8th EuCheMS Conference on Nitrogen Ligands

Program & Book of Abstracts

3 – 7 June 2024
Cassis, France

FOREWORD

On behalf of the Organizing Committee, it is our great pleasure to welcome you to the **8th EuCheMS Conference on Nitrogen Ligands** taking place in Cassis (France) from Monday 3rd to Friday 7th June 2024. The conference aims to bring together scientists, academic and industrial attendees from around the globe to provide all aspects of the role of nitrogen ligands, following the spirit and style of the seventh preceding conferences during its 32-year-long history.

The book contains the abstracts of the 5 plenary lectures, 9 keynotes, 7 invited, 41 oral contributions and 58 posters presented at the 8th EuCheMS Conference on Nitrogen Ligands.

Cassis was chosen by the international committee to host this event taking place in France. Cassis is a small seaside resort snuggled between two exceptional natural sites (the famous Massif des Calanques and the majestic Cap Canaille) offering its visitors a concentrate of Provence and the Mediterranean Sea.

We hope you will enjoy the scientific program and the beautiful place of Cassis. We wish you every success for your contributions.

Olivier Siri (Chair) and Aura Tintaru (Co-chair)

https://www.cinam.univ-mrs.fr/site/NLigands2024/

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History of the International Conference on Nitrogen Ligands

1992: Symposium on Nitrogen Ligands
Location: Alghero (Italy)
Organizer: Giovanni Minghetti (University of Sassari)

1996: Symposium on Nitrogen Ligands
Location: Como (Italy)
Organizer: Girolamo La Monica (University of Insubria)
and Sergio Cenini (University of Milano)

2004: 3rd International Conference on Nitrogen Ligands
Location: Camerino (Italy)
Organizer: Claudio Pettinari (University of Camerino)

2008: 4th International Conference on Nitrogen Ligands
Location: Garmisch Partenkirchen (Germany)
Organizer: Bernard Lippert (University of Dortmund)

2011: 5th International Conference on Nitrogen Ligands
Location: Granada (Spain)
Organizer: Jorge Navarro (University Grenada)

2015: 6th International Conference on Nitrogen Ligands
Location: Beaune (France)
Organizer: Claude Gros (University Burgundy)

2018: 7th International Conference on Nitrogen Ligands
Location: Lisbon (Portugal)
Organizer: Armando Pombeiro (University Lisbon)

SPECIAL ISSUE OF DALTON TRANSACTIONS

We are pleased to announce that a special issue of Dalton Transactions will be produced in conjunction with the N-ligands'2024 conference. Prof. Gabriel Canard and Dr. Olivier Siri are assigned as the guest editors of this special issue.

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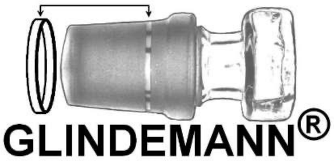

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PTFE ("TEFLON") Sealing Ring for hermetic greaseless Glass Joints

There is a prejudice that PTFE (often called "Teflon") is too inelastic to be a hermetic sealant for greaseless conical joints. Therefore, teaching books [1,2] recommend threaded or flanged "O-ring joints" for hermetic manipulation of air- and moisture sensitive chemicals if joint grease is no option.

Here we show [3] (Figure 1) that the common ground conical glass joint can be sealed relatively hermetic and at low cost with a narrow flat PTFE sealing ring (less than 1 mm wide and 0.1 mm thick, weight only 5 mg PTFE).

The sealing ring is high-vacuum tight (air leakage rate 10-8… 10-6 mBar*Liter/sec), solvent tight (loss of ethyl acetate out of containers < 0.1 mg/day) and resistant to fluctuation of temperature (freezing-thawing-heating cycles). The reusable PTFE sealing ring prevents stuck joints, is thin enough to be used with all joint clamps and is fixed elastically (without groove) on the glass joint. We demonstrate also a new all-glass-syringe ((Figure 1, 1 - 100 mL) that is gastight at fluctuating temperatures (freezing-thawing-cycles) by a similar exchangeable sealing ring (PTFE) in a groove of the glass piston [4].

Figure 1. Figure caption. Left: PTFE-sealing ring fixed elastic (no groove necessary). Middle: Sealing ring intransparent without pressure. Right: Sealing ring transparent under sealing pressure. Far right: A similar PTFE ring and a piston groove make an all-glass-syringe gastight.

[1] Manipulation of Air-Sensitive Compounds. D. F. Shriver, M. A. Drezdzon, Wiley, 1986; pp. 153-159.
[2] Advanced Practical Inorganic and Metalorganic Chemistry. R. J. Errington, Blackie; 1997, pp. 37-39.
[3] D. Glindemann, U. Glindemann, Fusion (American Society of Glass Blowers) 48 (2001) 29.
[4] D. Glindemann, All-glass syringe. Utility patent, DE 20 2006 020 555.1 (2009.03.05.).

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PROGRAM

Monday 3 June 2024

16:45 Welcome

17:10 – 18:45 Session 1 – Chair: Armando POMBEIRO

17:10 PL1 Makoto FUJITA (University of Tokyo, Japan)
Molecular Confinement Effects in Self-assembled Cages

17:55 KN1 Sonja HERRES-PAWLIS (Aachen University, Germany)
Manipulating the entatic state by biomimetic guanidine copper complexes

18:25 IL1 Mark GANDELMAN (Israel Institute of Technology)
Nitrenium Ions: Platform for Cationic N-Ligands, Reagents and Catalysts

19:00 - 22:00 Welcome Cocktail (*Ousteau-Calendal* congress center, Cassis).

Tuesday 4 June 2024

8:30 – 10:30 Session 2 – Chair: Claudio PETTINARI

8:30 PL2 Angela CASINI (University of Munich)
Expanding the Imaging Toolbox with Metal-based Molecules Featuring N-ligands

9:15 KN2 Alceo MACCHIONI (University of Perugia, Italy)
Organometallic Biomimetic Catalysts for Energy Applications

9:45 OC1 Arkadi VIGALOK (Tel Aviv University, Israel)
Selective Reductive Elimination of Polar Bonds: from Mechanistic Studies to Protein Bioconjugation

10:00 OC2 Cédric COLOMBAN (Aix Marseille University, France)
Unusual O_2 Activation at Bioinspired Caged Copper(I) Complexes

10:15 OC3 Fabio RAGAINI (Università degli Studi di Milano, Italy)
A New Type of Trimeric Formally Zerovalent Palladium Complexes only Supported by Nitrogen Ligands

10:30 – 11:00 Coffee Break

11:00 – 12:35 Session 3 – Chair: Stéphane BELLEMIN-LAPONNAZ

11:00 OC4 Grzegorz HRECZYCHO (Adam Mickiewicz University, Poland)
Cobalt complexes with PN5P ligands as catalysts in the synthesis of Si, B, and Ge compounds

11:15 OC5 Stéphane LE GAC (University of Rennes, France)
Parallel Chirality Inductions in Möbius Zn(II) Hexaphyrin Transformation Networks

11:30 IL2 Macarena POYATOS (University of Jaume, Spain)
Tuning the Catalytic Activity of Pincer Complexes of Rhodium (I) by Supramolecular and Redox Stimuli

11:50 OC6 Gilles LEMERCIER (University of Paris Cité and University of Reims, France)
Photophysical properties of 1,10-phenanthroline derivatives and related Ru(II) (nano-)edifices

12:05 OC7 Piotr PAWLUC (Adam Mickiewicz University, Poland)
Cobalt(II) complexes with Schiff base-type 3N-donor ligands as catalyst precursors for alkyne hydrosilylation and hydroboration

12:20 OC8 Zakaria HALIME (University of Paris-Saclay, France)
Ligand Modification Shifts CO_2 to CO Reduction by Iron Porphyrin from Fe(0) to Fe(I)

12:35 – 14:00 Lunch

14:00 – 16:05 Session 4 – Chair: Angela CASINI

14:00 KN3 Violetta PATRONIAK (Adam Mickiewicz University, Poland)
New Multifunctional Complexes of d- and f-Metal Ions with N-Donor Ligands

14:30 OC9 Alexander SOROKIN (University of Claude Bernard Lyon 1, France)
N-Bridged Diiron Phthalocyanine: Particularly Nitrogen-Rich Scaffold for Challenging Catalysis

14:45 OC10 Cristina PERONA (University of Granada, Spain)
Zirconium metal-organic polyhedra assemblies incorporating nitrogen-ligands as systems for energy and environmental applications

15:00 OC11 Olivier CHUZEL (Aix Marseille University, France)
Efficient and Selective Anion Capture Using Self-Assembled Boronium Macrocycles

15:15 OC12 Alborz BAVANDSAVADKOUHI (Université du Québec à Trois-Rivières, Canada)
Novel Benzene- and Triphenylene-based Ligands for Coordination Chemistry

15:30 OC13 Arno ESTIVAL (Laboratoire de Chimie de Coordination, CNRS, Toulouse)
Design and synthesis of new heptacoordinated molybdenum complexes supported by NNN pincer ligand

15:45 Sponsor 1: GLINDEMANN

15:55 Sponsor 2: LNI

16:05 – 16:35 Coffee Break

16:35 – 17:55 Session 5 – Chair: Gabriel CANARD

16:35 IL3 Wen-Hua SUN (Chinese Academy of Sciences, Beijing, China)
Bi-& Tri-dentate N-Ligated Late transition metal precatalysts: New Era of Ethylene Products

16:55 OC14 Charles H. DEVILLERS (Université de Bourgogne, France)
Redox Reactivity of Porphyrins with Imines

17:10 OC15 Nicolai BURZLAFF (Friedrich-Alexander Univ. Erlangen-Nürnberg, Germany)
Broadening the Scope of Bis(pyrazol-1-yl)acetato Ligands

17:25 OC16 Renaud HARDRE (Aix Marseille University, France)
Bioinspired hydrogen production via N-non-innocent ligands

17:40 OC17 Chanjuan XI (Tsinghua University, China)
[NiX2/N-ligand]-Catalyzed Allylation Reaction using Allylic Alcohols in the presence of CO_2

Wednesday 5 June 2024

8:30 – 10:30 Session 6 – Chair : Jens MUELLER

8:30 PL3 Jeanne CRASSOUS (University of Rennes, France)
Nitrogen-Containing Helical Ligands: from Organic Chromophores to Chiral Metallo-Organic Emitters

9:15 KN4 Simona GALLI (University of Insubria, Italy)
Bipyrazolate Metal-Organic Frameworks for Carbon Capture and Pollutants Sequestration

9:45 OC18 Josef HAMACEK (University of Orléans, France)
Supramolecular Lanthanide-Containing Cages: Insight into the Formation Mechanism

10:00 OC19 Fabio MARCHETTI (University of Pisa, Italy)
Dinuclear Iron Complexes with Pyridine Ligands as Promising Anticancer Agents

10:15 OC20 Nicolas DESBOIS (Université de Bourgogne, France)
Antimicrobial properties of porphyrins and corroles functionalized with carboxylic acids

10:30 – 11:00 Coffee Break

11:00 – 12:35 Session 7 – Chair: Aura TINTARU

11:00 KN5 Carole DUBOC (University of Grenoble Alpes, France)
Bio-Inspired Catalyst Design for Small Molecule Activation in Multi-Electron Reduction Processes

11:30 OC21 Jean WEISS (University of Strasbourg, France)
Porphyrins and Schiff Bases Combination: Anything New ?

11:45-12:20 Flash presentations (1-8)

12:20 Sponsor 3: ABCR

12:30 – 14:00 Lunch

14:00 – 16:05 Session 8 – Chair: Simona GALLI

14:00 KN6 Paolo FALCARO (Graz University of Technology, Austria)
Zeolitic Imidazolate Framework-based biocomposites

14:30 OC22 Yann PELLEGRIN (Nantes University, France)
Turning on the excited state properties of a Cu(I)-phenanthroline complex by covalent binding of the ligand inside a silica matrix

14:45 OC23 Charlie McTERNAN (The Francis Crick Institute, London, UK)
Metal-Peptidic Cages–Helical Oligoprolines Generate Highly Anisotropic Nanospaces with Emergent Isomer Control

15:00 OC24 Stéphanie DUROT (University of Strasbourg, France)
Allosteric control of the assembly of [2]rotaxanes thanks to a multi-site bis(Zn(II)-porphyrin) cage

15:15 OC25 Pavel LHOTAK (UCT, Prague, Czech Republic)
Application of meta-Nitrosocalix[4]arenes in Supramolecular Chemistry

15:30 OC26 Mohamed AMEDJKOUH (University of Oslo, Norway)
Enabling a Bioinspired N,N,N- Copper Coordination Motif through Spatial Control in UiO-67: Synthesis and Reactivity

15:45 IL4 Elisabetta IENGO (University of Trieste, Italy)
Metal-Mediated Porphyrin Assemblies based on Pyridyl Ligands

16:05 – 16:35 Coffee Break

16:35 – 18:15 Session 9 – Chair: Anthony KERMAGORET

16:35 IL5 Denis JACQUEMIN (Nantes University, France)
Using ab initio Tools to Predict the Optical Spectra of N-Containing Ligands and Complexes

16:55 OC27 Ewa PACHOLSKA-DUDZIAK (University of Wrocław, Poland)
Two metal ions inside a porphyrin core – activation of metal-metal interactions

17:10 OC28 Jean-Christophe LACROIX (University of Paris Cité, France)
Viologen/cobalt(terpyridine)2 based molecular wires

17:25-18:05 Flash presentations (9-17)

18:05 Sponsor 4: ADVION INTERCHIM

18:10 Sponsor 5: HEIDOLPH

18:15 Poster Session and Beer Session

Thursday 6 June 2024

8:30 – 10:30 Session 10 – Chair: Claude GROS

8:30 PL4 David LEIGH (University of Manchester, UK)
Much Ado about Knotting

9:15 KN7 Abhik GHOSH (The Arctic University of Norway, Norway)
Corroles as a Platform for Exotic Coordination Chemistry: Binuclear, Metal-Metal–Bonded and Sandwich Compounds

9:45 OC29 Sébastien GOEB (University of Angers, France)
Chiral Truxene-Based Self-Assembled Cages: Triple Interlocking and Supramolecular Chirogenesis

10:00 OC30 Karim ABDEL HADY (University of Trieste, Italy)
Pd(II)-catalyzed ethylene/methyl acrylate copolymerization: toward catalyst recycling

10:15 OC31 Alla LEMEUNE (University of Claude Bernard Lyon 1, France)
Phosphonate-substituted N-donor Ligands for Efficient and Sustainable Photocatalysis

10:30 – 11:00 Coffee Break

11:00 – 12:35 Session 11 – Chair: Andrew PHILLIPS

11:00 KN8 **Chemistry Europe Lecture**
Stéphane BELLEMIN LAPONNAZ (Université de Strasbourg, France)
Nonlinear Behaviour and the Limits of Mechanistic Understanding in Asymmetric Catalysis

11:30 IL6 Biprajit SARKAR (University of Stuttgart, Germany)
Metal Complexes of Diamido-and Tetraamido-benzene Ligands: Privileged Compounds in Organometallic Chemistry and Molecular Magnetism

11:50 OC32 Ally AUKAULOO (University of Paris-Saclay, France)
Porphyrins as Programmable Components for Artificial Photosynthesis

12:05 OC33 Werner THIEL (Rheinland-Pfälzische Tech. Univ. Kaiserslautern-Landau, Germany)
Electronic fine-tuning of ruthenium(II) catalysts

12:20 OC34 Véronique PATINEC (University of Brest, France)
New Triazamacrocycle-Based Chelates for Potential Ga^{3+} *Radiopharmaceuticals*

12:35 – 14:00 Lunch

Friday 7 June 2024

8:30 – 10:30 Session 12 – Chair: Jeanne CRASSOUS

8:30 PL5 Armando POMBEIRO (University of Lisboa, Portugal)
Organonitrogen Ligand Complexes in Selected Catalytic Reactions

9:15 KN9 Claude PIGUET (University of Geneva, Switzerland)
Iron Spin Crossover and Nitrogen Ligands: a Tale of Thwarted Love

9:45 OC35 Clémence QUEFFÉLEC (Nantes University, France)
Plasmonic Au-nanocatalysts based on porphyrins for the N-dealkylation of amines

10:00 OC36 Tom J. N. OBEY (University of Edinburgh, UK)
Probing Uranyl Reduction Chemistry with a Tripodal Pyrrole-Imine Ligand

10:15 OC37 Ling PENG (Aix-Marseille University, France)
Self-assembling supramolecular dendrimers bearing N-ligand terminals for biomedical applications

10:30 – 11:00 Coffee Break

11:00 – 12:20 Session 13 – Chair: Carole DUBOC

11:00 OC38 Rafael GRAMAGE-DORIA (University of Rennes, France)
Re-purposing the Reactivity of Metalloporphyrins

