to produce methanol from CO_2 or CO is Co phthalocyanine (CoPc).[3-4] Membrane electrode assemblies (MEAs), integrating ion exchange membranes, gas diffusion layers, and catalytic electrodes, are central to performance (Figure 1).[2]

The integration of molecular catalysts such as CoPc has shown promise toward this aim. Building on previous results, we implemented a two-step strategy: CO_2-to-CO followed by CO-to-CH_3OH in MEA cells. A CoPc-based catalytic ink on gas diffusion electrodes allowed high CO conversion and methanol production. I will discuss key parameters optimizing CO_2 and CO electroreduction in MEA cells, highlighting the role of CoPc molecular catalyst and the impact of its loading, the gas flow, and electrolyte pH on activity and selectivity.

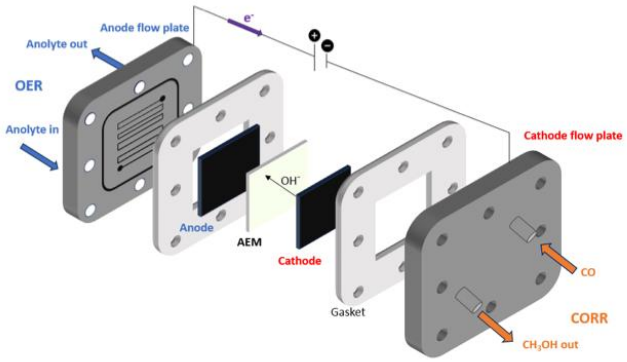


Figure 1. Scheme of membrane electrode assembly for CO-to-methanol conversion

References

1 Birdja, Y. Y.; Pérez-Gallent, E.; Figueiredo, M. C.; Göttle, A. J.; Calle-Vallejo, F.; Koper, M. T. M. Advances and Challenges in Understanding the Electrocatalytic Conversion of Carbon Dioxide to Fuels. *Nat. Energy* **2019**, *4* (9), 732–745.

2 Zhang, Z.; Huang, X.; Chen, Z.; Zhu, J.; Endrődi, B.; Janáky, C.; Deng, D. Membrane Electrode Assembly for Electrocatalytic CO_2 Reduction: Principle and Application. *Angew. Chem. Int. Ed.* **2023**, *62* (28).

3 Boutin, E.; Wang, M.; Lin, J. C.; Mesnage, M.; Mendoza, D.; Lassalle-Kaiser, B.; Hahn, C.; Jaramillo, T. F.; Robert, M. Aqueous Electrochemical Reduction of Carbon Dioxide and Carbon Monoxide into Methanol with Cobalt Phthalocyanine. *Angew. Chem. Int. Ed.* **2019**, *58* (45), 16172–16176.

4 Boutin, E.; Salamé, A.; Merakeb, L.; Chatterjee, T.; Robert, M. On the Existence and Role of Formaldehyde During Aqueous Electrochemical Reduction of Carbon Monoxide to Methanol by Cobalt Phthalocyanine. *Chem. – Eur. J.* **2022**, *28* (27).

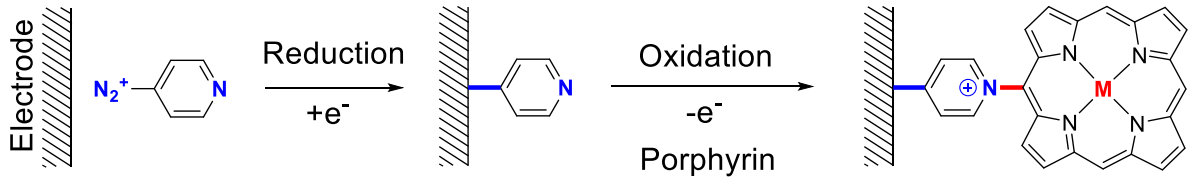
Synthesis of Porphyrin Material via Oxidative C-N Coupling of Porphyrin with Pyridinyl Functionalized Electrodes

Fatima Akhssas,[1] Moad Bouzid,[1] Abhishek Kumar,[1] Anna Krystianiak,[2] Eric Lesniewska,[2] Régis Parvaud,[2] Olivier Heintz,[2] Rita Meunier-Prest,[1] Charles H. Devillers[1*]

[1] Institut de Chimie Moléculaire de l'Université de Bourgogne UMR6302, CNRS, Université Bourgogne Europe, 9 avenue Alain Savary, 21000 Dijon, France. [2] Laboratoire Interdisciplinaire Carnot de Bourgogne UMR5209, CNRS, Université Bourgogne Europe, 9 avenue Alain Savary, 21000 Dijon, France.
E-mail: charles.devillers@ube.fr

Immobilization of functional molecules on an electrode surface is a crucial step towards the development of functional devices. Among these molecules, porphyrins exhibit unique physico-chemical properties. These molecules have been exploited for many applications in various research fields such as electrocatalysis,[1] photoluminescent biosensors[2] nonlinear and optical limiting devices.[3] Several approaches have been developed to graft the porphyrin moiety by post-functionalization of modified substrate. The coupling method can be performed *via* the formation of different chemical bonds: amide,[4] ester,[5] coordination[6] or using Huisgen cycloaddition reaction.[7]

We will show during this presentation that it is possible to immobilize a porphyrin *via* its oxidation on a pyridinyl-functionalized working electrode surface.[8] UV-vis. spectroscopy, cyclic voltammetry, XPS, SEM, AFM and TOF-sims analyses have been performed to confirm the chemical composition of the porphyrin material.



This work was supported by Région Bourgogne Franche Comté, Université de Bourgogne Europe and CNRS

References

1. Marianov, A. N.; Jiang, Y. *ACS Sustain. Chem. Eng*. **2019**, 7 (4), 3838–3848.
2. Khairutdinov, R. F.; Serpone, N. *J. Phys. Chem.* **1995**, 99 (31), 11952–11958.
3. Wang, A.; Yu, W.; Huang, Z.; Zhou, F.; Song, J.; Song, Y.; Long, L.; Cifuentes, M. P.; Humphrey, M. G.; Zhang, L.; Shao, J.; Zhang, C. *Sci. Rep.* **2016**, 6 (1), 23325.
4. Rocklin, R. D.; Murray, R. W. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, 100 (1), 271–282.
5. Baskaran, D.; Mays, J. W.; Zhang, X. P.; Bratcher, M. S. *J. Am. Chem. Soc.* **2005**, 127 (19), 6916–6917.
6. Zuo, G.; Yuan, H.; Yang, J.; Zuo, R.; Lu, X. *J. Mol. Catal. Chem.* **2007**, 269 (1), 46–52.
7. Mennel, J. A.; Pan, H.; Palladino, S. W.; Barile, C. J. *J. Phys. Chem. C* **2020**, 124 (36), 19716–19724.
8. Akhssas, F.; Bouzid, M.; Kumar, A.; Krystianiak, A.; Heintz, O.; Lesniewska, E., Parvaud, R., Meunier-Prest, R.; Devillers, C. H., *manuscript in preparation*.

Clear the Air! Redesigning Iron Porphyrin Catalysts to Tackle CO_2 Reduction Amid Oxygen

Philipp Gotico,[1]* Haroon Rashid,[1] Diana Dragoe,[2] Atanu Rana,[3] Serena De Beer,[3] Winfried Leibl,[1] Ally Aukauloo[2]*

[1]*Institut de Biologie Intégrative de la Cellule, CEA, 91191 Gif sur Yvette, France*
[2] *Institut de Chimie Moléculaire et des Matériaux d'Orsay, 91405, Orsay, France*
[3] *Max Planck Institute for Chemical Energy Conversion, D-45470 Mülheim, Germany*

E-mail: philipp.gotico@cea.fr, ally.aukauloo@universite-paris-saclay.fr

The electrocatalytic reduction of CO_2 to energy rich forms such as CO or hydrocarbons is typically realized with pure CO_2. This is primarily to exclude O_2, which is a far better oxidant and a major competitor upon reduction of CO_2:O_2 feed gas. Further, the presence of O_2 can deactivate the catalytic material and reduce its effectiveness for CO_2 reduction. To confront this major challenge, different strategies are being pursued (Figure 1).[1-3] We utilize a molecular design approach by adjoining to a known catalyst a redox active module that can competitively divert the deleterious O_2 activity. We tailored an iron porphyrin, a prominent catalyst for CO_2 reduction, flanked with viologen units known for its efficient O_2 reduction. Electrochemical studies in homogeneous phase of the pre-catalyst, the iron(III)-μ-oxo form, show the independent activity of both modules. When heterogenized with carbon nanotubes on carbon paper electrode, we found that the catalyst could sustain the aerobic (5% O_2) reduction of CO_2 to CO with a Faradaic efficiency of 62% while the activity of the unmodified iron porphyrin fell to 18% under the same experimental conditions.