11:15 OC39 Ankita JAISWAL (Indian institute of Technology Kanpur, India)
SERS Based bio screening Platform for Selective Detection of β-Amyloid peptide

11:30 IL7 Matthias TAMM (Technische Universität Braunschweig, Germany)
Iron(I) and Cobalt (I) Amido-Imidazolin-2-imine Complexes as Catalysts for H/D Exchange in Hydrosilanes

11:50 OC40 Matteo MAURO (University of Strasbourg, France)
Binuclear Copper(I) Complexes for Near-Infrared Light-Emitting Electrochemical Cells

12:05 OC41 Andrew PHILLIPS (University College Dublin, Ireland)
Highly Stable Coniage Metal α,α-Dimine Catalysis that Incorporates Carbon Dioxide Into Alkyne Frameworks

12:20 **Poster Awards & Closing**

PLENARY LECTURES

PL1 Molecular Confinement Effects in Self-assembled Cages

Makoto Fujita[1,2]

[1] The University of Tokyo; [2] Institute for Molecular Science (IMS)
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Since our first report on a self-assembled coordination cage in 1995,[1] we and others have been developing the molecular confinement effects of the self-assembled cages (Fig. 1). The cavities of our cages are extraordinarily large and are capable of binding neutral guests. A triazine-cored N-ligand (2,4,6-tris(4-pyridlyl)triazine, takes an important role in exhibiting the unique molecular confinement effects of the cages. Through molecular recognition, new properties, reactions, and functions have been created.[2,3] One of the recent topics in the course of our study is protein encapsulation in a self-assembled gigantic cage.[4]

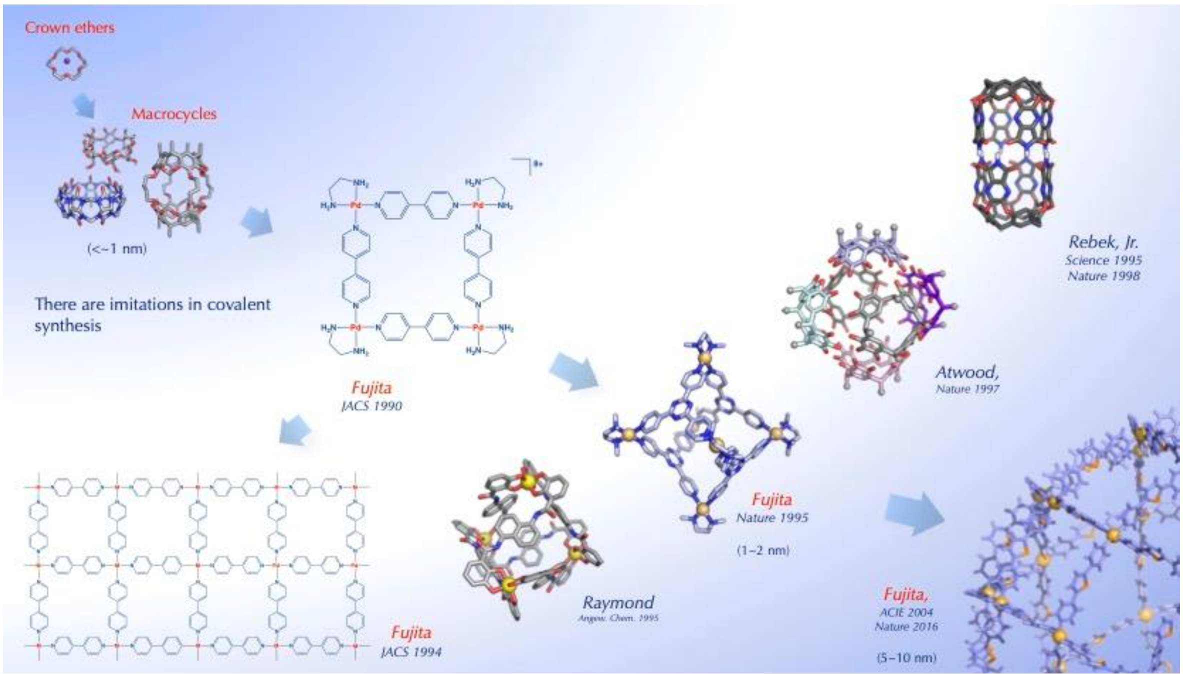

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Figure 1. An overview on the history of chemically defined cavities.

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2. M. Yoshizawa**,** J. K. Klosterman, and M. Fujita, *Angew. Chem. Int . Ed.* **2009**, *48*, 3418-3438.
3. H. Takezawa, M. Fujita*Bull. Chem. Soc. Jpn.* **2021**, *94*, 2351–2369
4. D. Fujita, R. Suzuki, Y. Fujii, M. Yamada, T. Nakama, A. Matsugami, F. Hayashi, J.-K. Weng, M. Yagi-Utsumi, M. Fujita, *Chem* **2021**, *7*, 2672–2683.

PL2 Expanding the Imaging Toolbox with Metal-based Molecules Featuring N-ligands

Angela Casini

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Complexes of metals with N-ligands are a highly important class of compounds in chemistry, biochemistry, medicinal chemistry and material science. In this lecture, I will showcase their role in the design of metal-based molecules for applications in biomedical imaging. Specifically, the case of ruthenium-based ‘mass-tags’ for mass spectrometry imaging (MSI) will be presented, as well as the application of pyridyl ligands for the self-assembly of supramolecular coordination complexes (SCCs) as targeted imaging and therapeutic agents.

In the first case, the use of metal compounds as chemical tools to enhance resolution in mass spectrometry imaging techniques includes the synthesis and bio-conjugation of photoactivable transition metal complexes to peptides/antibodies to implement MSI in complex biological samples (e.g. cancer tissues).[1] Recently, we have developed a Ru(II)-based probe, consisting of a cyclic peptide (binding motif) bound to a polypyridine-Ru(II) complex (reporter group) via a photosensitive D-biotin, to image $\alpha_v\beta_3$ integrins in hypopharynx tumour tissue from a human patient with head and neck cancer by LDI-MSI.[2]

On the other hand, the biomedical application of discrete SCCs, specifically self-assembled 3D-metallacages, is an emergent field of study.[3] In this context, I aim at summarizing the key concepts and challenges in this fascinating research area, starting with the main synthetic and design principles and illustrating representative examples from our group. Thus, the case of “lantern-shaped” cationic $[M_2L_4]^{4+}$ cages ($M = Pd^{2+}$, Pt^{2+}, L = bitopic monodentate N-donor ligand) will be presented, as well as their use either as targeted drug delivery systems or as new *theranostic* agents.[4,5]

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5 Deiser, S.; Drexler, M.; Moreno-Alcántar, G.; ...Günther, T.; Casini, A.. *Inorg. Chem.* **2023**, 62, 20710-20720.

PL3 Nitrogen-Containing Helical Ligands: from Organic Chromophores to Chiral Metallo-Organic Emitters

Jeanne Crassous

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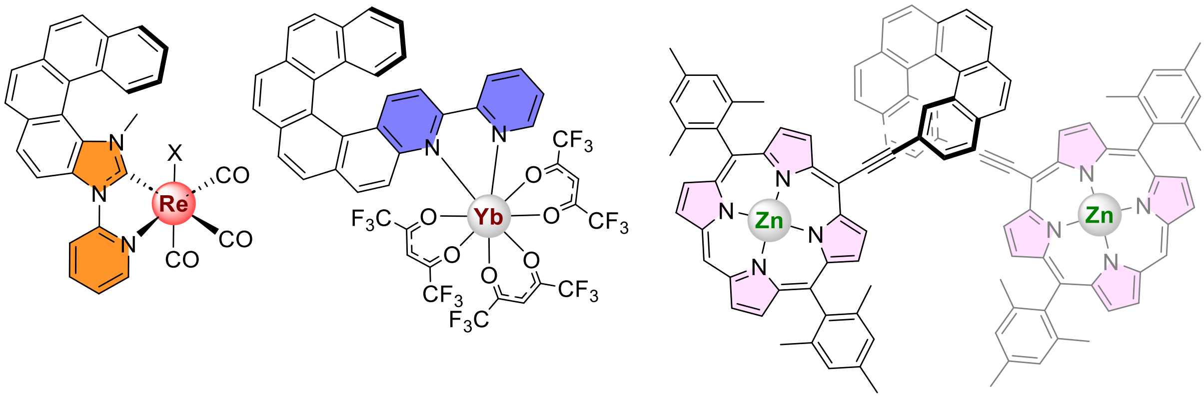
Ortho-fused aromatic rings form helically shaped chiral molecules named helicenes that wind in a left-handed (*M*) or a right-handed (*P*) sense.[1] The helical topology combined with extended π-conjugation provides helicenes with appealing properties such as strong photophysical and chiroptical properties (high optical rotation values, intense electronic circular dichroism and circularly polarized emission). Introducing nitrogen atoms into these helical architectures enables not only to generate a diversity of chemical organic structures and create original chiral chromophores with optimized properties but also to have access to efficient ligands for coordination to a diversity of metallic ions. I will present a set of representative examples, like helicenes containing NHC-pyridine, bipyridine, or porphyrine ligands.[2] Their combination with metallic units leads to chiral molecular materials with appealing properties (circularly polarized phosphorescence, magnetochirality, spin selectivity) for applications in materials science (Chiroptoelectronics, Spintronics).



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PL4 Much Ado about Knotting

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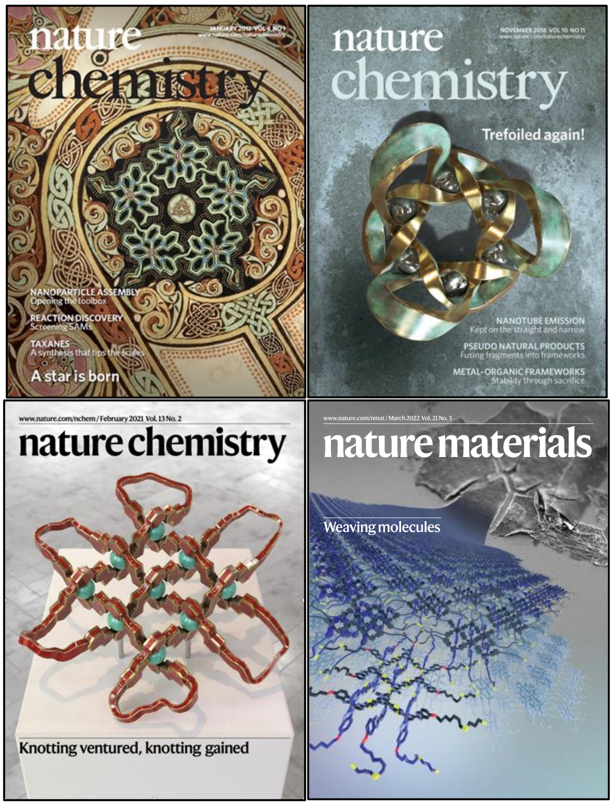
Knots are important structural features in DNA and some proteins, and play a significant role in the physical properties of both natural and synthetic polymers.[1] Although billions of prime knots are known to mathematics, few have been realized through chemical synthesis.[2] Here we will discuss the latest progress from our laboratory, including the synthesis of some of the most complex molecular knots and links (catenanes) to date[3-8] and the introduction of 2D molecular weaving[9].



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PL5 Organonitrogen Ligand Complexes in Selected Catalytic Reactions

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Nitrogen ligands can be of a fundamental nature in many chemical and biological processes, often displaying key roles in fields of chemical, biological, materials and related sciences. The binding of an entity (ligand) to a central atom leads to the formation of a coordination centre which can activate other molecules of different or the same species, determining the behavior of the system.

This talk addresses the work of the author's group (also with collaboration of others) on the synthesis and application of a diversity of organonitrogen ligands, often unsaturated ones, bi- or multifunctional (e.g., of N,O-type), chelating and hemilabile, with appended functional groups. They include arylhydrazones, aroylhydrazines, Schiff bases, aromatic amino- and amide-carboxylates, pyrazole-triazopentadienes, tris(pyrazolyl)methanes, tetrazole-amides, etc., forming a diversity of molecular complexes, coordination polymers and MOFs.

The use of their complexes and metal assemblies (namely with 3d transition metals) as catalysts is illustrated with selected examples, namely with the involvement of metal-ligand cooperation. Adsorption (concerning the removal of organic dyes in water medium) and antitumor properties are also outlined.

The catalytic reactions include alkane oxidations, water electrocatalytic oxidation and reduction (oxygen evolution and hydrogen evolution reactions), CO_2-epoxide coupling, azide-alkyne cycloaddition, nitroaldol reaction, etc.

The role of nitrogen ligands in the formation of supramolecular assemblies via non-covalent interactions (such as, halogen and chalcogen bonds) and the involvement of such weak bonds in the structure and chemical behavior are also disclosed. Possible reaction mechanisms are discussed.

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KEYNOTE LECTURES

KN1 Manipulating the Entatic State by Biomimetic Guanidine Copper Complexes

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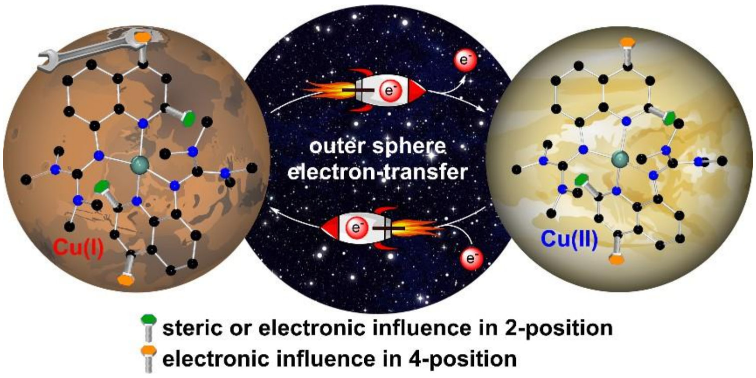
Copper guanidine quinoline complexes act as good entatic state models due to their distorted structures leading to a high similarity between Cu(I) and Cu(II) complexes.[1] This principle can be transferred even to photochemistry.[2] For a better understanding of the entatic state principle regarding the electron transfer a series of guanidine quinoline ligands with different substituents have been synthesised to examine the influence on the electron-transfer properties of the corresponding copper complexes.[3] Substituents with different steric or electronic influences were chosen. The effects on the properties of the copper complexes were studied applying different experimental and theoretical methods. The molecular structures of the bis(chelate) copper complexes were examined in solid state by single-crystal X-ray diffraction and in solution by X-ray absorption spectroscopy and density functional theory (DFT) calculations revealing a significant impact of the substituents on the complex structures. For a better insight natural bond orbital (NBO) calculations of the ligands and copper complexes were performed. The electron transfer was analysed by the determination of the electron self-exchange rates following the Marcus theory. The obtained results were correlated with the results of the structural analysis of the complexes and of the NBO calculations. Nelsen´s four-point method calculations give a deeper understanding of the thermodynamic properties of the electron transfer. These studies reveal a significant impact of the substituents on the properties of the copper complexes.