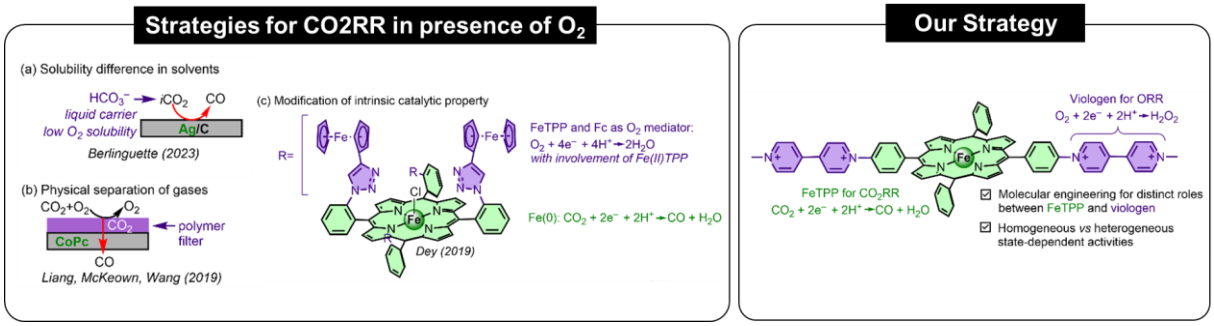


Figure 1. (Left) Strategies for performing CO_2 reduction reaction (CO2RR) in presence of oxygen and (right) our strategy with porphyrin appended viologen units.

References

1. D. J. D. Pimlott, A. Jewlal, Y. Kim and C. P. Berlinguette, *J. Am. Chem. Soc.,* **2023**, *145*, 25933–25937
2. X. Lu, Z. Jiang, X. Yuan, Y. Wu, R. Malpass-Evans, Y. Zhong, Y. Liang, N. B. McKeown and H. Wang, *Sci. Bull.,* **2019**, *64*, 1890–1895.
3. B. Mondal, P. Sen, A. Rana, D. Saha, P. Das and A. Dey, *ACS Catal.,* **2019**, *9,* 3895–3899.

Urea Functionalized Second Coordination Sphere on Iron Porphyrin Catalyst for CO_2 Reduction Under Aprotic and Protic Conditions

Ashutosh Vishwakarma[1], Philipp Gotico[2], Zakaria Halime[1]

[1]*Institut de Chimie Moléculaire et des Matériaux d'Orsay, Université Paris Saclay, Orsay, France;*
[2]*Institut de Biologie Intégrative de la Cellule, CEA Saclay, Gif-sur-Yvette, France;*
ashutosh.vishwakarma@uinverite-paris-saclay.fr

Global warming driven by rising CO_2 emissions has prompted intense research into efficient, cost-effective catalysts for CO_2 capture and reduction. While geological CO_2 storage offers a temporary solution, its long-term stability and cost remain uncertain. A more sustainable strategy involves converting CO_2 into energy-rich compounds or C1 building blocks for organic synthesis, forming a closed carbon cycle. The goal is to use solar energy to power the electrocatalytic transformation of CO_2 into fuels, mimicking natural photosynthesis where metalloenzymes convert CO_2 and water into hydrocarbons. Effective catalysts must activate CO_2 and promote its reduction through proton-coupled multi-electron steps, avoiding high-energy intermediates. Current research focuses on molecular catalysts, particularly metal complexes both noble (Ru, Rh, Pd, Re, Ir) and earth-abundant first-row transition metals (Mn, Fe, Co, Ni, Cu) coordinated with nitrogen-based ligands. Iron porphyrins have emerged as especially promising electrocatalysts for CO_2 reduction to CO, showing high efficiency and selectivity.

In this poster, we have developed a new iron-porphyrin catalyst featuring four urea groups in the second coordination sphere, with an $\alpha_2\beta_2$ geometry where the two adjacent groups are positioned adjacently on one side with respect to the porphyrin plane and two other groups in the opposite side (Figure 1). We have found that this specific spatial arrangement enables efficient CO_2 reduction even in the absence of an external proton source. The catalyst exhibits a significantly higher turnover frequency compared to its *αβαβ* atropisomer where the urea groups are positioned alternately on the porphyrin plane[1]. This difference highlights the critical role of symmetry in modulating reactivity. Moreover, a pronounced kinetic isotope effect (KIE) suggests that protonation is the rate-determining step in the reaction mechanism. These findings emphasize how strategic placement of hydrogen-bond donors in the second coordination sphere can enhance CO_2 activation and reduction, offering valuable insights into the design of next-generation catalysts for sustainable carbon conversion.

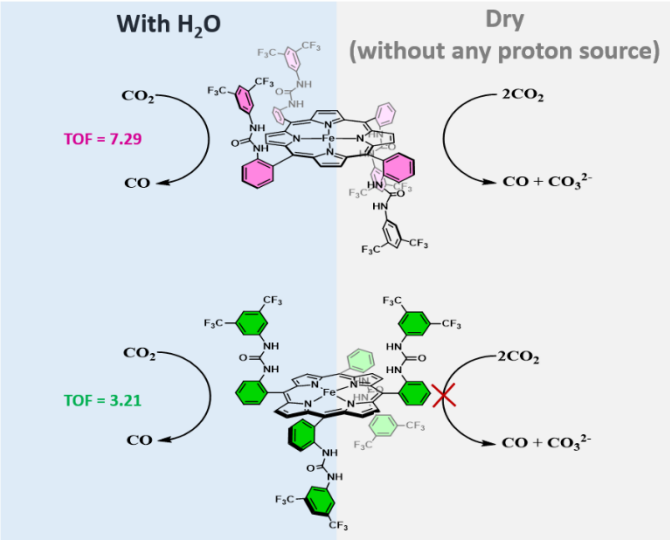


Figure 1. Electrocatalytic CO_2 reduction to CO by iron porphyrin catalysts ($\alpha_2\beta_2$ in pink *and αβαβ* in green) in absence and presence of an external proton source.

References

1. P. Gotico, B. Boitrel, R. Guillot, M. Sircoglou, A. Quaranta, Z. Halime, W. Leibl, A. Aukauloo, *Angew. Chem. Int. Ed*. **2019**, *58*, 4504

Corrole-based cages : getting closer to biological receptors.

A. Baidiuk,[1] M. Orio,[1] A. Martinez,[1] G. Canard,[2] C. Colomban*[1]

[1] *iSm2, UMR-7313, Aix Marseille Univ., CNRS, Marseille, France*

[2] *CINaM, UMR-7225, Aix Marseille Univ., CNRS, Marseille, France*

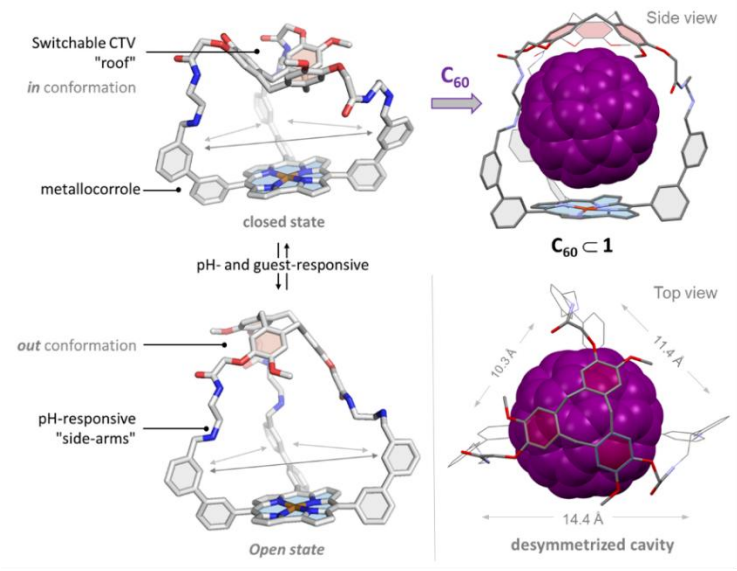
E-mail: cedric.colomban@univ-amu.fr

We develop metalloprotein-inspired metal complexes entrapped in artificial cavities. These cage architectures enable advanced reactivity studies,[1] and enhanced catalysts (eg CH_4 oxidation).[2]

Inspired by biological receptors, interests in desymmetrized, guest-adaptive,[3] and stimuli responsive,[4] artificial hosts are currently increasing. However, the major challenge remains to combine these “biological” features in one artificial cavity.

In this study, we establish a key precedent of a single host regrouping these important features and introduce a new design of molecular cages based on corroles, the low symmetrical analogue of porphyrins. Introduction of a concave–convex shape-switching “roof”, and pH-responsive “side-arms”, enables the first mettalocorrole cage to reversibly bind fullerenes in a guest-adaptive, stimuli-responsive and low-symmetrical environment.[5]

Discussion on i) how our synthetical strategy allow convenient access to caged metallocorrole complexes and ii) how the shapeshifting cavity enable selective guest encapsulation and controlled guest-release, will be the core of this communication, which aims at giving a better understanding of this challenging caged complexes.



References

1. D. Diao, … , X. Ribas, A. Martinez, P. Nava, J. Simaan, C. Colomban, *JACS-Au.*, **2024**, 4, 1966
2. D. Diao, J. Simaan, A. Martinez, C. Colomban, *Chem.Commun.*, **2023**, 59, 4288
3. J.R. Nitschke and co., *Nat.Chem.*, **2025**, 17, 289
4. J.L. Sessler, H.Y. Gong and co. *Angew.Chem.Int.Ed.*, **2024**, e202407805
5. A. Baidiuk, … , G. Canard, C. Colomban, *ChemRxiv*, **2025** DOI: 10.26434/chemrxiv-2025-lprmp

Dynamic porphyrin cages: supramolecular catalysis, allosteric encapsulation of guests and application to [2]rotaxanes

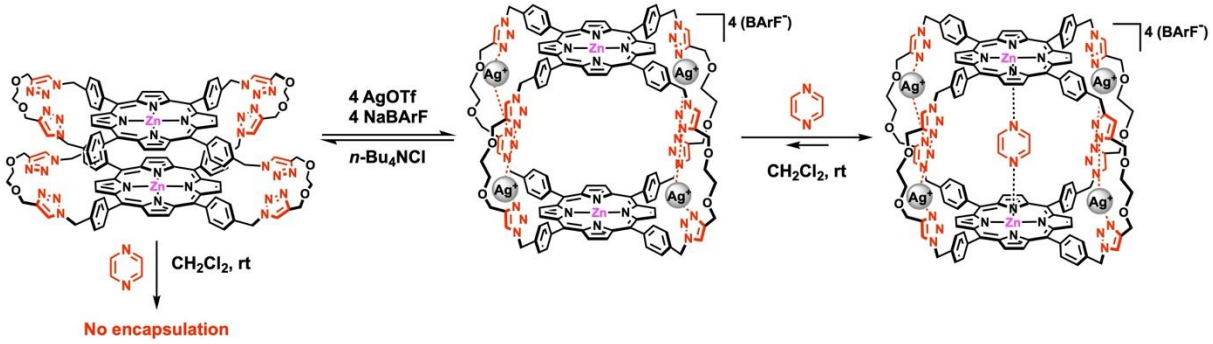
Laetitia Schoepff,[1] Sonia Adrouche,[1] Ryan Djemili,[1] Valérie Heitz,[1] Stéphanie Durot*[1]

[1] *Laboratoire de Synthèse des Assemblages Moléculaires Multifonctionnels,*
Université de Strasbourg et Institut de Chimie de Strasbourg CNRS UMR 7177,
Institut Le Bel, 4, rue Blaise Pascal, F-67000 Strasbourg, France ;
E-mail: sdurot@unistra.fr

Molecular cages are hollow structures with a well-defined three-dimensional cavity that can encapsulate guest molecules or perform reactions in their cavity.[1] Metalloporphyrins are attractive constituents of cages thanks to their various properties and catalytic activities.[2]

Flexible covalent cages, endowed with two zinc(II) or cobalt(III) porphyrins and eight peripheral 1,2,3-triazolyl ligands were prepared and used as bimetallic catalysts.[3]

Coordination of four silver(I) ions to the peripheral ligands switched the Zn(II) porphyrin cage from a flattened to an open and locked conformation, allowing the allosteric control of encapsulation of neutral guest molecules, such as pyrazine (Fig.).[4]



The receptor properties of our covalent cages can be leveraged for the assembly of [2]semirotaxanes[4b] and allosteric-driven motion in [2]rotaxanes, since such control of the threading step or macrocycle translation by effector binding to additional sites has rarely been reported.[5]

This work was supported by the ANR (projects "Switchables cages" ANR 14-CE06-0010, the French Ministry of Education and Research, LabEx-CSC and the GDR MAPYRO (Pyrrolic Macrocycles).

References

1. M. Yoshizawa, J. K. Klosterman, M. Fujita, *Angew. Chem. Int. Ed.* **2009**, *48*, 3418.
2. S. Durot, J. Taesch, V. Heitz, *Chem. Rev.* **2014**, *114*, 8542.
3. a) L. Kocher, S. Durot, V. Heitz, *Chem. Commun.* **2015**, *51*, 13181; b) L. Schoepff, L. Kocher, S. Durot, V. Heitz, *J. Org. Chem.* **2017**, *82*, 5845; c) L. Schoepff, L. Monnereau, S. Durot, S. Jenni, C. Gourlaouen, V. Heitz, *ChemCatChem* **2020**, *12*, 5826.
4. a) R. Djemili, L. Kocher, S. Durot, A. Peuronen, K. Rissanen, V. Heitz, *Chem. – Eur. J.* **2019,** *25*, 1481. b) R. Djemili, S. Adrouche, S. Durot, V. Heitz, *J. Org. Chem.* **2023**, *88*, 14760.
5. a) J. Kuwabara, C. L. Stern, C. A. Mirkin, *J. Am. Chem. Soc.* **2007**, *129*, 10074; b) S. Cantekin, A. J. Markvoort, J. A. A. W. Elemans, A. E. Rowan, R. J. M. Nolte, *J. Am. Chem. Soc.* **2015**, *137*, 3915; c) D. S. Marlin, D. González Cabrera, D. A. Leigh, A. M. Z. Slawin, *Angew. Chem. Int. Ed.* **2006**, *45*, 1385; d) F. Durola, V. Heitz, F. Reviriego, C. Roche, J.-P. Sauvage, A. Sour, Y. Trolez, *Acc. Chem. Res.* **2014**, *47*, 633.

DESIGN AND SYNTHESIS OF A STABLE POROUS PORPHYRINIC ZIRCONIUM MOF FOR APPLICATIONS IN PHOTOCATALYSIS

Fangbing Liu[1], Alexandra Fateeva*[1]

[1] *Université Claude Bernard Lyon 1, CNRS, LMI UMR 5615, Villeurbanne, F-69100, 6 rue Victor Grignard, 69100 Villeurbanne, France.*

E-mail: fangbing.liu@univ-lyon1.fr

In recent years, porphyrin-based metal organic frameworks (PMOFs) have particularly attracted attention for their photoactivity.[1,2] Inspired by the enhanced hydrophobicity and higher stability to oxidation and light on fluorinated MOFs,[3,4] we have ignited an effort to explore the synthesis and functional properties of fluorinated PMOFs. Specifically, we developed the gram scale synthesis of the fluorinated analog of tetrakis(4-carboxyphenyl)porphyrin (TCPP), named F_{16}TCPP to be used as linker.

It is established that the strong interaction between Zr(IV) and carboxylate make the resultant MOFs chemically stable, bearing this in mind, we constructed a polyfluorinated porphyrinic zirconium MOF by combining Zr precursor and F_{16}TCPP through adjusting the reaction conditions. By carefully choosing different metal precursors and exploring the reactivity in different solvents, a new Zr-F-PMOF could be isolated in a reproducible manner with good yield. Synchrotron diffraction data revealed that Zr-F-PMOF crystallizes in the P_{432} space group, the structure is arranged in cubes formed of eight corner-sharing $Zr_6O_4(OH)_4$ units and six face-occupying F_{16}TCPP porphyrins, leading to a cubic structure and ~19.3 Å pore size. The topology of this framework can be classified as a 3-D (4,12)-connected **ftw** net. Furthermore, achieving precise size control of Zr-F-PMOF crystals while retaining their intrinsic physicochemical properties and high uniformity represents a critical challenge in advancing their functional applications. Notably, nano-sized crystals usually show an enhanced catalytic activity than their bulk analogues, attributed to their increased exposure of active sites and reduced mass transfer limitations. In our work, through an ultrasound-assisted method, we successfully tuned the size of Zr-F-PMOF crystals from 8 µm to 130 nm, to achieve nano Zr-F-PMOF with high crystallinity and uniform morphology (**Fig. 1**). In this communication, relevant structural, spectroscopic and textural properties will be discussed.

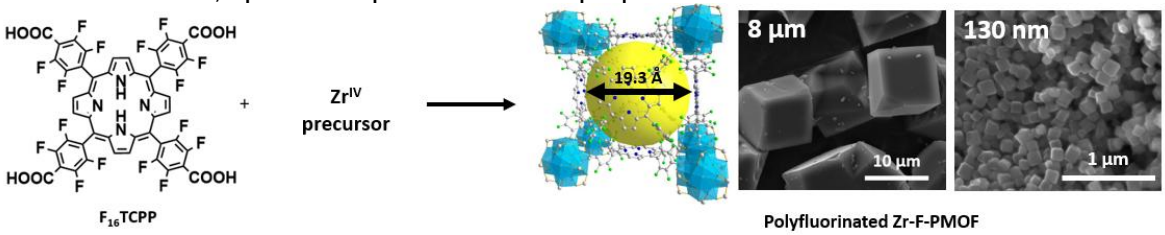


Fig. 1. Schematic Diagram of Polyfluorinated PMOF synthesis and SEM pictures illustrating the particle size tunability.

This work was supported by ARQUS European University Alliance.

References

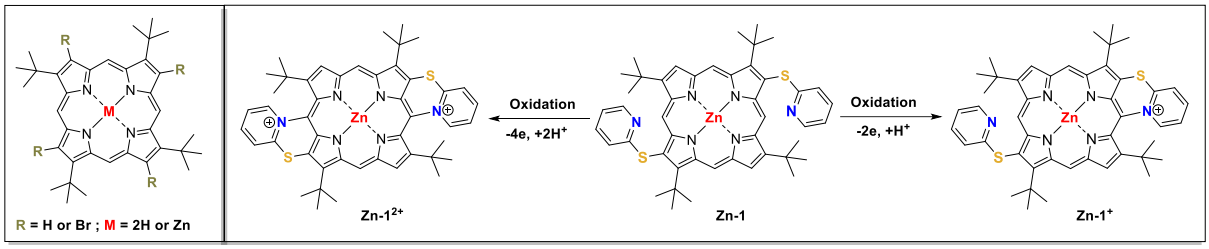
1. Q. Deng, P. Sun, L. Zhang, *Adv. Funct. Mater.*, **2019**, 29, 1903018.
2 . B. Gikonyo, E. Montero-Lanzuela, H. G. Baldovi, *J. Mater. Chem. A*, **2022**, 10, 24938–24950.
3 . P. T. Nyffeler, S. G. Durón, M. D. Burkart, *Angewandte Chemie International Edition*, **2005**, 44, 192–212.
4 . C. Yang, U. Kaipa, Q. Z. Mather, *J. Am. Chem. Soc.*, **2011**, 133, 18094–18097.