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KN2 Organometallic Biomimetic Catalysts for Energy Applications

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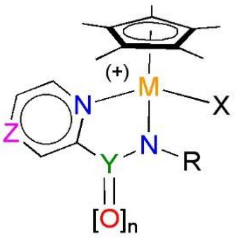
In this contribution, the recent results of our research group aimed at developing functional mimics of enzymes will be illustrated. Particularly, it will be shown that rather simple organometallic complexes, bearing amidate ligands (Figure), can be successfully applied in many important reactions relevant to energy production: hydrogen evolution from formic acid and water,[1] water oxidation,[2] NADH and $FMNH_2$ regeneration,[3,4] hydrogenation of α-ketoacids and glycerol dehydrogenation.[5]

A key aspect of the success of organometallic catalysts shown in Figure stems from the versatility of N-amidate ligands, whose electronic, steric and solubility features and their possibility to be anchored onto supports can be easily tuned by a proper selection of X, Y, Z and R groups. For instance, the installation of a carbohydrate R functionality makes complexes highly soluble in water and capable of establishing intermolecular hydrogen bonding that contribute to facilitating the activation of polar substrates such as α-ketoacids (M = Ir, X = Cl, Y = C, Z = C).[5] Alternatively, the utilization of a sulphur bridge (Y = S) has a twofold effect: it decreases the electron donation of ligand to metal, consequently increasing its electrofilicity, and makes the N,N-bidentate ligand hemilabile (M = Ir, X = NO_3, Z = C). All results in catalysts extremely active for NADH regeneration.[3]



M = Ir, Co
X = anion, solvent
Y = C, n=1; S, n=2
R = H, Me, $(CH_2)_3Si(OEt)_3$, carbohydrate
Z = C, N

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KN3 New Multifunctional Complexes of *d*- and *f*-Metal Ions with N-Donor Ligands

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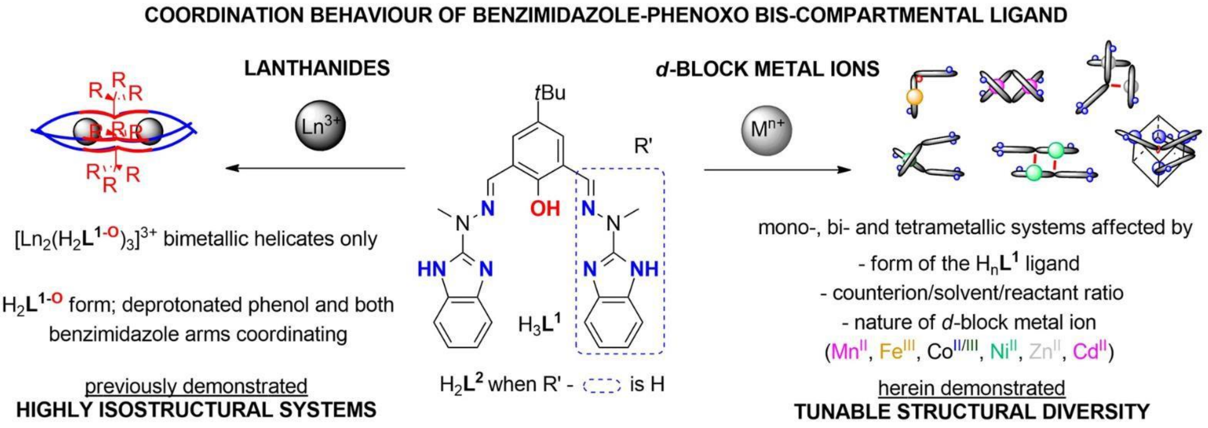
The synthesis of supramolecular complexes is currently one of the most explored areas of coordination chemistry due to their chemical and physical properties, unusual structures, and potential applications.[1] Characterization and study of the properties of new complexes of d- and f-metal ions are scientific goals pursued for many years by our research group. The presented topic of the talk will concern transition metal complexes with N-heterocyclic ligands, with special emphasis on their luminescent, magnetic, catalytic, photocatalytic, electrochemical, electrocatalytic and biological properties.[2-8]



This work was supported by IDUB-UAM "Scientific conferences - support for the participation of scientists and doctoral students in prestigious scientific conferences" and National Science Center, Poland; OPUS—grant UMO-2022/47/B/ST4/02310.

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KN4 Bipyrazolate Metal-Organic Frameworks for Carbon Capture and Pollutants Sequestration

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Metal-organic frameworks[1] (MOFs) are crystalline open frameworks deriving from the self-assembly of metal ions or metal-based clusters (the nodes) and electron-donor organic molecules (the linkers). The vast library of candidate nodes and linkers allows the concomitant tailoring of MOFs crystallochemical features and functional properties[2]. Polyazolate linkers generally form stronger coordinative bonds than polycarboxylate ones, thus imparting higher thermal and chemical stability to the corresponding MOFs[3].

In this context, the present contribution will showcase the results obtained by our research group upon exploiting single- and mixed-ligand bipyrazolate MOFs in the applicative contexts of carbon capture and pollutants sequestration. Focusing on Zn(BPZ-X)[4-6], $Fe_2(BPEB)_3$[7,8], $Fe_2(BDP)_3$[9], and Zn(BPE)[10] [H_2BPZ-X = 3-X-4,4′-bipyrazole, X = H, NO_2, NH_2; H_2BPEB = 1,4-bis(1*H*-pyrazol-4-ylethynyl)benzene; H_2BDP = 1,4-bis(1*H*-pyrazol-4-yl)benzene; H_2BPE = 1,2-bis(1*H*-pyrazol-4-yl)ethyne)] as representative examples, special attention will be paid to the invaluable role played by multi-technique approaches, juxtaposing (*in situ*) powder X-ray diffraction, volumetric adsorption, electronic-transition spectroscopy, and theoretical calculations, in disclosing and mutually relating key structural and functional features. This strategy not only leads to the in-depth characterization of a study case, but also provides a relevant knowledge advancement, paving the way to improved new-generation materials for the application under investigation.

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KN5 Bio-Inspired Catalyst Design for Small Molecule Activation in Multi-Electron Reduction Processes

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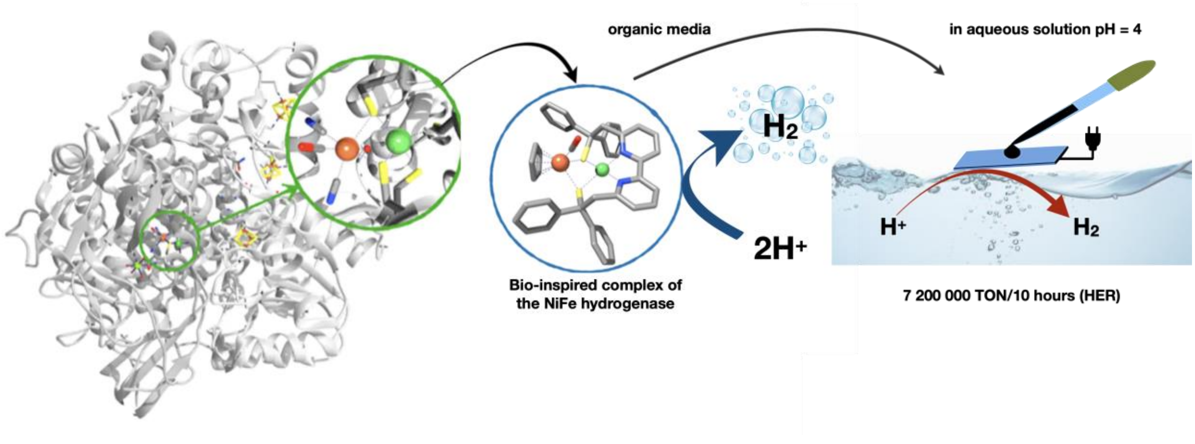
The activation of small molecules in multi-electron reduction catalysis has become an important area of research due to the challenges associated with the energy and environmental problems facing our society. These redox processes are generally promoted by metal ions. In our aim to develop efficient complexes for such catalytic processes, we focused on thiolate-based scaffolds, as thiolate-metal complexes are widely present in the active site of enzymes catalyzing the reactions of interest. Examples include the hydrogenases, which reversibly reduce protons to generate H_2 (see Figure). Our aim is to design innovative catalysts (for H_2 production and O_2 reduction) that are robust and active in water, based on the use of thiolate-based ligands and noble-free metal ions.

In particular, we will describe how we have designed our most efficient catalytic systems. This involved a systematic exploration of series of complexes to assess the impact of the metal, the first coordination sphere, particularly with regard to the pivotal role of the thiolate during catalysis, and the second coordination sphere, where a potential proton relay can be introduced. We will also present mechanism studies, including the generation and characterization of intermediate species, to unveil the key factors for enhanced activity. Finally, we will also discuss how we can modify the catalytic conditions to optimize the catalytic process (homogeneous or heterogeneous conditions, how to supply electrons, i.e., chemically, via electro-assisted or photo-assisted processes).



KN6 Zeolitic Imidazolate Framework-based biocomposites

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In aqueous systems, the presence of biomacromolecules can trigger the rapid self-assembly of 2-methylimidazole and Zn(II) into Zeolitic Imidazole Framework-based materials.[1] The building blocks of these frameworks can be arranged in different topologies (e.g. sodalite, diamondoid, and katzenite)[2] and diverse crystalline phases with distinct chemical compositions (e.g. ZIF-C[3], ZIF-EC1[4]). These different spatial arrangements and chemical compositions lead to different functional properties. Here we illustrate the research progress starting from the initial discovery up to the integration with functional therapeutics (e.g. CRISPR/Cas9 gene editing systems,[5] and antibodies[6]) and their potential application in biomedicine[1].

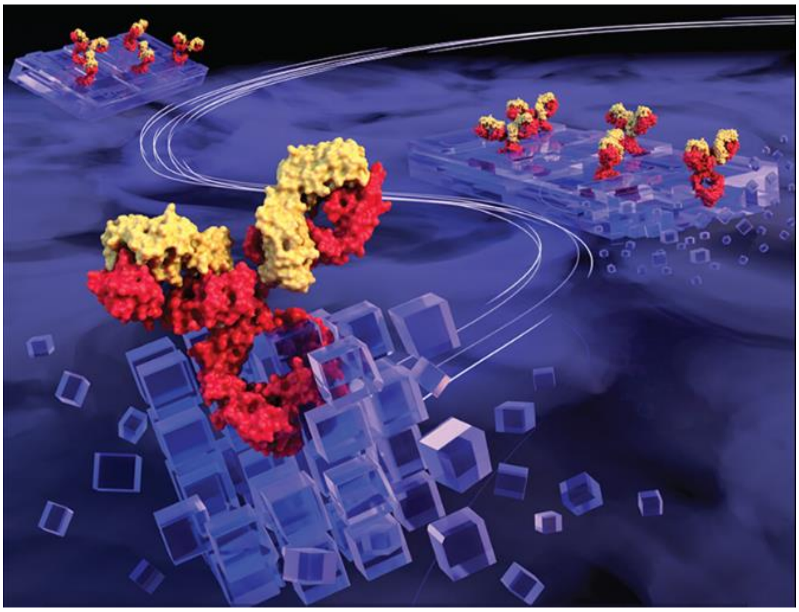

Figure illustrating the self-assembly of ZIF-C on antibodies.[6]

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KN7 Corroles as a Platform for Exotic Coordination Chemistry: Binuclear, Metal-Metal–Bonded and Sandwich Compounds

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Since the discovery of simple, one-pot syntheses of corroles at the end of the last century, their coordination chemistry has grown by leaps and bounds. In our laboratory, we have focused particularly on 5d transition metal complexes, somewhat unusual constructs in that they involve the encapsulation of a large metal ion by a sterically constrained macrocyclic ligand.[1] In spite of the steric mismatch inherent in their structures, the great majority of them are chemically and photochemically rugged, and amenable to a variety of applications. This talk will focus on the particularly versatile interactions of rhenium and corrole, which have led to rhenium-oxo and imido complexes, quadruple-bonded rhenium corrole dimers and rhenium biscorrole sandwich compounds. The talk will conclude with a sneak preview of our latest findings on rhenium as a thiophilic metal.

This work was supported by the Research Council of Norway.

Alemayehu, A. B.; Thomas, K. E.; Einrem, R. F.; Ghosh, A. The story of 5d metallocorroles: from metal–ligand misfits to new building blocks for cancer phototherapeutics. *Acc. Chem. Res.* **2021**, *54*, 3095-3107.

KN8 Nonlinear Behaviour and the Limits of Mechanistic Understanding in Asymmetric Catalysis

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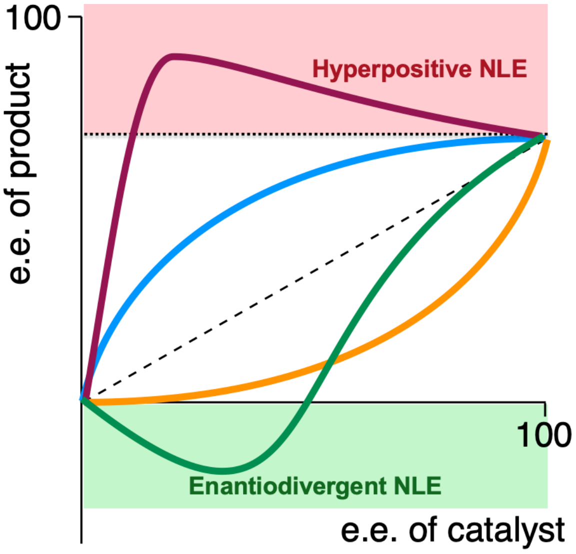
Asymmetric amplification is a phenomenon that plays a key role in the emergence of homochirality in life. In asymmetric catalysis, theoretical and experimental models have been investigated for understanding how chiral amplification is possible, in particular through non-linear effect.[1] Recently we have proposed models that have led to an understanding of more complex non-linear effects, such as hyperpositive and enantiodivergent non-linear effects, which include a coexistence of active monomeric and active dimeric species.[2,3] A higher degree of complexity seems attainable if one considers that higher levels of aggregation could be envisaged.[4]

We show here how different ligands, issued from the same privileged chiral structure, exhibit completely different systems-level behaviours and thus also different reaction outcomes – although they differ only by small chemical modifications. Mechanistic studies showed that the metal complexes aggregate and generate additional catalytic species in distinct ways. These results were obtained through a combination of nonlinear effect studies and other related studies and simulations have confirmed the possibility of such systems-level behaviour.

Overall, these results highlight the need to be cautious with certain paradigms of asymmetric catalysis, as structures alone do not necessarily predict systems-level behaviour that could bias the outcome of the catalytic reaction.



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KN 9 Iron Spin Crossover and Nitrogen Ligands: a Tale of Thwarted Love

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The concept of spin transition goes back to Pauling's description of the nature of chemical bonding and finds a satisfactory description within the ligand-field theory. The $3d^6$ open-shell metallic centers, as Fe(II), appear to be the most promising candidates for working as molecular-based magnetic and optical switches responding to thermal, pressure or light-induced stimuli. The target energy balance $0 \le \Delta E = 2(\Delta_{oct}-P) \le 10RT$ between the ligand-field splitting Δ_{oct} and the electron pairing energy $P = 2B+4C$, which is required for inducing a usable spin crossover (SCO) process, can be tuned by the geometry and the nature of the coordination sphere around Fe(II). It is now well-established that distorted octahedral $[FeN_6]$ units, where N are heterocyclic nitrogen donors, are pertinent for this purpose. Detailed modeling further exalts non-symmetrical didentate ligands, made of alternated heterocycles involved in five-membered chelates rings, as the grail for inducing valuable SCO in $[Fe(N{\cap}N')_3]$ chromophores.[1] The detection (i.e. reading) of the spin-state switching process at the molecular level appears as important as its implementation if profitable and socially acceptable applications as sensor or as Q-bit are to be proposed. The best (*i,e* easy, highly selective and cheap) solution relies on the indirect SCO modulation of a long-lived luminescent signal observed in the visible part of the electromagnetic spectrum and originating from an appended trivalent lanthanide metal, a strategy proposed more than two decades ago,[2] successfully realized once in a doped solid material[3] and detected only very recently in an isolated (supra)molecule (Figure 1).[4]

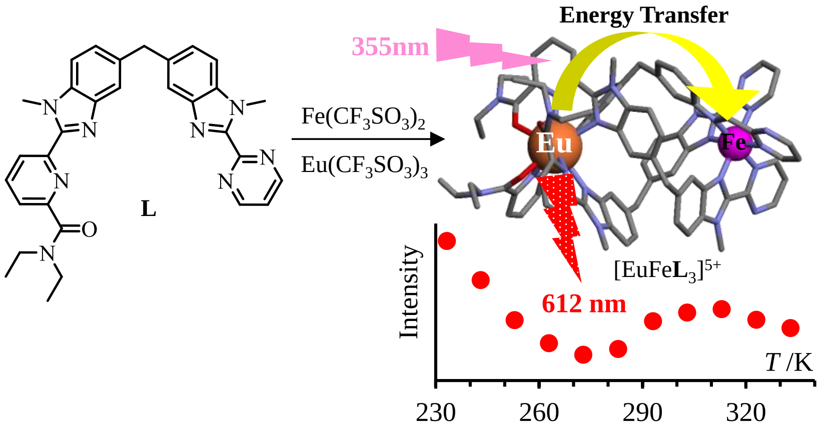

Figure 1: Molecular structure and light modulation of the spin crossover $FeEu\mathbf{L}_3]^{5+}$ complex.

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INVITED LECTURES

IL1 Nitrenium Ions: Platform for Cationic N-Ligands, Reagents and Catalysts

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N-heterocyclic carbenes (NHCs) have received a spectacular development in the last few decades. Possesing unique chemical properties, NHCs have found wide application in organometallic chemistry and catalysis. Not surprisingly, a chemistry of the main-group NHC- analogs (NEN species; E = B^-, Ga^-, Si, Ge, Sn, Pb, P^+, As^+, Sb^+), isoelectronic and isostructural to NHC, has attracted a great interest. The missing link in this series of ligands and catalysts was the nitrogen counterpart - the N-Heterocyclic Nitrenium ion (NHN). It is defined as a divalent cationic nitrogen center bearing a lone pair of electrons and an accessible vacant p- orbital in its singlet state.