β-Bromination of 2,7,12,17-Tetrabromoporphyrins. Functionalization of the Dibrominated Derivative with Thiopyridine Substituents for Oxidative C-N Fusion in *meso* Positions

Nesrine AMIRI, Amelle MANKOU-MAKAYA, Hélène CATTEY, Charles H. DEVILLERS*

Institut de Chimie Moléculaire de l'Université de Bourgogne UMR6302, CNRS, Université Bourgogne Europe, 9 avenue Alain Savary 21000 Dijon, France.
E-mail: Nesrine.Amiri@u-bourgogne.fr

Porphyrins are versatile *π*-conjugated macrocycles with applications in catalysis,[1] sensing,[2] photovoltaics,[3] and photodynamic therapy.[4] Chemical modifications at the *β*-pyrrolic positions are of particular interest, as they strongly influence the structural and electronic properties of the porphyrin core. In this work, we report the synthesis of a new series of *β*-brominated 2,7,12,17-tetra-tert-butylporphyrins and their zinc(II) complexes, using *N*-bromosuccinimide as the brominating agent. By controlling the reaction conditions, mono-, di-, tri- and tetra-brominated derivatives were isolated in moderate to excellent yields (Scheme 1, left). The compounds were fully characterized by NMR spectroscopy, mass spectrometry, UV–Vis absorption spectroscopy, and single-crystal X-ray diffraction. A progressive red-shift in the *Soret* and *Q* bands was observed with increasing bromination, highlighting the strong impact of bromine substituents on the optical properties. Furthermore, a dibrominated porphyrin was functionalized with two thiopyridinyl moieties to afford Zn(II) *β*-pyridin-2-ylthio-porphyrin Zn-1 (Scheme 1, right). Electrochemical oxidation of this precursor Zn-1 led to intramolecular C–N bond formation, giving mono- (Zn-1^{+}) and bis-fused (Zn-1^{2+}) macrocycles.[5] These fused derivatives exhibited significant spectral shifts, indicating enhanced conjugation.



***Scheme 1**: From β-bromoprphyrins to C-N fusion macrocyles*.

This work was supported by Université Bourgogne Europe, CNRS, Région Bourgogne Franche Comté, French "Investissement d'Avenir" Program, project ISITE-BFC (contract ANR-15-IDEX-03)

References

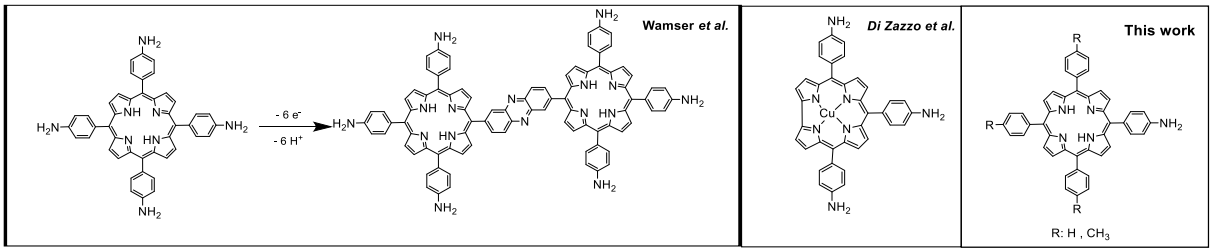
1. X. Li, H. Lei, L. Xie, N. Wang, W. Zhang, R. Cao, *Acc. Chem. Res*. **2022**, 6, 878–892.
2. G. Magna, L. D. Zazzo, M. Stefanelli, A. Catini, R. Capuano, R. Paolesse, C. D. Natale, *Meet. Abstr.* **2023**, 01, 1404.
3. S. Huang, Q. Li, S. Li, C. Li, H. Tan, Y. Xie, *Chem. Commun*. **2024**, 60, 4521-4536.
4. M. Ethirajan, Y. Chen, P. Joshi, R. K. Pandey, *Chem. Soc. Rev*. **2011**, 40, 340-362.
5. A. Nesrine, M. M. Amelle, C. Hélène, D. Charles H., *manuscript in preparation.*

Electrochemical Oxidation of *Meso*-substituted Mono-aminophenylporphyrins

Fatima AWADA, Marcel BOUVET, Charles H. DEVILLERS*

Institut de Chimie Moléculaire de l'Université de Bourgogne, UMR CNRS 6302, Université Bourgogne Europe, 9 avenue Alain Savary, BP 47870, 21078 DIJON Cedex, FRANCE
E-mail : fatima.awada@u-bourgogne.fr

In the material research field, electrochemistry is a powerful method to finely tuned the material thickness and properties thanks to the control of the potential or the current. For example, electropolymerized porphyrin films have been exploited for applications in electrocatalysis, fuel cell cathodes, and photovoltaic devices.[1] A variety of metallo and free base *meso*-substituted aminophenylporphyrins containing ortho, meta-, and para-substituted amino groups have been reported to electropolymerize under a wide range of conditions using both organic and aqueous electrolyte solutions.[1,2,3] Wamser *et al.*[1] reported the electropolymerization of variously substituted aminophenylporphyrins including the tetrakis-5,10,15,20-(4-aminophenyl)-porphyrin (TAPP). According to the authors and FT-IR analyses, upon oxidation of the TAPP, phenazine bridges were formed between the porphyrin units (Scheme 1, left). In addition, Di Zazzo *et al.*[4] reported the oxidative electropolymerization of [5,10,15-(4-aminophenyl)corrolato]copper(III) (Scheme 1, middle). This led to the *in-situ* synthesis of polycorroles conductive materials whose structure was proposed to include phenazine bridges between the corrole units. As the phenazine bridge was systematically proposed to be the spacer unit between the porphyrins or corroles, we embarked in the synthesis of porphyrins bearing only one aniline unit, with the aim to definitively prove the formation of the phenazine bridge by common solution analytical methods. Thus, our work has first consisted in the synthesis of 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin and 5-(*p*-aminophenyl)-10,15,20-tri(*p*-tolyl) porphyrin (Scheme 1, right). Their oxidation was then performed to verify the formation of the phenazine bridged porphyrin dimer. We will show in this presentation that no phenazine has been obtained and original porphyrin products were formed instead.



***Scheme 1**: Electropolymerization of meso-substituted aminophenylporphyrins/corroles*

This work was supported by ANR Porph4Sens (ANR-22-CE06-0039-01), Université Bourgogne Europe and CNRS

References

1. M.G. Walter, C. Wamser, *J. Phys. Chem. C* **2010**, *114* (17), 7563–7574.
2. G. Cornejo, G. Ramirez, M. Villagran, *Chem. Soc.* **2003**, *48*, 49–55.
3. S. Chen, Y. Chen, R.J.Thangamuthu, *Solid State Electrochem*. **2007**, *11*, 1441–1448.
4. L. Di Zazzo, A. Kumar, R. Meunier-Prest, *Chem. Eng. J.* **2023**, *458*, 141465.

Flash Communication

Synthesis of bis-acridinium-Zn(II)porphyrin tweezer for chiral substrat recognition.

Axel Eisenbeth[1], Henri-Pierre Jacquot de Rouville*[1], Valérie Heitz*[1]

[1]*Laboratoire de synthèse des assemblages moléculaires multifonctionnels, Institut de chimie de Strasbourg, UMR 7177 – Université de Strasbourg, 4 rue Blaise Pascal, 67000 Strasbourg, France.*
E-mail: aeisenbeth@unistra.fr

Porphyrins are well known as excellent chromophores and fluorophores, thanks to their intense absorbance and fluorescence which can be tuned by metal coordination.[1] These optical properties make metalloporphyrins highly attractive for the chiroptical detection of chiral coordinating substrates. In particular, the close spatial arrangement of two porphyrin units can lead to a pronounced exciton coupling in the visible range.[2] In addition, our group has explored the pH switching of acridinium units coupled to porphyrins in a tweezer architecture, and has recently demonstrated the possibility of switching the porphyrin luminescence in an on/off manner.[3] We are now focusing on developing novel porphyrin–acridinium systems to investigate the chiroptical detection of substrates via circularly polarized luminescence (CPL), an approach still rarely applied to porphyrinic frameworks.[4] In this context, we have synthesized a bis-acridinium–porphyrin Zn(II) tweezer, which should enable sensitive and intense chiroptical detection in the visible range, even for non-absorbing substrates (Figure 1).

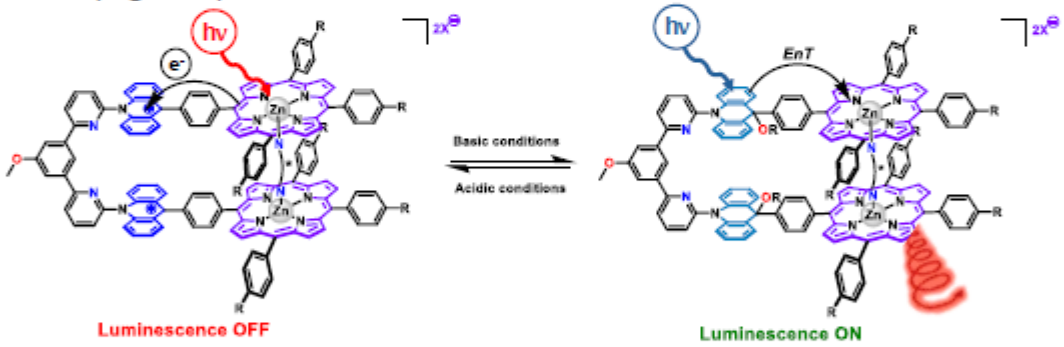


Figure 1. Expected chiral diamine recognition by a bis-acridinium-Zn(II)porphyrin tweezer and his luminescence switching properties.