In my lecture, we will discuss versatile chemistry of NHN species. We will demonstrate coordination ability of these unusual cationic ligands, analyze their properties and their utilization in stabilization of elusive species.[1,2] Moreover, we will demonstrate that nitrenium ions can be used as Lewis acid.[3] The chemistry of such nitrogen-based Lewis acids was completely unknown. We will demonstrate versatile and intriguing reactivity of nitrenium in organocatalysis, frustrated Lewis pairs chemistry and radical-based chemistry.[4]

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IL2 Tuning the Catalytic Activity of Pincer Complexes of Rhodium (I) by Supramolecular and Redox Stimuli

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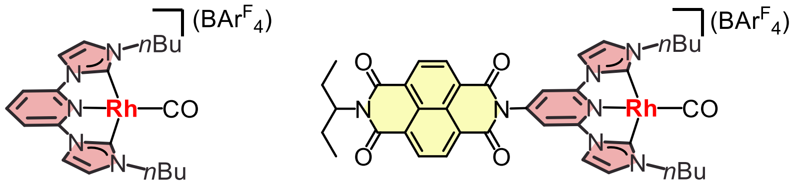
Oxidative addition (OA) and reductive elimination (ER) are two of the most important steps in transition metal-based homogeneously catalyzed reactions. To design efficient organometallic catalysts, it is crucial to understand the factors that determine the kinetics and thermodynamics of these steps. For OA, it is commonly assumed that electron-rich metal centers favor this step. In traditional studies investigating the influence of ligands on OA and ER, the steric and electronic properties of spectator ligands have been used to control the catalyst's performance. In this regard, we recently proposed the use of redox-switchable ligands to study the influence of the electronics while maintaining the steric parameters intact.[1]

We present a novel approach for achieving supramolecular or redox control over the electronic properties employing two Rh(I) complexes supported by a pyridine-bis-imidazolylidene pincer ligand (complexes **1** and **2**, respectively). We demonstrated that **1** has a high affinity with coronene, which can be explained by means of π-stacking interactions. This interaction has a strong impact on the electrondonating strength of the pincer CNC ligand and, in turn, on the reactivity of the complex towards the oxidative addition of MeI, which is greatly enhanced.[2] Additionally, the activity of complex **2**, supported by a CNC-pincer ligand decorated with a naphthalenediimide (NDI) fragment, can be tuned by introducing either a supramolecular (adding a π-π-stacking additive) or a redox (adding a fluoride source) stimuli.[3] In both cases, the addition of coronene (for **1** and **2**) or a fluoride source (for **2**) produces a positive effect on the performance of the rhodium-catalyzed cyclization of 4-pentynoic acid.



1 **2**

Scheme 1. Pincer complexes of Rh(I) under study

This work was supported by the Ministerio de Ciencia e Innovación (PID2021-127862NB-I00), and the Universitat Jaume I (UJI-B2020-01 and UJI-B2021-39). We also are grateful to the Serveis Centrals d'Instrumentació Científica (SCICUJI) for providing with spectroscopic facilities.

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IL3 Bi-& Tri-dentate N-Ligated Late transition metal precatalysts: New Era of Ethylene Products

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The concept of using late-transition metal precatalysts, such as α-diimino Ni/Pd1 and bis(imino)pyridyl Fe/Co2 by the teams of Prof. Brookhart and Prof. Gibson, was initiated for ethylene polymerization in 1990s. Subsequently, the extensive investigations were mushroomed approving the characteristic features of resulting products as highly branched by Ni/Pd and highly linear by Fe/Co; however, the critical problems have been realized with the limited models of ligands as well as less thermos-stability. To overcome the model shortage of catalysts, multiple frameworks with ring-fused pyridine derivatives for potential complexes have been developed through both philosophic3 and new catalytic syntheses.4 To enhance the stability of active species, the benzhydryl substituent was introduced and approved the efficiency of derivative complex catalysts.5 Therefore the practicing complex precatalysts could be further developed to achieve from wax (even oligomer) to high molecular weight polyethylenes by using tridentate N,N,N-ligated iron/cobalt7 while for highly branched polyethylenes by bidentate N,N-ligated nickel complexes.8 The narrower dispersity of resultant polyethylenes is a common feature as its advantage of new catalytic system, more importantly, various differences of their molecular weights could be controlled through finely turning the steric and electronic properties of ligands used. Followed with our experience of late transition metal precatalysts for ethylene reactivity in two dozen years, the process of iron-promoted ethylene oligomerization has operated for alpha-olefins with 50 Ktons annually since 2021 and its 200 Ktons process is under construction. In addition, the pilot processes with tons/year have efficiently performed for highly linear polyethylenes (waxes) by the iron/cobalt precatalysts7 and polyethylene elastomers (highly branched polyethylenes from sole ethylene) by nickel precatalysts.8 No doubt, late-transition metal precatalysts could provide highly efficient catalytic systems and the truly tailoring polyethylenes are successfully achieved with targeting any types of microstructural designed and purpose-oriented polyethylenes.

Acknowledgements: I am sincerely grateful to all of my colleagues for their contributions as well as all referees' (critical) comments on our submissions.

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IL4 Metal-Mediated Porphyrin Assemblies based on Pyridyl Ligands

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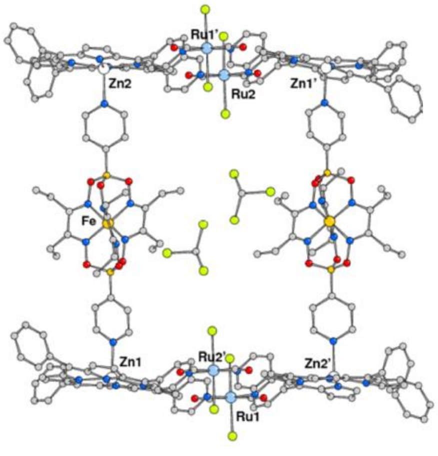
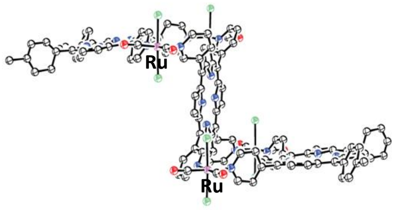
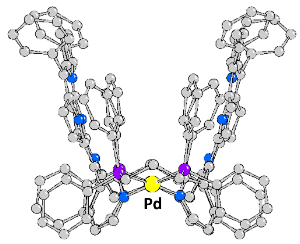
Porphyrins, and their metallated derivatives, play a pervasive role in major biochemical enzymatic functions and natural processes, so great efforts were made to integrate metalloporphyrins as structural elements in functional discrete assemblies.[1a] In particular, the metal-mediated assembling approach has led to a variety of spectacular arrays.[1b] The vast majority of these consist of homoleptic systems, while examples containing different kind of porphyrins are relatively more rare. Over the years we have employed metal-coordination of pyridyl ligands for the obtainment of multi-component porphyrin systems, mostly for artificial photosynthesis mimic, with specific focus on the control of the number and disposition of the active units.[2] More recently we expanded our interests in the design of heretoleptic architectures, by exploiting both *inert/labile* and *hard/soft* discriminations of coordination bonds.[3] An excursion on the most fascinating past and recent examples will be presented (see also Figure below).







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IL5 Using *ab initio* Tools to Predict the Optical Spectra of *N-C*ontaining Ligands and Complexes.

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In this contribution, I will illustrate how theoretical tools can be applied to obtain not only insights into the nature of electronic excited states, but also quantitative estimates of absorption and emission features for several *N*-bearing systems. To this end, the use of advanced theoretical protocols, explicitly accounting for vibronic couplings are often necessary, since these give access to band shapes, molar absorption coefficients, and, sometimes even fluorescence quantum yields.[1,2] Illustrations of the strengths and shortcomings of theory in such context will be provided for several experimentally-relevant examples treated in close collaboration with experimental groups, with an effort to underline the progresses of theory during the last few years.[3-7]

This work was supported by Nantes Université, the CNRS, the IUF, as well as the ANR (Condor grant)

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IL6 Metal Complexes of Diamido- and Tetraamido-benzene Ligands: Privileged Compounds in Organometallic Chemistry and Molecular Magnetism

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The deprotonated forms of diamino- and teteraamino-benzenes (Figure 1) are typical examples of non-innocent ligands.[1] Traditionally metal complexes of these ligands have either been studied because of their intriguing electronic structures,[2] or because of their proton-responsive nature[3]. In this contribution, we will focus on recent contributions from our groups in which we have used these ligands to generate “masked” low-valent or high-valent compounds with intriguing organometallic reactivity.[4] Additionally, we will present modifications on the substitution pattern in these ligands that have led to air- and moisture-stable radical-bridged organometallic compounds.[5] Furthermore, we will discuss the relevance of such complexes, and in particular of the radical-bridged forms for generating state-of-the-art single-ion magnets.[6]

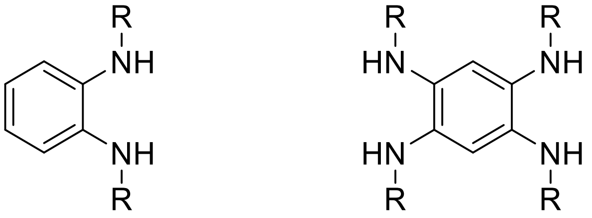

Figure 1. The ligands 1,2-diaminobenzene (left) and 1,2,4,5-tetraaminobenzene (right).

This work was supported by the Deutsche Forschungsgemeinschaft (DFG).

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IL7 Iron(I) and Cobalt (I) Amido-Imidazolin-2-imine Complexes as Catalysts for H/D Exchange in Hydrosilanes

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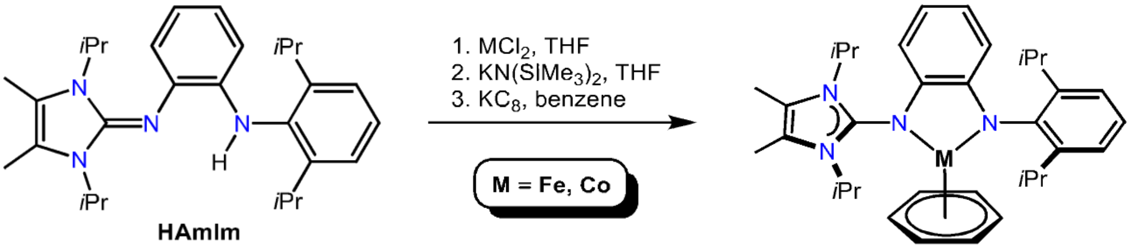
Imidazolin-2-imine ligands have proven to be very useful as ancillary ligands in a wide variety of homogeneous transition metal, lanthanide, and actinide catalysts.[1] Due to the ability of the imidazole ring to efficiently stabilize a positive charge, imidazolin-2-imines can act as $2\sigma,2\pi$-electron donors and can therefore be considered as neutral amido-type ligands. This feature has been exploited in the design of a phenylene- bridged amido-imidazolin-2-imine (AmIm) ligand that served as a suitable scaffold for the stabilization of unusual triel(I) compounds.[2] More recently, this AmIm ligand has been introduced into transition metal chemistry with the synthesis of high-spin iron(I) and cobalt(I) complexes [(AmIm)M(η^6-C_6H_6)] (Scheme 1), which have served as catalysts for H/D exchange in hydrosilanes, among other applications.[3] Notably, the reactivity and magnetic properties of these complexes differ significantly from those of related *β*-diketiminate (NacNac) systems,[4] which will be discussed in detail.



Scheme 1. Synthesis of AmIm-supported iron(I) and cobalt(I) benzene complexes.

In-depth mechanistic studies revealed that the deuteration of silanes proceeds via activation of the iron(I) precatalyst to give catalytically active iron(II)-hydride/deuteride species and that the catalytic cycle proceeds via *σ*-bond metathesis with the silane substrates.[3a] In contrast, the cobalt(I) precatalyst gives rise to a mechanism that follows a classical oxidative addition/reductive elimination pathway with the formation of intermediate Co(III) silyl hydride complexes.[3b]

This work was supported by the Deutsche Forschungsgemeinschaft (Germany) and the National Science Centre (Poland).

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ORAL COMMUNICATIONS

OC1 Selective Reductive Elimination of Polar Bonds: from Mechanistic Studies to Protein Bioconjugation

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Reductive elimination of an Aryl-X bond (X= N, O or Halogen) is a difficult reaction compared with the more common C-H or C-C coupling. It becomes even more complicated when competing coupling reactions can potentially take place, such as in the case of Pd(IV) or Pt(IV) complexes. In this presentation, I will briefly describe our journey toward a Pt(IV) system that can eliminate a variety of Aryl-X bonds under mild conditions (Figure 1),[1,2] before focusing on the most recent applications of this chemistry in the bioconjugation reactions. In particular, I will present our results on the selective arylation of different types of N-H bonds in unmodified peptides and proteins (Figure 2).[3]

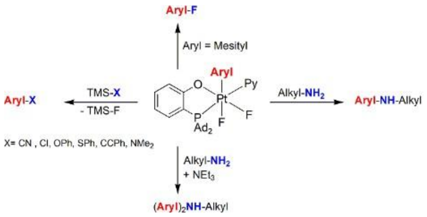

Figure 1.

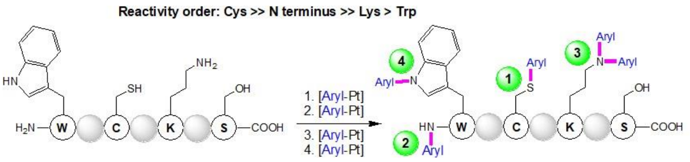

Figure 2.

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OC2 Unusual O_2 Activation at Bioinspired Caged Copper(I) Complexes.

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O_2-activating metalloproteins (containing Cu, Fe or Mn metals) perform challenging functionalization of inert C-H bonds, under physiological conditions, in a remarkably efficient manner. [1] The binding cavities found in these systems govern the selectivity and efficiency of reactions. In their hydrophobic channels, destabilizing (like steric repulsion) and stabilizing (like H-bonding) forces allow for substrate positioning and activation/stabilization of highly reactive intermediates. In order to reproduce the efficient chemistry found in nature, we therefore develop bioinspired complexes where the reactive metal center is entrapped in chiral cage architectures describing well- defined hydrophobic cavities. We have recently demonstrated that these organic supra-structures allow for protection of Cu(I) active sites,[2] control of the chirality around the metal core,[3] and lead to enhanced oxidation catalysts (eg CH_4 oxidation).[3] On this basis, we are developing caged O_2-activating Cu(I) catalysts displaying an H- bonding hydrophobic cavity,[4] aiming at controlling substrate positioning and/or stabilizing metastable superoxo intermediates.

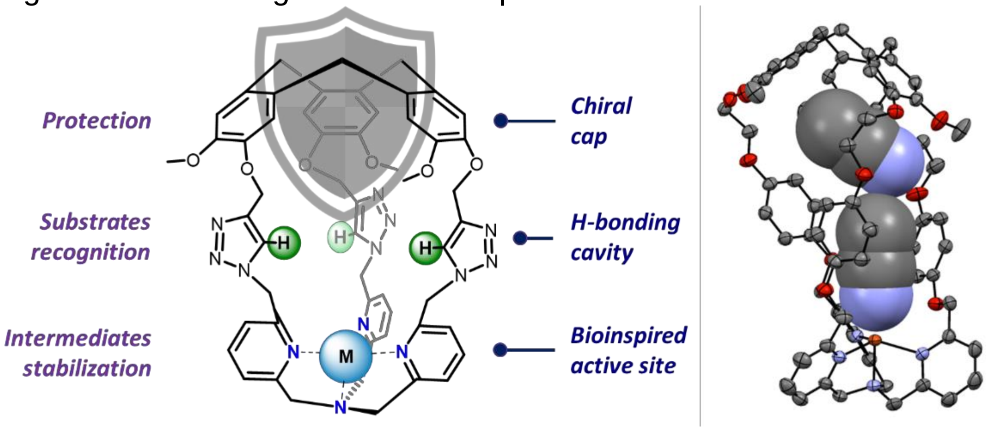

Figure 1. Schematic representation of the targeted caged catalysts along with an example of XRD structure of a caged copper complex.

Discussion about (*i*) the crucial role of these hydrophobic cavities for efficient and selective transformations and (*ii*) the unprecedented light-induced reactivity observed at related Cu(I) catalysts, will be the core of this communication, which aims at giving a better understanding of the benefits of these novel confined oxidation catalysts.

*This work was supported by the ANR (ANR-22-CE50-0009-01) and the “Initiative d’Excellence d’Aix-Marseille Université” – A*MIDEX (AMX-21- PEP-041).*

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OC3 A New Type of Trimeric Formally Zerovalent Palladium Complexes only Supported by Nitrogen Ligands

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Ar-BIAN (bis(arylimino)acenaphthene) Schiff bases have found wide application as ligands for both transition and main group metals because their rigid structure imparts the correct geometry for chelation and improves the stability of the compounds against hydrolysis and rupture of the central C-C bond. We have previously reported on the synthesis of the reduced form of the BIAN compounds, Ar-BIANH_2.[1,2] We now report that treatment of palladium acetate with these ligands results in the reduction of palladium(II) to palladium(0) and coordination of the so formed Ar-BIAN to the latter. In the absence of other ligands, an unprecedented trinuclear complex was obtained, which is formally the first palladium(0) compound only stabilized by nitrogen ligands. Its X-ray structure shows that each palladium atom is coordinated in a standard κ^2N chelating way to an Ar-BIAN ligand and in a η^2 way to a C=N double bond of another Ar-BIAN ligand. The latter is itself chelating a second palladium atom and the same bonding scheme extend to a third Pd(Ar-BIAN) unit, which closes the loop over the first palladium atom (Figure 1).