This work was supported by Université de Strasbourg, CNRS and by the Interdisciplinary Thematic Institute SysChem via the IdEx Unistra (ANR-10-IDEX-0002). A.E. gratefully thanks the ENS Paris-Saclay for his PhD grant.

References

1. Sekhar, A. R.; Chitose, Y.; Janoš, J.; Dangoor, S. I.; Ramundo, A.; Satchi-Fainaro, R.; Slavíček, P.; Klán, P.; Weinstain, R. *Nat Commun* **2022**, *13* (1), 3614.
2. Huang, X.; Rickman, B. H.; Borhan, B.; Berova, N.; Nakanishi, K. *J. Am. Chem. Soc.* **1998**, *120* (24), 6185–6186.
3. Edo-Osagie, A.; Serillon, D.; Ruani, F.; Barril, X.; Gourlaouen, C.; Armaroli, N.; Ventura, B.; Jacquot de Rouville, H.-P.; Heitz, V. *J. Am. Chem. Soc.* **2023**, *145* (19), 10691–10699.
4. Dhbaibi, K.; Matozzo, P.; Abella, L.; Jean, M.; Vanthuyne, N.; Autschbach, J.; Favereau, L.; Crassous, J. *Chem. Commun.* **2021**, *57* (82), 10743–10746.

Posters

Design of new molecular cages combining porphyrins and cyclotriveratrylenes

Louise Pfeiffer,[1] Cédric Ollier,[2] Alexandre Martinez,[2] Christophe Gourlaouen,[3] Valérie Heitz,[1] Stéphanie Durot*[1]

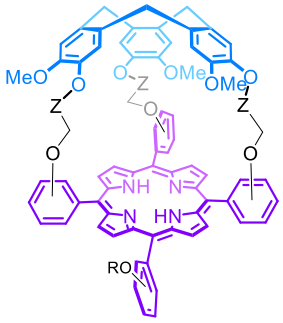
[1] *Laboratoire de Synthèse des Assemblages Moléculaires Multifonctionnels,* Université de Strasbourg, Institut de Chimie de Strasbourg CNRS UMR 7177, *Institut Le Bel, 4, rue Blaise Pascal, F-67000 Strasbourg, France ;*
[2] *Chirosciences team, iSm2, Aix-Marseille Université,CNRS UMR 7313, Centrale Marseille, 52 avenue Escadrille Normandie-Niemen,13013 Marseille, France.*
[3] *Chimie de la Matière Complexe, Université de Strasbourg,* CNRS UMR 7140, *Institut Le Bel, 4 rue Blaise Pascal, 67070 Strasbourg, France.*

E-mail: *louise.pfeiffer@unistra.fr*

Molecular cages are discrete compounds with cavities able of encapsulating smaller molecules through non-covalent interactions. They are designed for applications in molecular recognition, catalysis or transport.[1]

Among the various building blocks used, porphyrins stand out as versatile aromatic macrocycles. They can coordinate metals, absorb light and display redox and photophysical properties that can be useful in catalysis. Porphyrin cages[2] exhibit good host properties for neutral molecules and provide effective catalytic activities for reactions, like the conversion of CO_2 and epoxides into cyclic carbonates[3a] or size-selective cyclopropanation.[3b] Another important building block is cyclotriveratrylene (CTV), which forms a chiral capping unit in hemicryptophanes. CTV-based cavities are known to encapsulate neutral and charged guests and have demonstrated catalytic activity in cyclic carbonates formation[4a] or Diels-Alder reactions.[4b]

In this collaborative project, porphyrin and CTV are combined to access molecular cages able to stabilize aromatics and cations. The volume of the cavity can be modulated by changing the length of the linkers. Herein, we describe the design and the preliminary results about the synthesis of a cage by a templated approach.



Structure of targeted porphyrin-CTV molecular cages

This work was supported by the ANR (ANR-23-CE07-0035 AtropoPhotoCat).

References

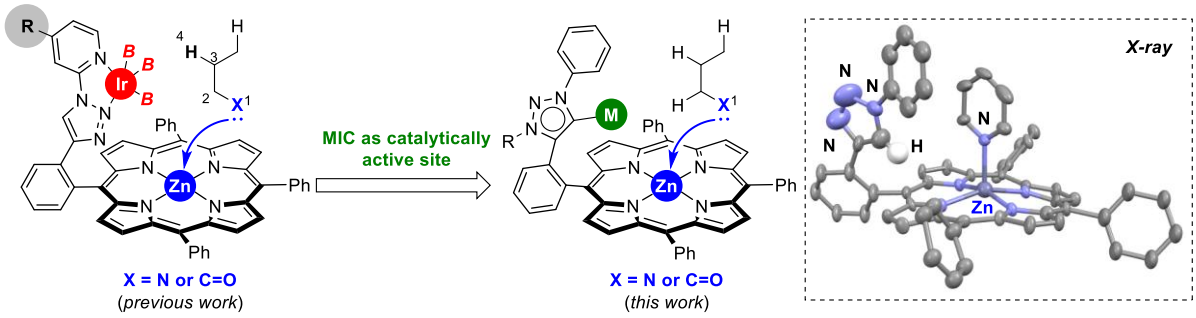
1. E. Ortiz-Gómez, R. Martínez-Máñez, V. Martí-Centelles, *Trends Chem.* **2025**, *7*, 429–443.
2. S. Durot, J. Taesch, V. Heitz, *Chem. Rev.* **2014**, *114*, 8542-8578
3.a. L. Schoepff, L. Monnereau, S. Durot, S. Jenni, C. Gourlaouen, V. Heitz, *ChemCatChem* **2020**, *12*, 5826–5833; 3.b. M. Otte, P. F. Kuijpers, O. Troeppner, I. Ivanović-Burmazović, J. N. H. Reek, B. de Bruin, *Chem. Eur. J.,* **2014**, 20, 4880–4884.
4.a. B. Bousquet, A. Martinez, V. Dufaud, *ChemCatChem* **2018**, *10*, 843–848 ; 4.b. B. Chatelet, V. Dufaud, J.-P. Dutasta, A. Martinez, *J. Org. Chem.,* **2014**, *79*, 8684–8688.

Merging mesoionic NHC-carbenes with metalloporphyrins for supramolecular catalysis

Elisa Travers, Mathieu Achard, Rafael Gramage-Doria,

University of Rennes, CNRS, Rennes Institute of Chemical Sciences, 263 Avenue du General Leclerc, 35042 Rennes, France
E-mail: elisa.travers.1@univ-rennes.fr

Incorporating molecular recognition features in the second coordination sphere of transition metal catalysts mimics the action mode of highly active and selective natural metalloenzymes.[1] Hydrogen bonding and ion pairing have proven beneficial for such purposes enabling substrate selection and reaching pre-organization that leads to exquisite of levels of selectivity in challenging organic transformations.[2] In this context, our laboratory has designed supramolecular iridium catalysts displaying remote weak coordination bonds between zinc-porphyrins and substrates containing electron lone pairs from nitrogen or oxygen (Zn…N or Zn…O=C).[3,4] Such supramolecular iridium catalysts enabled C-H borylation of pyridine derivatives and carbonyl-containing benzene substrates at a precise four-chemical bond distance from the molecular recognition site.[5,6] In order to expand such approach to systems compatible with first-row transition metals, we present herein a strategy that leads to zinc-porphyrins comprising mesoionic NHC carbenes (**MIC**). NHC carbenes are known coordinating units to first-row transition metal ions, such as copper, and their catalytic behavior has been documented although with limited success for nitrogen substrates due to the poisoning effect (over-coordination) of the nitrogen lone pair towards the metal active species.[7] Herein, we will present the synthesis and preliminary coordination chemistry studies as well as initial catalytic tests for new bond-forming processes.



This work was supported by ANR, CNRS and University of Rennes.

References

1. G. Olivo, G. Capocasa, D. Del Giudice, O. Lanzalunga, S. Di Stefano, *Chem. Soc. Rev,* **2021**, *50*, 7681-7724.
2. J. Trouvé, R. Gramage-Doria, *Chem. Soc. Rev*, **2021**, *50*, 3565-3584.
3. J. Trouvé, P. Zardi, S. Al-Shehimy, T. Roisnel, R. Gramage-Doria, *Angew. Chem. Int. Ed*. **2021**, *60*, 18006-18013.
4. J. Trouvé, V. Delahaye, M. Tomasini, P. Rajeshwaran, T. Roisnel, A. Poater, R. Gramage-Doria, *Chem. Sci*. **2024**, *15*, 11794-11806.
5. J. Trouvé, P. Rajeshwaran, M. Tomasini, A. Perennes, R. Roisnel, A. Poater, R. Gramage-Doria, *ACS Catal*. **2023**, *13*, 7715-7729.
6. M. Tomasini, L. Caporaso, J. Trouvé, J. Poater, R. Gramage-Doria, A. Poater, *Chem. Eur. J*. **2022**, *28*, e202201970.
7. Q. Zhao, G. Meng, S. P. Nolan, M. Szostak, *Chem. Rev.* **2020**, *120*, 1981-2048.