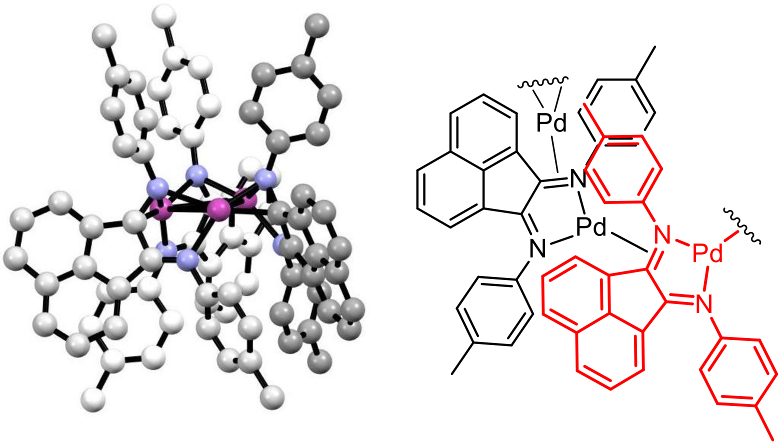

Figure 1 X-Ray structure of trimeric $[Pd(4\text{-}MeC_6H_4\text{-}BIAN)]_3$ and its partial bonding scheme.

Overall, the complex has a propeller shape, with the six aryl rings divided in two inequivalent groups. Other complexes have also been obtained showing unusual structures and their synthesis will be described.

This work was supported by MUR and Next Generation EU (PRIN2022ZJSCW3)

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OC4 Cobalt Complexes with PN$_5$P Ligands as Catalysts in the Synthesis of Si, B, and Ge Compounds

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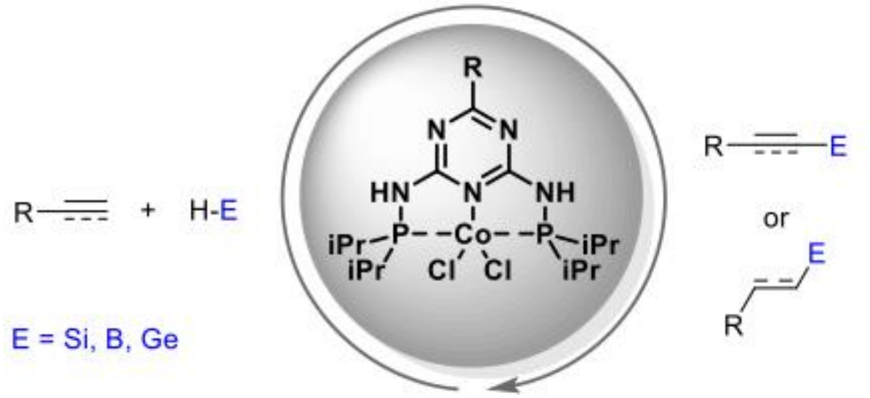

Modern chemical synthesis focuses on the sustainable development of conducted reactions, primarily by minimizing the amount of used and generated hazardous substances. This is mostly achieved by using catalysts that permit the activation of new reaction pathways which enable increased process selectivity and the utilization of less reactive substrates.[1]

An interesting example of recently intensively studied homogeneous catalysts is pincer cobalt complexes. They are known for their relatively simple synthesis, exhibiting high stability, activity, and selectivity in hydrogenation, hydroboration, hydrosilylation, or bond-forming reactions.[2] Their important feature is the possibility of affecting their selectivity by simply changing the reaction conditions or the structure of the ligand.

In this communication, I will present the synthesis of organogermanium, organoboron, and organosilicon compounds catalyzed by cobalt pincer complexes which have been synthesized gently and easily by using inexpensive and commercially available reagents. The presented methodology enables ligand-controlled synthesis regarding the principles of sustainable chemistry leading to a valuable group of compounds.[3-6]

This work was supported by a National Science Centre Grant: UMO-2018/30/E/ST5/00045.

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OC5 Parallel Chirality Inductions in Möbius Zn(II) Hexaphyrin Transformation Networks

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

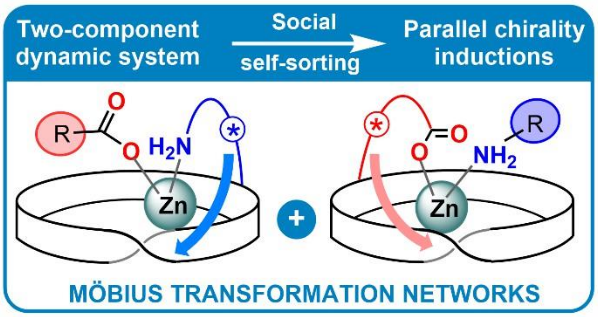

Figure 1. Multiple chirality inductions in mixtures of Möbius rings.

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OC6 Photophysical Properties of 1,10-Phenanthroline Derivatives and Related Ru(II) (Nano-)edifices

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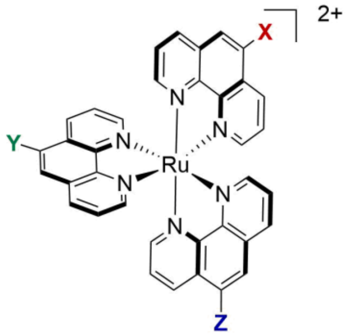
The presentation will concern studies developed in collaborations in the field of linear and nonlinear optical properties of 1,10-phenanthroline ligands and related Ru(II) complexes (Figure below)[1]. One- and two-photon induced access to ^{3}MLCT excited states will be discussed either for fundamental interest than in the perspective of potential applications[2]. We will describe (*i*) the huge solvatochromism and dual emission phenomena evidenced for an original 1,10-phenanthroline derivative[3], (*ii*) Ru(II) complexes-based ^{3}MLCT excited-states for applications (optical power limiting[4], photodynamic therapy, (a-)PDT[5]), and (*iii*) surface functionalized nano-edifices[6] for potential applications in physics[7] and medicine[8].



Homoleptic (X=Y=Z), and heteroleptic 1,10-phenanthroline derivatives-based ligands Ru(II) complexes

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*This work was supported by **ANR-17-CE07-0033-02** "Isogate" and **ANR-20-AMRB-0009-01** "Target Therapy".*

OC7 Cobalt(II) Complexes with Schiff Base-type *3N*-Donor Ligands as Catalyst Precursors for Alkyne Hydrosilylation and Hydroboration

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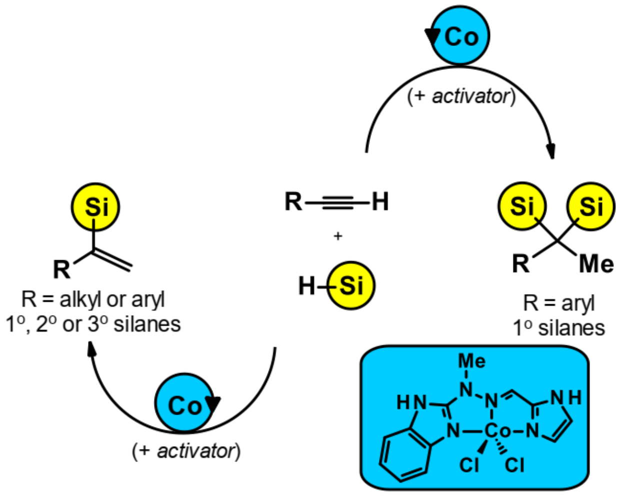
The hydrometallation reactions are the most important catalytic reactions used in the synthesis and modification of organometalloid compounds.[1] The catalysts commonly used in these processes are platinum, rhodium and ruthenium complexes. The high price of noble metals and the inability to reuse them in technological processes lead to the search for alternative, cheaper and similarly effective catalysts based on more abundant first-row transition elements (*3d* electron metals) of the periodic table, such as iron, cobalt and nickel.

In the communication we present the results of research on the development of new, effective and selective catalytic systems of Markovnikov hydrosilylation[2] and double hydrosilylation[3] reactions of functionalized alkynes based on cobalt(II) complexes with Schiff base-type *3N*-donor ligands and alkali metal trialkylborohydrides (Scheme 1). An extension of the research is the use of cobalt(II) complexes with tridentate *N*-donor ligands as catalyst precursors for *anti*-Markovnikov hydroboration of terminal alkynes.



Scheme 1. Markovnikov hydrosilylation vs. double hydrosilylation of terminal alkynes

An important aspect of the research is the optimization of procedures aimed at increasing the efficiency and selectivity of the tested systems, as well as an attempt to explain the mechanism of catalytic transformations. Particular emphasis will be placed on the influence of the ligand structure on the catalytic activity and selectivity of cobalt (pre)catalysts.

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OC8 Ligand Modification Shifts CO_2 to CO Reduction by Iron Porphyrin from Fe(0) to Fe(I).

Eva Pugliese, Amanullah sk, Philipp Gotico, Marie Sircorglou, Ally Aukauloo,

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Iron porphyrins are among the best molecular catalysts for the electrocatalytic carbon dioxide (CO_2) reduction reaction. Taking inspiration from the active sites of enzymes, the reactivity of this class of catalysts is constantly being improved through the implementation of chemical functionalities in the second coordination sphere.[1] As commonly advocated, these functionalities have been introduced on ligand scaffolds of metal complexes to establish a hydrogen bonding network with the incoming substrate, acting as proton relays or providing an electrostatic interaction with reaction intermediates.

We have recently found that a multipoint hydrogen bonding scheme may also shift the redox activation step from the well-admitted Fe(0) to the Fe(I) state for both photo- and electrocatalytic reduction of CO_2 to carbon monoxide (CO). [2-4] Such a remarkable shift opens new lines of research in the design of molecular catalysts to perform a more efficient catalytic CO_2 photo- and electroreduction. An alternative reaction mechanism with an early activation of CO_2 at Fe(I) oxidation state is proposed by combining different spectroscopic methods and DFT calculations.

This work has been supported by the French National Research Agency (LOCO, grant N°: ANR-19-CE05-0020-02 and LABEX CHARMMMAT, grant N°: ANR-11-LABX-0039). DFT calculations were performed using HPC resources from GENCI (grant A0070810977).

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OC9 N-Bridged Diiron Phthalocyanine: Particularly Nitrogen-Rich Scaffold for Challenging Catalysis

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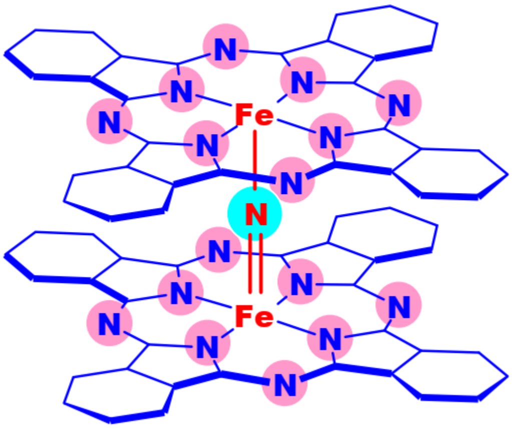
Among tetrapyrrolic macrocycles, the phthalocyanine ligand is particularly nitrogen-rich. When their iron complexes are connected via bridging nitrogen to the dimeric platform they form a conctruction containing 17 nitrogen atoms per molecule.

Compared to well-investigated in catalysis the mononuclear counterparts, the μ-nitrido diiron complexes have not been considered as catalysts until recently.[1-3] Of particular interest are their unusual catalytic properties, in particular, in the oxidation of methane[3] and in the oxidative transformation of the aromatic C-F bonds.2 These N-bridged diiron complexes are capable of reacting with oxidants to form extremely reactive ultra highvalent diiron species. These short-living species were detected and characterized by UV-vis, EPR, ESI-MS, Fe K edge EXAFS, XANES and Mössbauer techniques.



All these catalytic reactions can be efficiently performed under mild and clean conditions using H_2O_2 oxidant. μ-Nitrido diiron species show the same mechanistic features as enzymes but exhibit unprecedented reactivity.

Current challenge in bio-inspired catalysis is the development of efficient catalysts readily accessible on a large scale. In this context, *N*-bridged diiron phthalocyanine complexes seem to be promising candidates combining availability and high reactivity in many reactions. They show a new unexpected reactivity and provide a novel promising approach to challenging catalytic transformations under mild and clean conditions. Mechanistic issues of their unusual reactivity are briefly discussed.

This work was supported by the Agence Nationale de Recherche (ANR), France (grants ANR-16-CE29-0018 and ANR-23-CE07-0039).

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OC10 Zirconium Metal-Organic Polyhedra Assemblies Incorporating Nitrogen-Ligands as Systems for Energy and Environmental Applications

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In the last decade, different crystalline porous materials with porosity and modulable chemical functionality (MOFs, COFs, etc.) have been developed. Among them, we can especially mention metal-organic polyhedra (MOP). They are formed between linkers (carboxylic acid, pyridine, pyrimidine, etc.) and metal clusters. The robustness, permanent porosity, appropriate cavity size, hydrophobic nature, thermal and chemical stability of these discrete structures can be useful for a variety of applications [1].

In a previous study, we demonstrated the formation of stable Zr-MOPs based on zirconium(IV) [2]. These structures exhibit a range of favorable characteristics for various applications such as catalysis, gas adsorption or drug delivery. The $Zr_3(OH)_2$ metal clusters in these materials combine Lewis acidity and Brönsted basicity; and the modular structure allows for the control of porosity, structural charge, and the surface polarity of the MOP, resulting in discrete and soluble systems. For all these reasons, our current work focuses on the development of Zr-MOPs with different nitrogen ligands. These novel materials have a high potential for applications in energy-related processes, such as green hydrogen (H_2) generation and water oxidation.

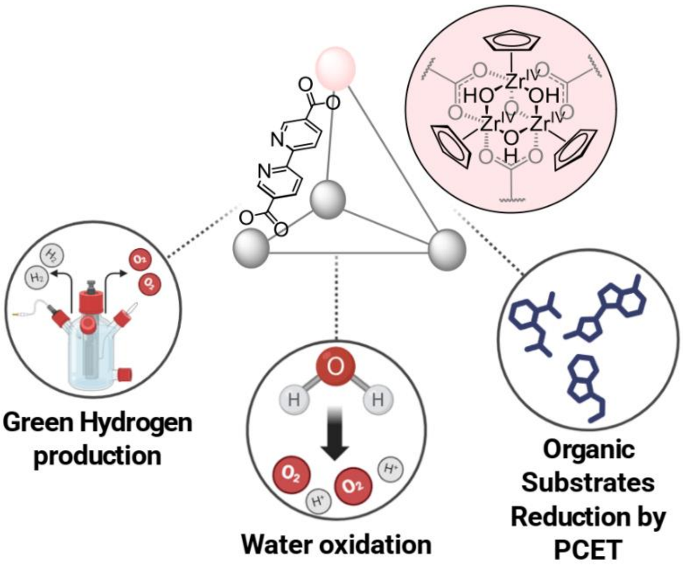

Figure 1. Different applications by Zr-MOP-bipyridine system.

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OC11 Efficient and Selective Anion Capture Using Self-Assembled Boronium Macrocycles

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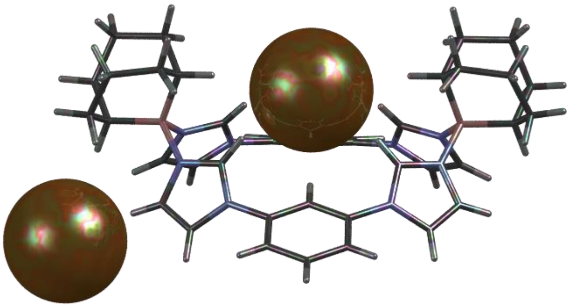
Considering the fundamental role played by anions in biological, environmental and chemical processes, detection, selective recognition and sensing of anions are topics of importance.[1] Consequently, the use of organic ligands with weak non-covalent interactions (e.g., ionic interaction, hydrogen bonds, Van der Waals forces, etc.) is an active field in anion supramolecular chemistry.[2] However, designing highly selective with strong binding affinity receptors for anions is extremely challenging, in part because of large ionic radius, low charge density, and low hydrogen-bonding ability. Thereby, the design of selective anions receptors with high binding associative constant, notably in water, is particularly difficult.[3]

Synthesis and physical properties of an air- and water stable family of bis-cationic macrocyclic imidazolylboronium anion receptors (BIB) will be presented here. By taking advantage of the structure and reactivity of 9-borabicyclo[3.3.1]-nonyl derivatives, boron atom becomes a keystone to offer rigid and highly stable dimeric imidazolylboronium macrocycles.[4] These macrocycles are designed around a functionalized aromatic linker allowing the modulation of physical-chemical properties. Interactions in these anion receptors come in part from several C-H binding sites, including C_{sp^2}-H and C_{sp^3}-H hydrogen-bond donors.



This work was supported by the French Research Ministry (Grant to M.T.), the Agence Nationale de la Recherche (Project - ANR-17-CE07-0021 - ROASTA) (Grant to P.D.), Aix Marseille University, Ecole Centrale Méditéranée, and the CNRS.

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OC12 Novel Benzene- and Triphenylene-based Ligands for Coordination Chemistry

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Benzene and triphenylene derivatives have received wide interest in the field of material science, exhibiting various applications such as organic light-emitting diodes (OLEDs), photovoltaic solar cells, and gas sensors.[1]

In this study, we present the synthesis of novel organic compounds with benzene and triphenylene cores designed for coordination reactions. To reinforce the coordination bonding of these derivatives with metal ions, we introduced various functional groups, such as carboxylic acid, amide, cyanopyridine, and diamino triazine.[2]

The selection of these ligands was driven by their advantageous coordination motifs. In addition, the aromatic nature and extended conjugated systems of their benzene and triphenylene cores foster anticipation of unique thermal and optical properties in the final metal-organic frameworks (MOFs) or complexes. Notably, compounds containing triphenylene, have exhibited stability up to 400 °C. Furthermore, our focus is directed toward studying intermolecular interactions present in the solid state of the compounds, particularly through the exploration of hydrogen bonding. Thus, the effect of functional groups and atomic positioning on intermolecular interactions is highlighted for these ligands.

Our findings bring valuable insights into the design and synthesis of organic ligands, opening avenues for the development of advanced materials with tailored properties.

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OC13 Design and Synthesis of New Heptacoordinated Molybdenum Complexes Supported by NNN Pincer Ligand

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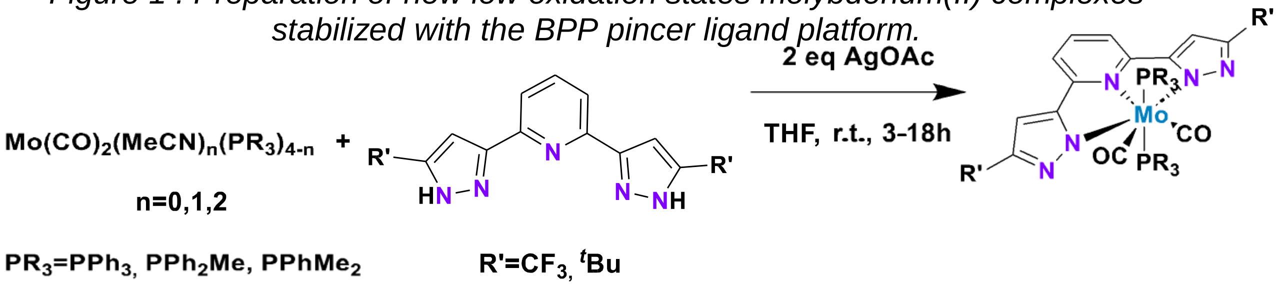
Pincer ligands have been widely explored over the past decades and became a powerful tool in organometallic chemistry for several application in recent years.[1] They are mainly used to stabilize active catalytic species by enabling precise tuning of electronic and steric properties, by rigidification of the coordination sphere. Introduction of metal-ligand cooperativity has led to the discovery of catalysts with exquisite activities for difficult reactions.[2] Aiming at the replacement of rare and expensive platinum group metals (PGMs) in homogeneous hydrogenation and dehydrogenation methods, we decided to investigate the coordination of molybdenum with a 2,6-bis(3- pyrazolyl)pyridine (BPP) pincer ligand platform, with two pyrazole arms to propose a proton responsive position that can be relevant for (de)hydrogenation catalysis (figure 1).[3–5]

We started our investigation by attempting the coordination of BPP ligands to Mo^0 precursors. Unexpectedly, mixtures of Mo^0 and Mo^{II} were systematically obtained, with deprotonated pyrazole arms for the Mo^{II} species. Suspecting the BPP platform to not be adequate for Mo^0 stabilization, we decided to run the reaction under oxidative conditions. Addition of two equivalent of AgOAc as both oxidant and base in THF let us achieve the selective synthesis of BPP-supported, hepta-coordinated Mo^{II} complexes (figure 1). They were fully characterized by NMR, X-Ray diffraction, infrared and elemental analysis. We are now exploring the reactivity of these compounds for hydrogen activation and the catalytic hydrogenation of unsaturated compounds.

Figure 1 : Preparation of new low oxidation states molybdenum(II) complexes stabilized with the BPP pincer ligand platform.



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OC14 Redox Reactivity of Porphyrins with Imines

Fatima Akhssas, Nesrine Amiri, Asmae Bousfiha, Michal Trojan, Rongning Lin,
Mathieu Berthelot, Abdou K. D. Dimé, Dominique Lucas, Hélène Cattey, Julien
Roger, Paul Fleurat-Lessard, Charles H. Devillers*

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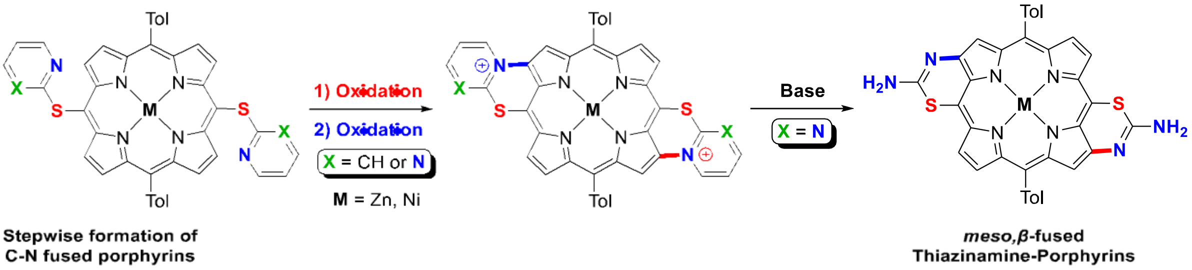
The functionalization of porphyrin is an important area of research since this macrocycle is involved in numerous applications. Despite the considerable efforts that have been devoted to this task for several decades, more efficient and (regio)selective functionalizations of porphyrins are still being developed today. Most of these functionalizations are based on chemical transformations, *i.e.*, involving chemical reagents. For more than a decade, our group has been interested in the electrochemical transformation of porphyrins. We will present our latest results on the anodic nucleophilic substitution (SNAn) of porphyrins with imine-based nucleophiles. We will show how the pyridination of porphyrins yields original amino-porphyrins with perfect regioselectivity and good yields.[1] The second part will be dedicated to the (electro)chemical oxidation of pyridinyl-based-porphyrins that will afford unprecedented C-N fused bis-pyri(mi)dinium derivatives in a stepwise manner.[2,3] The mono- and bis-pyrimidinium-porphyrins are not stable and evolve towards the original *meso*,*β*-fused thiazinamine-porphyrins (Scheme).[4] Their physicochemical properties (NMR, UV-vis., CV) will be also presented.



Scheme: *Oxidative C-N fusion of meso-pyri(mi)din-2-ylthio-porphyrins.*

This work was supported by the ANR (ANR-15-CE29-0018-01, ANR-15-IDEX-03), CNRS, Regional Council of Bourgogne Franche-Comté, Univ. Bourgogne Franche- Comté, FEDER

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OC15 Broadening the Scope of Bis(pyrazol-1-yl)acetato Ligands

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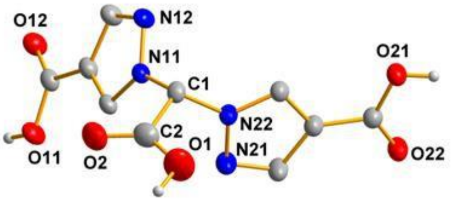
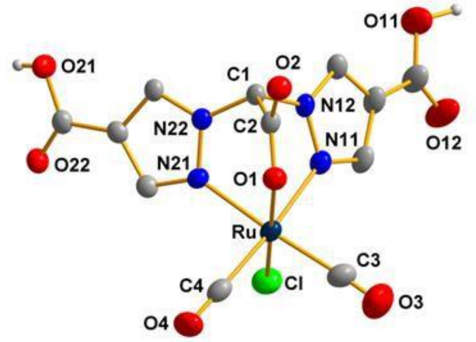
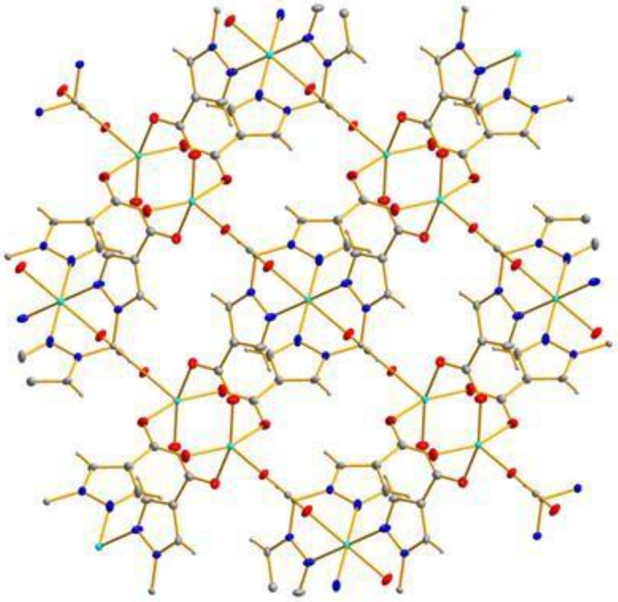
Since their introduction by Otero *et. al.* in 1999, the heteroscorpionate ligand class of bis(pyrazol-1-yl)acetic acids has been investigated extensively by several groups. The most commonly known of these ligands, bis(pyrazol-1-yl)acetate (bpza) and bis(3,5-dimethyl-pyrazol-1-yl)acetate (bdmpza), have been coordinated to a considerable number of transition metals, so far. Recently, our group reported on some p-block metal complexes e.g. of gallium(III) and tin(II).[1] To pursue this topic further and to gain insight into the coordination behavior of these ligands towards other group 13 and 14 metals, we now focused on various new aluminum(III), gallium(III), indium(III), germanium(II) and tin(II) complexes.

In another project bis(4-carboxylpyrazol-1-yl)acetic acid (H_3bcpza) and bis(3,5-dimethyl-4-carboxylpyrazol-1-yl)acetic acid (H_3bdmcpza) have been synthesized. These ligands offer a scorpionate carboxyl group for κ^3-*N,N,O* metal coordination next to two peripheral carboxyl groups that significantly enhance the water solubility of the corresponding complexes.[3]

Apart from this, the H_3bcpza ligand also allows the formation of metal organic frameworks (MOFs) with water capacities up to 29 wt%.[4]







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OC16 Bioinspired Hydrogen Production via N-non-Innocent Ligands

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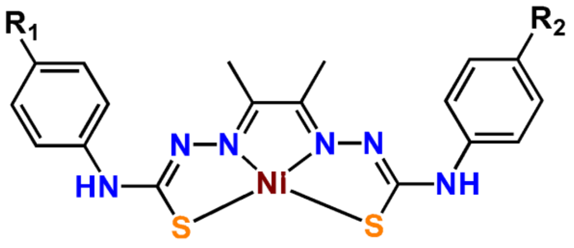
Hydrogen is the most abundant element in the universe and is considered an “ideal” fuel because, when burned, only water vapor is released into the environment. In recent years, efforts have been made to develop new methods to generate H_2 from renewable and sustainable resources, such as electrocatalytic and photocatalytic hydrogen evolution (HER) reactions [1].

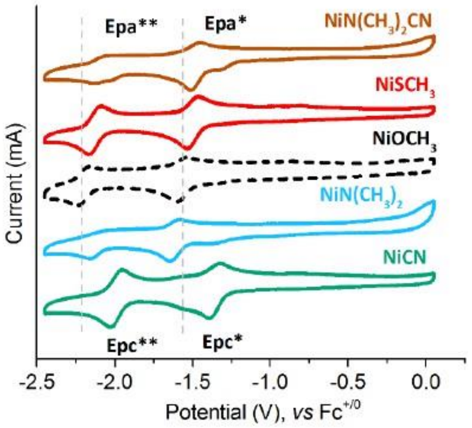
We have been working for several years on the use of nickel bis-thiosemicarbazone (NiTSC-R) complexes and their use as electrocatalysts in HER. The first molecule tested, NiTSC-OCH3, was found to be one of the best catalysts compared to the literature [2]. Substitution of the methoxy groups ($-OCH_3$) gave us new complexes to study, three symmetrical and one asymmetrical [3]. The thiomethyl group ($-SCH_3$) gave the improved results.

Some new substitutions on the phenyl ring, but not only, will be presented as well.

Mechanistic insights, thanks to DFT calculations, will be detailed.



R_1= R_2= -CN, -N(CH_3)$_2$, -OCH_3., -SCH_3
R_1= -CN R_2= -N(CH_3)$_2$



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OC17 [NiX_2/N-ligand]-Catalyzed Allylation Reaction using Allylic Alcohols in the Presence of CO_2

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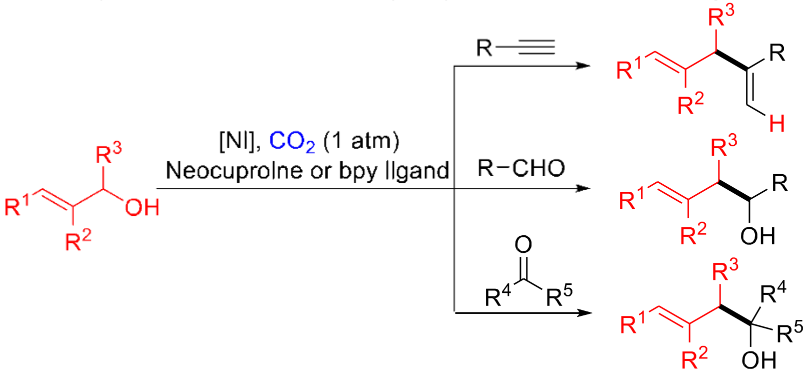
Allylation reaction is one of the most fundamental and productive C−C bond-forming transformations, as the allyl group can provide a useful handle for further manipulation. Utilizing alcohols bearing higher C-O bond dissociation energy in the cross coupling-electrophile protocol is not only chemically challenging but also avoids the cumbersome preparation of esters, troflates or tosylates from alcohols.[1] On the other hand, carbon dioxide (CO_2) is a nontoxic and abundant chemical and has been widely used as a C1 building block for the synthesis of highly important chemicals. CO_2 also has the ability to trigger changes in the chemical properties of certain chemicals without being incorporated into the product, namely CO_2 as a promoter/catalyst can potentially replace toxic reagents that are used in the fine chemical and pharmaceutical sectors.[2] Herein, we would like to report [NiX_2/N-ligand]-catalyzed allylation reaction using allylic alcohols in the presence of CO_2.



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OC18 Supramolecular Lanthanide-Containing Cages: Insight into the Formation Mechanism

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In supramolecular chemistry, lanthanide cations may play an important role as building blocks in functional devices, and many appealing assemblies incorporating Ln(III) were already designed and described. A part of these compounds relies on the use of tripodal ligands that are particularly suited for building polynuclear edifices, such as tetranuclear helicates.[1] Indeed, such polydentate nitrogen containing ligands allow efficient coordination of Ln(III) and fine tuning of their properties.

Although the most of multicomponent molecular edifices have been characterized from the structural point of view in solid state as well as in solution, thermodynamic and especially kinetic data are quite scarce for such complex systems. Since lanthanide cations usually form labile complexes, the reaction kinetics is fast and more difficult to access with conventional spectrophotometry. Instead, a stopped flow device can be applied to ensure a fast mixing of ligands with Ln(III).

In this contribution we mainly focus on kinetic aspects of the formation of tetranuclear Ln(III) cages that were previously designed by us.[2,3] We will present new kinetic data recorded for fast initial complexation as well as for slower re-equilibrating steps leading to polynuclear species.[4] We will also discuss different parameters affecting these processes, such as the role of anions.[5] Finally, we will attempt to rationally reconstruct a self-assembly mechanism reflecting our investigations.