Urea Functionalized Second Coordination Sphere on Iron Porphyrin Catalyst for CO_2 Reduction Under Aprotic and Protic Conditions

Ashutosh Vishwakarma[1], Philipp Gotico[2], Zakaria Halime[1]

[1]*Institut de Chimie Moléculaire et des Matériaux d'Orsay, Université Paris Saclay, Orsay, France;*
[2]*Institut de Biologie Intégrative de la Cellule, CEA Saclay, Gif-sur-Yvette, France;*
ashutosh.vishwakarma@uinverite-paris-saclay.fr

Global warming driven by rising CO_2 emissions has prompted intense research into efficient, cost-effective catalysts for CO_2 capture and reduction. While geological CO_2 storage offers a temporary solution, its long-term stability and cost remain uncertain. A more sustainable strategy involves converting CO_2 into energy-rich compounds or C1 building blocks for organic synthesis, forming a closed carbon cycle. The goal is to use solar energy to power the electrocatalytic transformation of CO_2 into fuels, mimicking natural photosynthesis where metalloenzymes convert CO_2 and water into hydrocarbons. Effective catalysts must activate CO_2 and promote its reduction through proton-coupled multi-electron steps, avoiding high-energy intermediates. Current research focuses on molecular catalysts, particularly metal complexes both noble (Ru, Rh, Pd, Re, Ir) and earth-abundant first-row transition metals (Mn, Fe, Co, Ni, Cu) coordinated with nitrogen-based ligands. Iron porphyrins have emerged as especially promising electrocatalysts for CO_2 reduction to CO, showing high efficiency and selectivity.

In this poster, we have developed a new iron-porphyrin catalyst featuring four urea groups in the second coordination sphere, with an $\alpha_2\beta_2$ geometry where the two adjacent groups are positioned adjacently on one side with respect to the porphyrin plane and two other groups in the opposite side (Figure 1). We have found that this specific spatial arrangement enables efficient CO_2 reduction even in the absence of an external proton source. The catalyst exhibits a significantly higher turnover frequency compared to its *αβαβ* atropisomer where the urea groups are positioned alternately on the porphyrin plane[1]. This difference highlights the critical role of symmetry in modulating reactivity. Moreover, a pronounced kinetic isotope effect (KIE) suggests that protonation is the rate-determining step in the reaction mechanism. These findings emphasize how strategic placement of hydrogen-bond donors in the second coordination sphere can enhance CO_2 activation and reduction, offering valuable insights into the design of next-generation catalysts for sustainable carbon conversion.

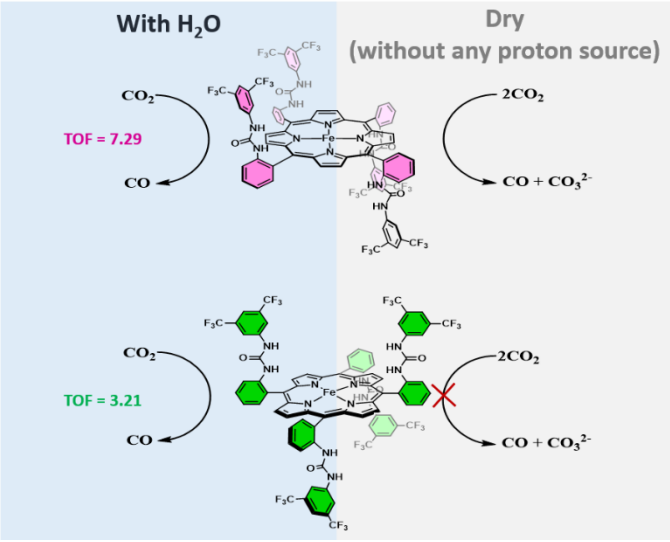


Figure 1. Electrocatalytic CO_2 reduction to CO by iron porphyrin catalysts ($\alpha_2\beta_2$ in pink *and αβαβ* in green) in absence and presence of an external proton source.

References

1. P. Gotico, B. Boitrel, R. Guillot, M. Sircoglou, A. Quaranta, Z. Halime, W. Leibl, A. Aukauloo, *Angew. Chem. Int. Ed*. **2019**, *58*, 4504

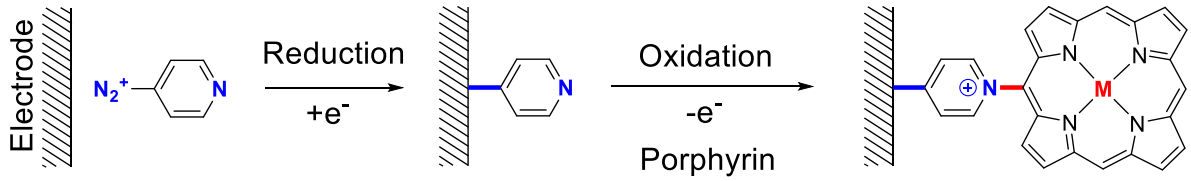
Synthesis of Porphyrin Material via Oxidative C-N Coupling of Porphyrin with Pyridinyl Functionalized Electrodes

Fatima Akhssas,[1] Moad Bouzid,[1] Abhishek Kumar,[1] Anna Krystianiak,[2] Eric Lesniewska,[2] Régis Parvaud,[2] Olivier Heintz,[2] Rita Meunier-Prest,[1] Charles H. Devillers[1*]

[1] Institut de Chimie Moléculaire de l'Université de Bourgogne UMR6302, CNRS, Université Bourgogne Europe, 9 avenue Alain Savary, 21000 Dijon, France. [2] Laboratoire Interdisciplinaire Carnot de Bourgogne UMR5209, CNRS, Université Bourgogne Europe, 9 avenue Alain Savary, 21000 Dijon, France.
E-mail: charles.devillers@ube.fr

Immobilization of functional molecules on an electrode surface is a crucial step towards the development of functional devices. Among these molecules, porphyrins exhibit unique physico-chemical properties. These molecules have been exploited for many applications in various research fields such as electrocatalysis,[1] photoluminescent biosensors[2] nonlinear and optical limiting devices.[3] Several approaches have been developed to graft the porphyrin moiety by post-functionalization of modified substrate. The coupling method can be performed *via* the formation of different chemical bonds: amide,[4] ester,[5] coordination[6] or using Huisgen cycloaddition reaction.[7]

We will show during this presentation that it is possible to immobilize a porphyrin *via* its oxidation on a pyridinyl-functionalized working electrode surface.[8] UV-vis. spectroscopy, cyclic voltammetry, XPS, SEM, AFM and TOF-sims analyses have been performed to confirm the chemical composition of the porphyrin material.



This work was supported by Région Bourgogne Franche Comté, Université de Bourgogne Europe and CNRS

References

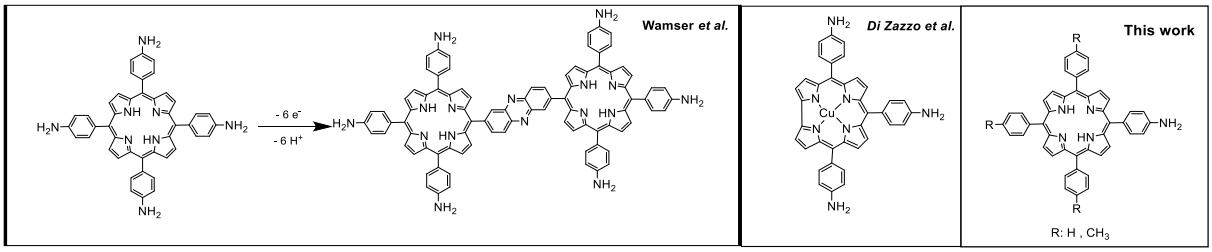
1. Marianov, A. N.; Jiang, Y. *ACS Sustain. Chem. Eng*. **2019**, 7 (4), 3838–3848.
2. Khairutdinov, R. F.; Serpone, N. *J. Phys. Chem.* **1995**, 99 (31), 11952–11958.
3. Wang, A.; Yu, W.; Huang, Z.; Zhou, F.; Song, J.; Song, Y.; Long, L.; Cifuentes, M. P.; Humphrey, M. G.; Zhang, L.; Shao, J.; Zhang, C. *Sci. Rep.* **2016**, 6 (1), 23325.
4. Rocklin, R. D.; Murray, R. W. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, 100 (1), 271–282.
5. Baskaran, D.; Mays, J. W.; Zhang, X. P.; Bratcher, M. S. *J. Am. Chem. Soc.* **2005**, 127 (19), 6916–6917.
6. Zuo, G.; Yuan, H.; Yang, J.; Zuo, R.; Lu, X. *J. Mol. Catal. Chem.* **2007**, 269 (1), 46–52.
7. Mennel, J. A.; Pan, H.; Palladino, S. W.; Barile, C. J. *J. Phys. Chem. C* **2020**, 124 (36), 19716–19724.
8. Akhssas, F.; Bouzid, M.; Kumar, A.; Krystianiak, A.; Heintz, O.; Lesniewska, E., Parvaud, R., Meunier-Prest, R.; Devillers, C. H., *manuscript in preparation*.