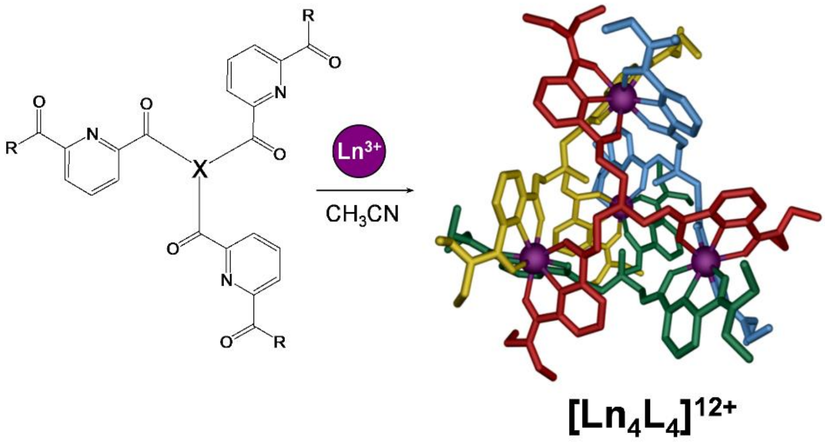

Figure 1: Self-assembly of supramolecular cages with Ln(III) as building blocks.

This work was supported by CNRS and the Ligue contre le cancer.

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OC19 Dinuclear Iron Complexes with Pyridine Ligands as Promising Anticancer Agents

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The commercial and inexpensive dimer [$Fe_2Cp_2(CO)_4$] (Cp = η^5-C_5H_5) represents a convenient starting material to access a variety of di-organoiron structures taking advantage of cooperative effects arising from the dimetallic scaffold.[1] Cationic complexes with bridging (hetero)-carbyne ligands are easily available from multigram scale synthesis and offer much opportunity for ligand diversity. We prepared new derivatives with terminal pyridine ligands, which display sufficient aqueous solubility and outstanding stability in physiological-like solutions (Figure 1). They exert a potent antiproliferative activity in vitro against a panel of cancer cell lines and significant selectivity compared to noncancerous cells. When applied in vivo under therapeutic conditions, **FETPY** led to a substantial reduction of tumor volume and animals subjected to treatment in both tumor models showed no visible signs of toxicity.[2]

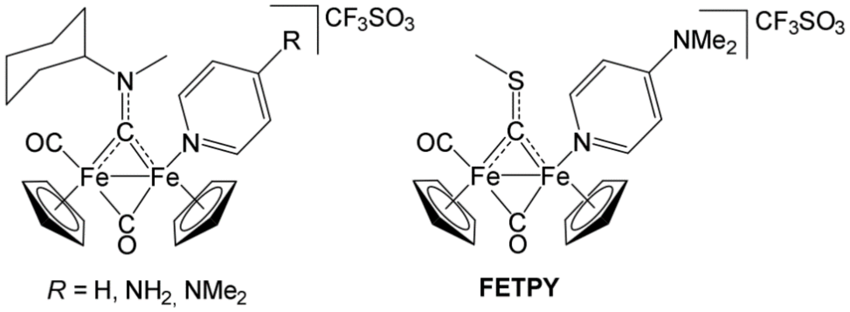

Figure 1. Diiron complexes with bridging carbyne and terminal pyridine ligands with promising anticancer activity.

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OC20 Antimicrobial Properties of Porphyrins and Corroles Functionalized with Carboxylic Acids

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

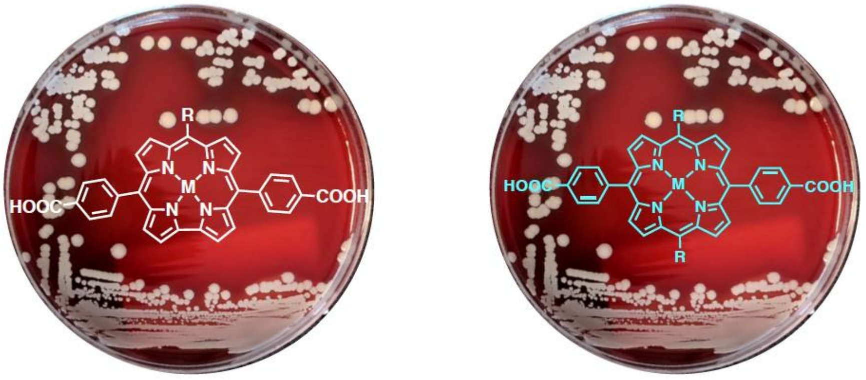

Figure 1: corroles *versus* porphyrins

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OC21 Porphyrins and Schiff Bases Combination: Anything New ?

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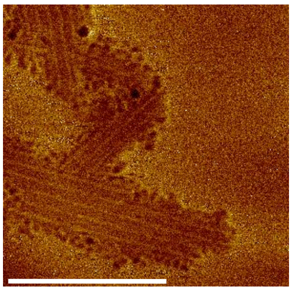
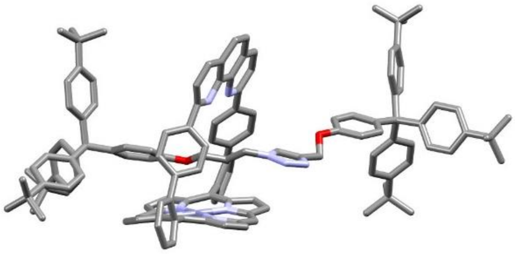
Over the last 30 years our group made an extensive use of strapped porphyrins structures. The introduction of a phenanthroline (phen) strap on a porphyrin core leads to the presence of six binding nitrogen atoms in a ditopic ligand that is significantly geometrically constrained. This phen strapped porphyrin found applications in selective imidazole recognition,[1] in the self-assembling of wire-like structures (left Figure),[2] in the synthesis of photoactivable rotaxanes (right Figure)[3,4] and as hetero-bimetallic hemoprotein active sites.[5]

In the past couple of years, the advantage of the rigidity imposed by the phenanthroline, especially when coordinating copper (II/I), was questioned and its replacement by bipyridine or other binding sites has now been addressed in several studies.





Synthetic consequences of the phenanthroline replacement by bipyridine will be detailed in the presentation. On the bio-inspired side, the introduction of terpyridine and bipyridine straps via self-assembly and the comparative properties of two water soluble cytochrome *c* oxidase models will be presented, as well as new structures involving the historical phenanthroline strapped porphyrin.

Over the years, this work was supported by the CNRS and the University of Strasbourg, the French Ministry of Research, the JSPS and a JST/ANR research grant.

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OC22 Turning on the Excited State Properties of a Cu(I)-Phenanthroline Complex by Covalent Binding of the Ligand Inside a Silica Matrix

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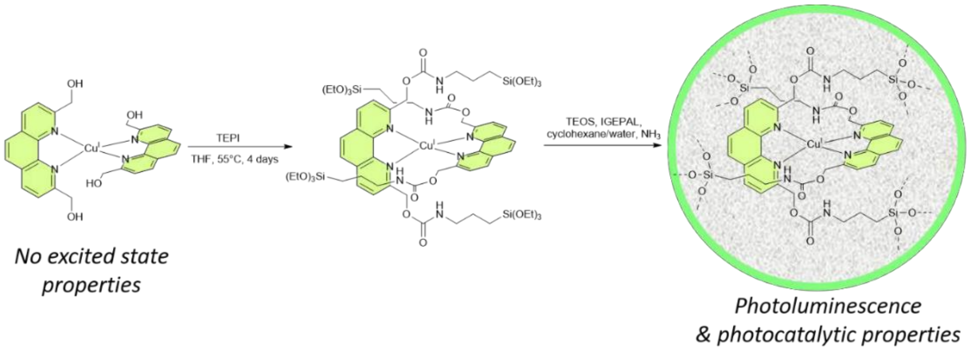
Copper(I)-diimine complexes CuL_2^+ (where L is a diimine sterically burdened in α of the nitrogen atoms) are very intriguing, cheaper and less noxious alternatives to ruthenium photosensitizers, featuring surprisingly similar properties. But the structural and photophysical properties of these complexes are severely threatened by exogenous ligands (e.g. solvent molecules).[1] In order to address these issues, we have trapped CuL_2^+ inside a rigid silica matrix (Scheme 1): by “freezing” the environment around the complex, the photophysical properties are enhanced and the structure is preserved *vs.* ligand scrambling. We report here the sol-gel micelle-assisted synthesis and the photophysical study of silica nanoparticles (from 12 to 25 nm diameter) embedding CuL_2^+ complexes within their core. L is a phenanthroline ligand, sterically burdened in positions 2 and 9 by linkers bearing alkoxysilane groups. During the sol-gel process, the complex is thus fully integrated within the walls of silica. We describe the morphological and photochemical studies of the obtained nanoobjects $CuL_2@SiO_2$. Summarily, the latter exhibit strongly improved properties compared to the corresponding free-standing molecular complex CuL_2^+. For example, $CuL_2@SiO_2$ is luminescent whereas CuL_2^+ is not.[2] In addition, the excited state properties of $CuL_2@SiO_2$ can be exploited in organic photochemistry (e.g. reductive dehalogenation) making it an efficient and durable new photocatalyst with many potential applications.



Scheme 1. Strategy developed to enhance the stability and photophysical properties of copper(I) complexes

This work was supported by the ANR (18-WTW7-0006-05) and the EU Water JPI 2018

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OC23 Metal-Peptidic Cages – Helical Oligoprolines Generate Highly Anisotropic Nanospaces with Emergent Isomer Control

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Advances in metal-organic cage self-assembly have enabled the construction of of increasingly complex, discrete three-dimensional architectures reminiscent of proteins from simple building blocks.[1] The current state-of-the-art, however, is almost exclusively built from rigid and flat aromatic panels, limiting binding selectivity and, often, water solubility.

Herein, we disclose a new class of cages - metal-peptidic cages - which utilise water-soluble, chiral and helical oligoproline strands of varying length with pyridine coordinating motifs, to generate highly anisotropic nanospaces.[2,3] We demonstrate the assembly of a range of Pd_2L_4 cages, with lengths from c. 1 - 4 nm, and find formation of the *cis* isomer of the cage is strongly favoured - an emergent property of using complex and chiral building blocks in the formation of defined nanospaces. Further, the use of biologically relevant components enables targeted binding of therapeutic molecules, highlighting the potential of these systems for selective drug delivery. Finally, we report recent breakthroughs in self-sorting, hierarchical assembly, and biological applications.

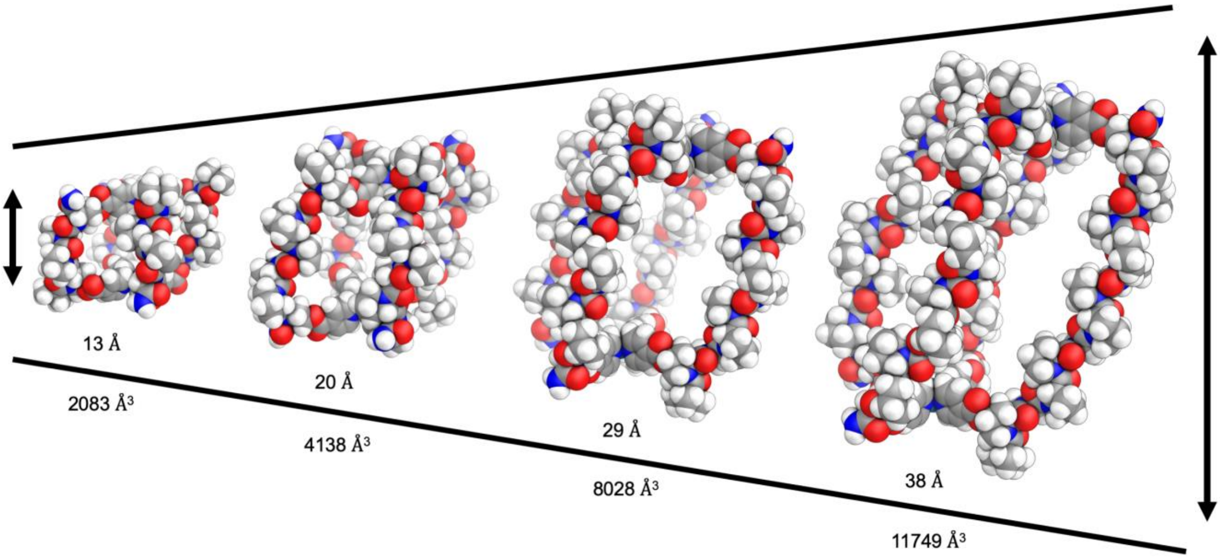

Figure 1. Metal-Peptidic Cages

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OC24 Allosteric Control of the Assembly of [2]Rotaxanes Thanks to a Multi-Site bis(Zn(II)-Porphyrin) Cage

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Mechanically interlocked molecules (MIM), used in a large variety of applications, are supramolecular assemblies in which at least two covalent subcomponents are held together not through a conventional covalent bond but through a mechanical one.[1] The assembly of [2]pseudorotaxanes or [2]rotaxanes by threading a molecular axis through a ring, by slipping the ring over a stopper, by clipping the ring precursor around a dumbbell, or by using a template to gather the ring and the string components requires specific interaction sites on both precursors.[1,2]

Allosteric control of the threading step by the binding of effectors to additional sites has seldom been reported.[3] To this purpose, a flexible covalent cage, endowed with two zinc(II) porphyrins and eight peripheral 1,2,3-triazolyl ligands,[4] is of particular interest, since it provides increased preorganization for a higher stabilization of the threaded species compared to simple macrocycles and extra sites to govern allosteric effects. The principle of this allosterically driven assembly of semirotaxanes is given in Figure 1. It was recently demonstrated by NMR studies.[5] This step can be followed by the addition of the second stopper to form the corresponding [2]rotaxane.

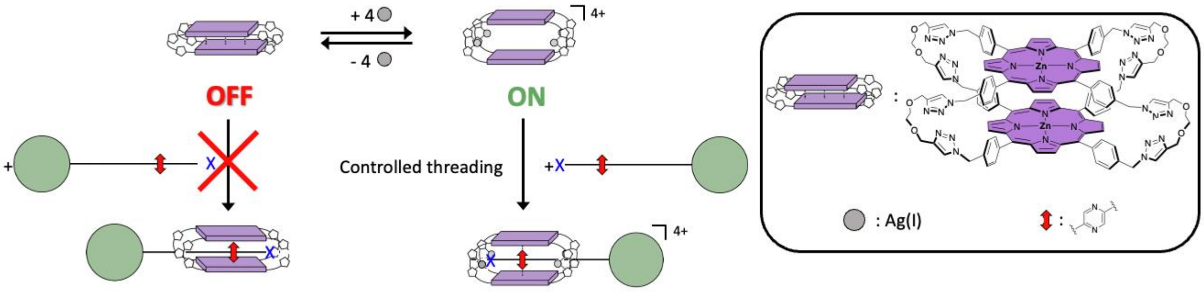

Fig. 1: Allosteric control of half-dumbbell threading through a molecular cage receptor.

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OC25 Application of *meta*-Nitrosocalix[4]arenes in Supramolecular Chemistry

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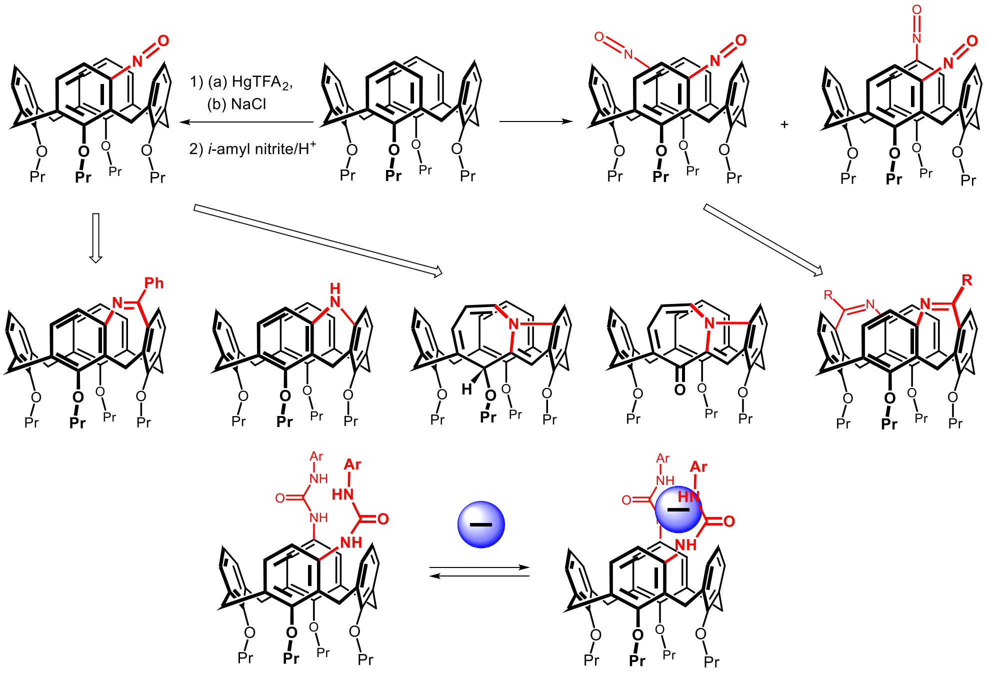
Direct mercuration[1] of calix[4]arenes allowed us to address hitherto virtually inaccessible *meta* position[2] of the macrocyclic skeleton. As we found, the -HgCl group can be smoothly substituted by *in situ* generated nitrosyl chloride to yield the corresponding nitrosocalixarenes. These inherently chiral compounds represent the starting point for the preparation of many calixarenes with unprecedented structures (Scheme).[3] Moreover, the *meta* substitution of calix[4]arenes dramatically changes dynamic behaviour of these compounds in solution as documented by various NMR techniques. A simple reduction into the amino functions allows the construction of new urea-based ligands exhibiting interesting complexation properties towards anions.