Electrochemical Oxidation of *Meso*-substituted Mono-aminophenylporphyrins

Fatima AWADA, Marcel BOUVET, Charles H. DEVILLERS*

Institut de Chimie Moléculaire de l'Université de Bourgogne, UMR CNRS 6302, Université Bourgogne Europe, 9 avenue Alain Savary, BP 47870, 21078 DIJON Cedex, FRANCE
E-mail : fatima.awada@u-bourgogne.fr

In the material research field, electrochemistry is a powerful method to finely tuned the material thickness and properties thanks to the control of the potential or the current. For example, electropolymerized porphyrin films have been exploited for applications in electrocatalysis, fuel cell cathodes, and photovoltaic devices.[1] A variety of metallo and free base *meso*-substituted aminophenylporphyrins containing ortho, meta-, and para-substituted amino groups have been reported to electropolymerize under a wide range of conditions using both organic and aqueous electrolyte solutions.[1,2,3] Wamser *et al.*[1] reported the electropolymerization of variously substituted aminophenylporphyrins including the tetrakis-5,10,15,20-(4-aminophenyl)-porphyrin (TAPP). According to the authors and FT-IR analyses, upon oxidation of the TAPP, phenazine bridges were formed between the porphyrin units (Scheme 1, left). In addition, Di Zazzo *et al.*[4] reported the oxidative electropolymerization of [5,10,15-(4-aminophenyl)corrolato]copper(III) (Scheme 1, middle). This led to the *in-situ* synthesis of polycorroles conductive materials whose structure was proposed to include phenazine bridges between the corrole units. As the phenazine bridge was systematically proposed to be the spacer unit between the porphyrins or corroles, we embarked in the synthesis of porphyrins bearing only one aniline unit, with the aim to definitively prove the formation of the phenazine bridge by common solution analytical methods. Thus, our work has first consisted in the synthesis of 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin and 5-(*p*-aminophenyl)-10,15,20-tri(*p*-tolyl) porphyrin (Scheme 1, right). Their oxidation was then performed to verify the formation of the phenazine bridged porphyrin dimer. We will show in this presentation that no phenazine has been obtained and original porphyrin products were formed instead.



***Scheme 2**: Electropolymerization of meso-substituted aminophenylporphyrins/corroles*

This work was supported by ANR Porph4Sens (ANR-22-CE06-0039-01), Université Bourgogne Europe and CNRS

References

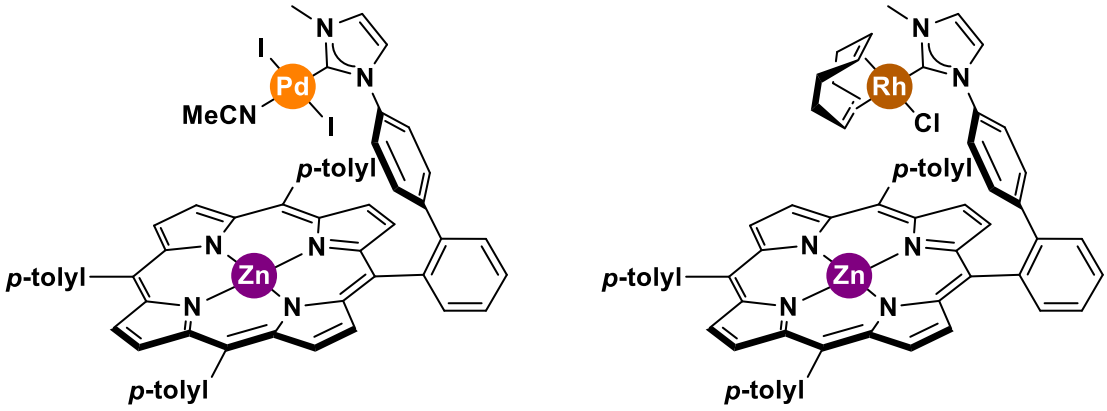
1. M.G. Walter, C. Wamser, *J. Phys. Chem. C* **2010**, *114* (17), 7563–7574.
2. G. Cornejo, G. Ramirez, M. Villagran, *Chem. Soc.* **2003**, *48*, 49–55.
3. S. Chen, Y. Chen, R.J.Thangamuthu, *Solid State Electrochem*. **2007**, *11*, 1441–1448.
4. L. Di Zazzo, A. Kumar, R. Meunier-Prest, *Chem. Eng. J.* **2023**, *458*, 141465.

Synthesis and characterization of N-heterocyclic carbene metal complexes linked to porphyrins

Dimitri Dessaint, Sébastien Clément, Michel Granier, Sébastien Richeter

University of Montpellier, CNRS, Institut Charles Gerhardt Montpellier, 1919 route de Mende, 34293 Montpellier, France
E-mail: dimitri.dessaint@umontpellier.fr

N-heterocyclic carbenes (NHCs) are ubiquitous ligands in organometallic chemistry and catalysis.[1] Knowing that natural metalloenzymes fix and organize substrates around their active sites via reversible, dynamic interactions in their second coordination spheres, we plan to incorporate this biologically relevant feature into NHCs to achieve unprecedented catalysis.[2] To this end, we introduced a zinc(II) porphyrin into the second coordination sphere of NHC-metal complexes, hoping that substrates bearing lone electron pairs would bind to the zinc(II) ion via coordination bonds formed in the vicinity of the catalytic active site.[3] We intend to perform difficult or novel reactions with these complexes. Here, we present the synthesis and characterization of novel Pd/Zn and Rh/Zn bimetallic complexes, where the peripheral catalytic sites are NHC-PdI_2(N≡C-CH_3) and NHC-RhCl(cod) (cod = 1,5-cycloocta-diene), respectively. We present also the preliminary results about the coordination of pyridine as a representative substrate onto zinc(II) porphyrins.



This project is supported by the ANR (project number: ANR-23-CE07-0020).

References

1. S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612-3676.
2. M. Raynal, P. Ballester, A. Vidal-Ferran, P. W. N. M. van Leeuwen, *Chem. Soc. Rev.* **2014**, *43*, 1660-1733 ; M. Raynal, P. Ballester, A. Vidal-Ferran, P. W. N. M. van Leeuwen, *Chem. Soc. Rev.* **2014**, *43*, 1734-1787.
3. L. Poyac, S. Scoditti, X. Dumail, M. Granier, S. Clément, R. Gramage-Doria, C. H. Devillers, S. Richeter, *Chem. Commun.* **2022**, *58*, 13270-1272.

Design of new peptide vectors for photodynamic therapy of pancreatic cancer

Souleymane SARR*[1], Céline FROCHOT[2], Samir ACHERAR[1]

[1]Laboratoire de Chimie Physique Macromoléculaire (LCPM), Université de Lorraine, ENSIC,1 rue Grandville, BP 20451, 54000 Nancy, France
[2]Laboratoire Réactions et Génie des Procédés (LRGP), Université de Lorraine, ENSIC,1 rue Grandville, BP 20451, 54000 Nancy, France
souleymane.sarr@uninv-lorraine.fr

Pancreatic cancer (PDAC) remains one of the most aggressive and least treatable cancers, with patient survival rates virtually unchanged for the past 50 years. Surgery is currently the only potentially curative treatment option for PDAC. However, it is generally only feasible in cases of early diagnosis. In all other cases, chemotherapy alone or in combination with radiotherapy is recommended as palliative treatment. Despite these therapeutic options, the overall 5-year survival rate (OS) is only 11% (INCa 2023). Photodynamic therapy (PDT) is emerging as a promising approach to specifically target tumor cells while limiting side effects. PDT combines a photoactibale molecule called photosensitizer, light and oxygen. Upon light excitation, the photosensitizer transfers electrons to biomolecules or energy to oxygen to form reactive oxygen species that destroy cancer cells. To better target receptors overexpressed in pancreatic cancers, we are developing third generation photosensitizers with new peptide vectors specifically designed to target receptors overexpressed in PDAC (**Figure 1**). Two targets have been selected: MUC1, a transmembrane mucin involved in tumor progression and highly expressed in pancreatic cancers and uPAR, a receptor involved in invasion and metastasis, also overexpressed in PDAC. Based on the crystallographic structure of the interaction between uPA and uPAR[1], as well as a set of peptide ligands described in the literature, we have designed new peptide vectors with promising affinity. We will present the synthesis, affinity for uPAR and MUC1 receptors of these peptides, as well as the first photosensitizers coupled to the peptides.”).

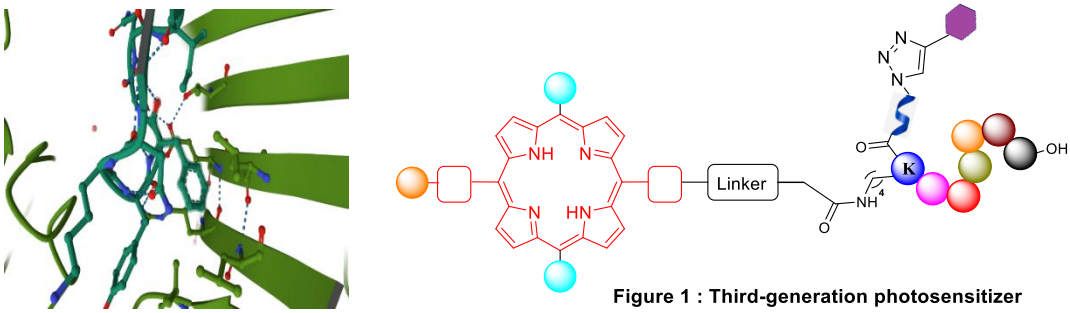


Figure 1 : Third-generation photosensitizer

Acknowledgements*: This work was supported by a French government grant managed by the Agence Nationale de la Recherche under the France 2030 program, reference ANR-23-EXLU-0002 (PEPR LUMA)*

References

1. Barinka C, Parry G, Callahan J. Mol. Biol, 2006, 363, 482–495

Participants

List of participants

AMIRI	Nesrine	Université Bourgogne Europe	Dijon
ANXOLABEHERE	Elodie	Sorbonne Université	Paris
AWADA	Fatima	Université Bourgogne Europe	Dijon
BOITREL	Bernard	Institut des Sciences Chimiques de Rennes	Rennes
CANARD	Gabriel	CINAM, Aix-Marseille Univ.	Marseille
CLEMENT	Sébastien	Institut Charles Gerhardt Montpellier	Montpellier
COLOMBAN	Cédric	Institut des Sciences Moléculaires	Marseille
DESSAINT	Dimitri	Université de Montpellier	Montpellier
DEVILLERS	Charles	Université Bourgogne Europe	Dijon
DURAND	Jean-Olivier	Institut Charles Gerhardt Montpellier	Montpellier
DUROT	Stéphanie	Institut de Chimie de Strasbourg	Strasbourg
EISENBETH	Axel	Institut de Chimie de Strasbourg	Strasbourg
EL-BEAINE	Emma	Sorbonne Université	Paris
GOTICO	Philipp	CEA Centre de Saclay	Saclay
GROS	Claude P.	Université Bourgogne Europe	Dijon
HAYASHI	Takashi	University of Osaka	Osaka, Japon
LIU	Fangbing	Univ. Claude Bernard Lyon 1	Lyon
MOINARD	Romane	Université de Lorraine	Nancy
PFEIFFER	Louise	Institut de Chimie de Strasbourg	Strasbourg
RIBAS	Xavi	Universitat de Girona	Girona, Espagne
RICHETER	Sébastien	Institut Charles Gerhardt Montpellier	Montpellier
SARR	Souleymane	Université de Lorraine	Nancy
SOL	Vincent	LABCiS, Univ. de Limoges	Limoges
TRAVERS	Elisa	Université de Rennes	Rennes
VISHWAKARMA	Ashutosh	Université Paris Saclay	Gif sur Yvettte
WEISS	Jean	Institut de Chimie de Strasbourg	Strasbourg
WYTKO	Jennifer	Institut de Chimie de Strasbourg	Strasbourg

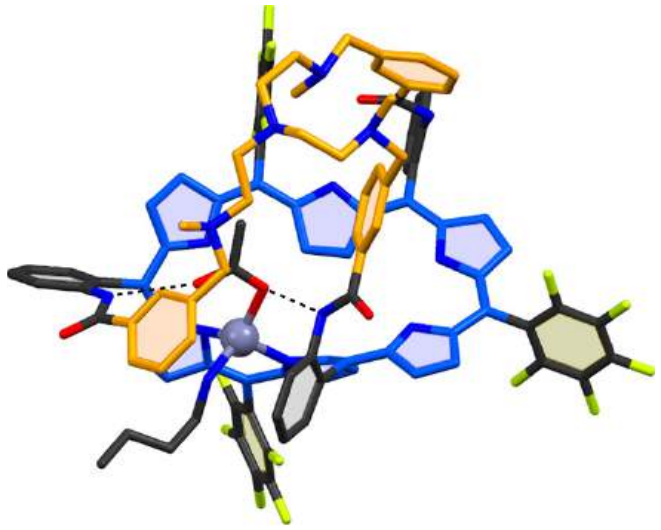
GDR MAPYRO
Macrocycles pyrroliques

75 chercheuses et chercheurs impliqués au sein de **23** laboratoires

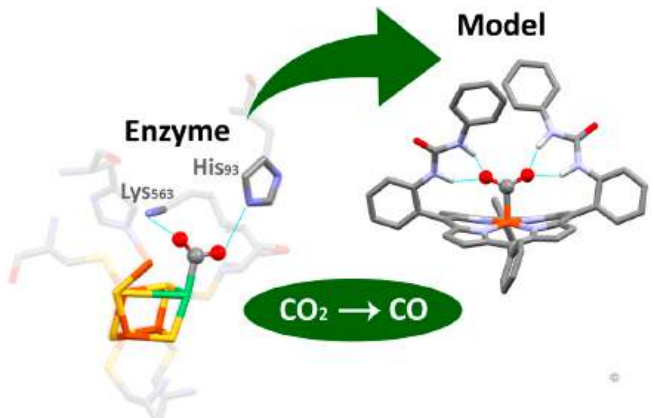
OBJECTIFS

La mission du GDR MAPYRO est de fédérer les différents groupes français impliqués dans la chimie des macrocycles polypyrroliques comprenant des spécialités très variées telles que la synthèse organique, la chimie de coordination, la chimie supramoléculaire, la catalyse homogène et hétérogène, l'activation de petites molécules, l'électro et la photoactivation.

Le GDR permet un échange régulier des connaissances, apporte des solutions à des problématiques précises via des collaborations au cours desquelles des chercheurs peuvent se déplacer dans un laboratoire du groupement pour être formés à des techniques et/ou pratiques nouvelles.



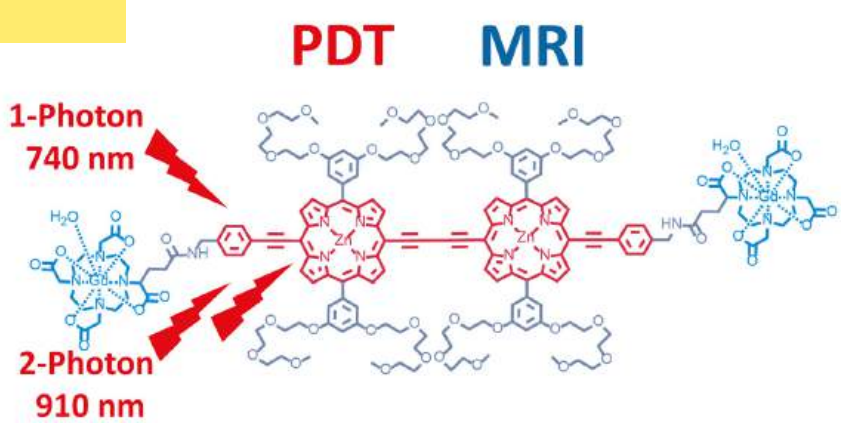
Hexaphyrine chapeautée : métallorécepteur chiral et Möbius-aromatique.
© Stéphane Le Gac, CNRS/Université de Rennes



Réduction biomimétique du CO_2
© Zakaria Halime, CNRS/Université Paris-Saclay

THÉMATIQUES

- Catalyseurs biomimétiques et activation de petites molécules
- Chimie supramoléculaire des assemblages porphyriniques
- Les macrocycles pyrroliques en chimie thérapeutique



Bis-porphyrine fonctionnalisée : agent thérapeutique bimodal.
© Sébastien Jenni, Université de Strasbourg

PROSPECTIVES

Les porphyrines et leurs dérivés sont impliqués dans des processus essentiels des mondes animal et végétal. Pour ces raisons, la porphyrine est souvent appelée "molécule de la vie". D'ailleurs, l'étude approfondie de l'implication de ces macrocycles dans les phénomènes biologiques indispensables à la vie sur Terre a rapidement attiré l'attention des chimistes, générant une communauté des polypyrroles cycliques large et variée que MAPYRO a pour but d'animer.

En structurant les différentes équipes partenaires au niveau national et en renforçant les liens de nombreuses d'entre elles à l'international, le défi de MAPYRO est de tirer parti des macrocycles pyrroliques pour trouver de nouvelles solutions dans trois axes de recherche majeurs et d'impact sociétal important :

ACTIVATION DE PETITES MOLÉCULES ET CATALYSEURS BIOMIMÉTIQUES

Parmi les réactions emblématiques concernées, priment la réduction du dioxygène, la réduction du dioxyde de carbone et l'oxydation des substrats organiques par transfert d'atomes d'oxygène ou d'azote. L'étude des mécanismes catalytiques, la caractérisation des intermédiaires réactionnels ainsi que la conception de modèles optimisés mobilisent une force importante dans ce GDR.

CHIMIE SUPRAMOLÉCULAIRE DES ASSEMBLAGES PORPHYRINIQUES

Il est possible de concevoir et d'étudier de nouveaux assemblages élaborés à partir de polypyrroles cycliques et présentant des propriétés spécifiques (optiques, électrochimiques, photochimiques...).
Les propriétés associées aux assemblages supramoléculaires porphyriniques ouvrent de nombreuses perspectives pour la transmission et le stockage de l'information grâce à la commutation des systèmes, le développement des matériaux auto-réparants, le transport et la restitution de molécules thérapeutiques. Qui plus est, la chimie de coordination de nouveaux macrocycles (isomériques, contractés, étendus...) reste entièrement à découvrir, à comprendre et à maîtriser.

LES MACROCYCLES PYRROLIQUES EN CHIMIE THÉRAPEUTIQUE

Depuis longtemps, les macrocycles pyrroliques, de par leur tropisme pour les cellules cancéreuses, leur capacité à coordiner des cations, leur stabilité et leurs propriétés de photosensibilisateurs, sont des acteurs crédibles dans différents domaines thérapeutiques majeurs tels que la lutte anticancéreuse, antimicrobienne... Ainsi, au niveau national, plusieurs groupes sont actifs pour la conception et l'élaboration de nouveaux macrocycles pyrroliques dans les domaines de la photothérapie, de la radio-immunothérapie, mais aussi de l'imagerie et de la théranostique.

CONTACTS

Directeur
Claude Gros (ICMUB, Dijon)
claude.gros@u-bourgogne.fr

Directrice adjointe
Stéphanie Durot (LSAMM, Strasbourg)
sdurot@unistra.fr

Directeur adjoint
Zakaria Halime (ICMMO, Saclay)
zakaria.halime@universite-paris-saclay.fr

https://mapyro.chimie.unistra.fr

GDR Groupement de recherche
MAPYRO Macrocycles pyrroliques