This work was supported by Czech Science Foundation 23-07154S.

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OC26 Enabling a Bioinspired *N,N,N*- Copper Coordination Motif through Spatial Control in UiO-67: Synthesis and Reactivity [1]

Mohamed Amedjkouh*[1,2] Isabelle Gerz,[1,2] Erlend S. Aunan,[1,2] Valeria Finelli,[3,4] Mouhammad Abu Rasheed,[1,2] Gabriele Deplano,[3] Rafael Cortez S. P.,[1,2] Inga L. Schmidtke,[1,2,5] David S. Wragg,[1,2] Matteo Signorile,[3] Knut T. Hylland,[1,2] Elisa Borfecchia,[3] Karl Petter Lillerud,[1,2] Silvia Bordiga,*[3] Unni Olsbye,*[1,2]

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Metal-organic frameworks (MOFs) featuring zirconium-based clusters are widely used for the development of functionalized materials due to their exceptional stability. In this study, we report the synthesis of a novel N,N,N-ligand compatible with a biphenyl dicarboxylic acid-based MOF.[2] However, the resulting copper(I) complex exhibited unexpected coordination behaviour, lacking the intended trifold coordination motif. Herein, we demonstrate the successful immobilization of a bioinspired ligand within the MOF, which preserved its crystalline and porous nature while generating a well-defined copper site. Comprehensive spectroscopic analyses, including X-ray absorption, UV/Vis, and infrared spectroscopy, were conducted to investigate the copper site and its thermal behaviour. The immobilized ligand exhibited the desired tridentate coordination to copper, providing access to a coordination motif otherwise unattainable. Notably, water molecules were also found to coordinate to copper. Upon heating, the copper centre within the MOF exhibited reversible dehydration, suggesting facile creation of open coordination sites. Furthermore, the copper site displayed reduction at elevated temperatures and subsequent susceptibility to oxidation by molecular oxygen. Lastly, both the molecular complexes and the MOF were evaluated as catalysts for the oxidation of cyclohexane using hydrogen peroxide. This work highlights the successful immobilization of a bioinspired ligand in a zirconium-based MOF, shedding light on the structural features, thermal behaviour, and catalytic potential of the resulting copper sites.

This work was supported by the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement Nº 856446 (CUBE)).

[1] Accepted for publication in *Dalton Trans*. **2024**.

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OC27 Two Metal Ions Inside a Porphyrin Core – Activation of Metal-Metal Interactions

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Agata Białońska

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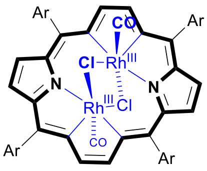
The porphyrin macrocycle with the four-nitrogen donor coordination core is rarely a ligand for more than one transition metal ion, and a single porphyrin macrocycle has rarely been used as a platform for a metal-metal bond investigation. The potential of porphyrinoid chemistry to construct binuclear species with two metal ions driven into close proximity was recently discovered with the synthesis of 21,23-dirhodaporphyrin **1**.[1] This aromatic and stable porphyrin contains two metal atoms incorporated into the porphyrin skeleton *in place of two NH* groups. The bridged Rh_2Cl_2 unit with two metal centres located approximately in the macrocyclic plane contains two 18-electron rhodium(III) ions surrounded by octahedral environments. Molecule **1** is formally derived from a porphyrin-annulene hybrid, 21,23-divacataporphyrin **2**.[2] However, the synthetic route began with 21,23-ditelluraporphyrin **3**,[3] and involved two heteroatom exchange steps.



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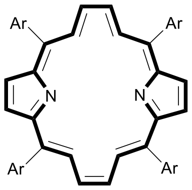

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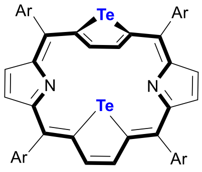

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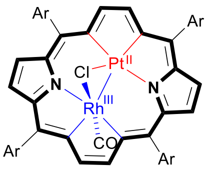

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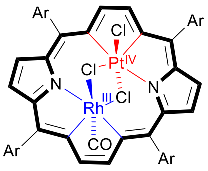

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Similarly, a substitution of two tellurium atoms for different transition metal atoms resulted in the formation of two 21-platina-23-rhodaporphyrins, **4** and **5**.[4] The degree of metal-metal interaction varied depending on the oxidation state of platinum. The Natural Bond Orbital (NBO) bond order of Pt–Rh equals 0.15 in **4**, with a platinum(II) center and 0.04 for **5**, which contains platinum(IV).

This work was supported by the National Science Center (grant 2020/37/B/ST4/00869) and Wroclaw Centre for Networking and Supercomputing, Grant 329.

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OC28 Viologen/Cobalt(Terpyridine)$_2$ Based Molecular Wires

Lacroix Jean Christophe,[1] Yara Al Chami, Frederic Lafolet, Romeo Bonnet,
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Thin layers of fully conjugated oligomers incorporating viologen (1) and cobalt terpyridine complexes (2) with thicknesses between 3 and 14 nm have been deposited on gold electrodes by electrochemical reduction of a diazonium salt, and used as active layers in a solid-state large area molecular junction (MJ). The devices show symmetric J–V curves and highly efficient long-range transport, attenuation factor as small as 0.25 nm–1 and record high current density. This is attributed to the fact that the oligomers are fully conjugated, strongly coupled to the electrodes and that their LUMO or HOMO energy lies between the energies of the Fermi levels of the two contacts and that the layers incorporate mobile ionic species. As a consequence, injection barrier at the interfaces are low and resonant tunneling combined to redox hopping prevails for all investigated thickness. Adding Cobalt terpyridine complexes in the transport path leads to enhanced transport properties and this effects will be discussed

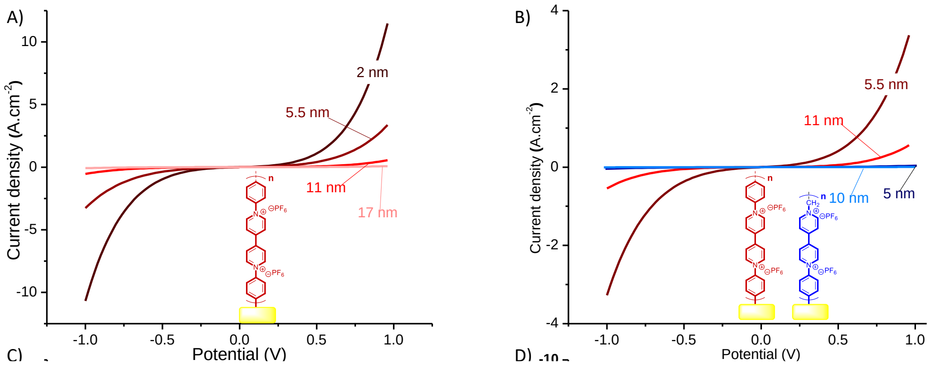

Figure 1: A) Superposition of averaged JV curves for different wide area junctions formed by Ph-VIO-Ph of various thicknesses 2 nm (black) 5.5 nm (wine) 11 nm (red) 17 nm (pink). B) Averaged JV curves representing the Au/Me-VIO/Ti/Au system (shades of blue) compared with those for the Au/Ph-VIO-Ph/Ti/Au system (shades of red) taken at ±1 V.

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OC29 Chiral Truxene-Based Self-Assembled Cages: Triple Interlocking and Supramolecular Chirogenesis

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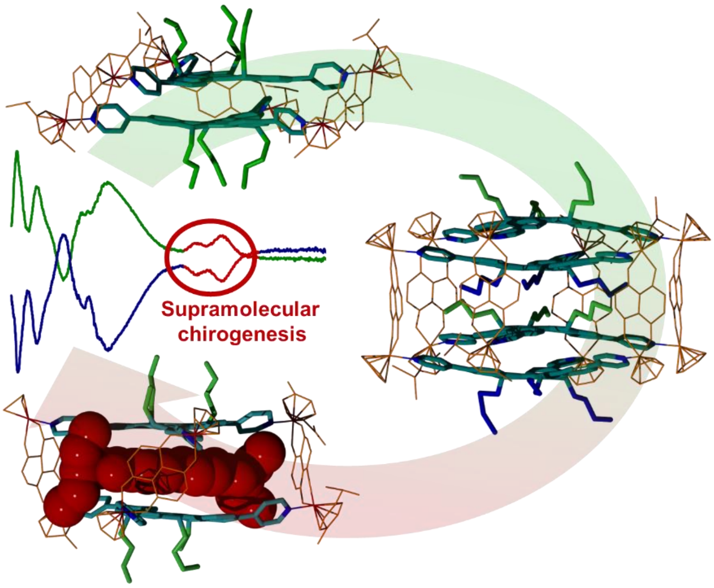
The coordination-driven self-assembly strategy is remarkably efficient for building sophisticated discrete polygons and cages by association under thermodynamic control of polytopic ligands and complementary metal complexes.[1] Those systems inherently feature a cavity, prone to be used for host-guest purposes.[2,3] Topologically more complex assemblies have appeared recently in the literature: interlocked cages. Similarly, to the class of [2]-catenanes, interlocked cages are based on interpenetrated systems. Whilst the first examples were essentially produced by serendipity as by-products along the metal-driven self-assembly process of discrete cages, the rationalization of their formation is subject to an intense attention.[4,5] On the other hand, a growing interest has emerged in the development of chiral host molecules since enantioselective interactions may occur with chiral guest molecules, a situation of interest for enantioseparation, asymmetric catalysis, or chiral sensing.[6,7]



In this context, we have shown that a chiral truxene-based ligand can be engaged in a self-assembly process to produce a chiral cage whose cavity allows for i) producing a chiral interlocked species and ii) binding achiral molecules with chirogenic behavior.[8]

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OC30 Pd(II)-Catalyzed Ethylene/Methyl Acrylate Copolymerization: Toward Catalyst Recycling.

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During the last two decades Pd(II)-based Brookhart-type complexes, of general formula [Pd(Me)(MeCN)(N-N][PF_6] (N-N = α-diimines) (Figure 1a), have been extensively studied as homogeneous catalysts for the copolymerization of ethylene with polar vinyl monomers, such as acrylic esters, to produce functionalized polyolefins (**FPO**),[1,2] very interesting macromolecules that could represent an environmental- friendly improvement with respect to simple polyolefins.[3]

Whereas, in catalytic systems reported in literature, dichloromethane (**DCM**) is the typical reaction medium, we have recently discovered that working in 2,2,2-trifluoroethanol (**TFE**) positively affects both catalyst activity and macromolecule microstructure.[4]

We have now investigated the role of the reaction medium in the target ethylene/methyl acrylate copolymerization, by carrying out the catalysis in **DCM**/**TFE** mixtures. We have discovered that when mixtures of specific composition are used, the spontaneous separation of two phases takes place at the end of the copolymerization runs (Figure 1b), with the upper layer mainly formed by **FPO** and the catalyst confined in the lower layer.

Starting from this unprecedented phenomenon, we have been able to establish a protocol to effectively separate the two layers and recycle the lower one. The catalyst resulted to be active up to three cycles and, more importantly, the obtained copolymer was made by macromolecules with always the same microstructure, thus indicating the same nature of the active species.

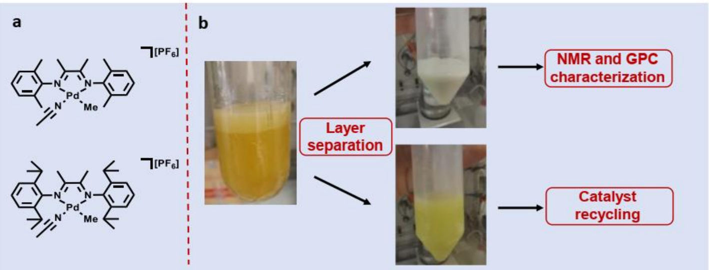

Figure 1. **(a)** Pd(II)-based Brookhart-type complexes. **(b)** New protocol for catalyst recycling.

This discovery results very promising since catalysts for polyolefin synthesis usually remain embedded into the macromolecules and are never recovered and recycled.

Acknowledgement:
MUR (PhD PON Program) is acknowledged for the fellowship (K.A.H.).

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OC31 Phosphonate-substituted *N*-donor Ligands for Efficient and Sustainable Photocatalysis

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Visible light-mediated photocatalytic reactions have garnered enormous interest over the last two decades as they offer unconventional synthetic strategies for the preparation of complex organic compounds with diverse functional groups, simultaneously addressing the growing demand for renewable energy usage. However, several notable drawbacks still need to be addressed to make these reactions truly suitable for achieving the ultimate goals of sustainable chemistry and industrial production. The optimization of available photocatalysts has emerged as a crucial objective in the development of photocatalysis, aiming for shorter irradiation times, reduced photocatalyst loading, and the use of more environmentally friendly solvents. *N*-containing ligands play a particular role in the development of this field because efficient photocatalysts generally incorporate these ligands.

In this work,[1–3] we discuss how the introduction of phosphonate groups Ru(II) complexes, bearing *N,N'*-bipyridine-type ligands, and porphyrins, both renowned for their remarkable photophysical properties, serves to enhance the efficiency of classical*meso*-tetraphenylporphyrins and $[Ru(bpy)]_3$ photocatalyst.

The synthesis of the phosphonate-substituted ligands and the corresponding complexes (Figure) is discussed. Next, their efficiency in typical photocatalytic processes, such as photoredox catalytic transformations of *N*-aryl-1,2,3,4-tetrahydroisoquinolines and selective oxidation of sulfide to sulfoxide by molecular oxygen, is demonstrated. Finally, we show that the introduction of phosphonate substituents allows for the recycling of photocatalysts through liquid–liquid phase separation processes or through grafting these photocatalysts onto mesoporous titanium(IV) oxide. Several examples of processes involving efficient recovery and reuse of the photocatalysts are provided.

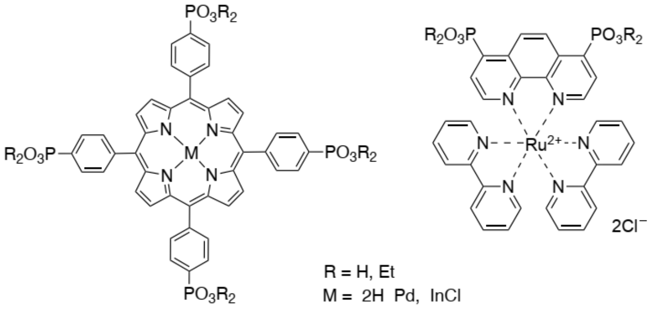

Figure. Examples of phosphonate-substituted complexes studied in this work.

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OC32 Porphyrins as Programmable Components for Artificial Photosynthesis.

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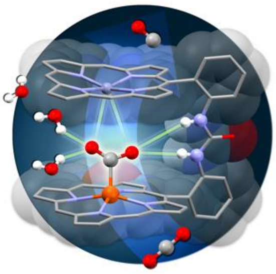
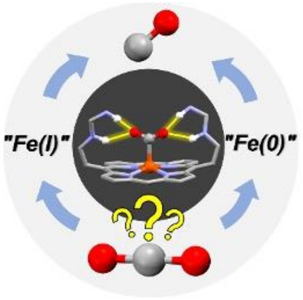
We developed porphyrin based catalysts to cover the three aspects of artificial photosynthesis, ie. light induced electron transfer processes,[1] catalyst for CO_2 reduction[2] and water oxidation. We have found that bringing urea groups as a two point hydrogen bonding clefts on the periphery of the porphyrinic ring can boost the CO_2 reduction at lower overpotential.[3,4] Another grand challenge of the CO_2 reduction is the presence of O_2. O_2 often kills the catalyst! We will expose our approach to realize this challenge task.





Acknowledgements: This work was supported by the ANR, CNRS, Université Paris-Saclay, CEA-Saclay and Institut Universitaire de France

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OC33 Electronic Fine-Tuning of Ruthenium(II) Catalysts

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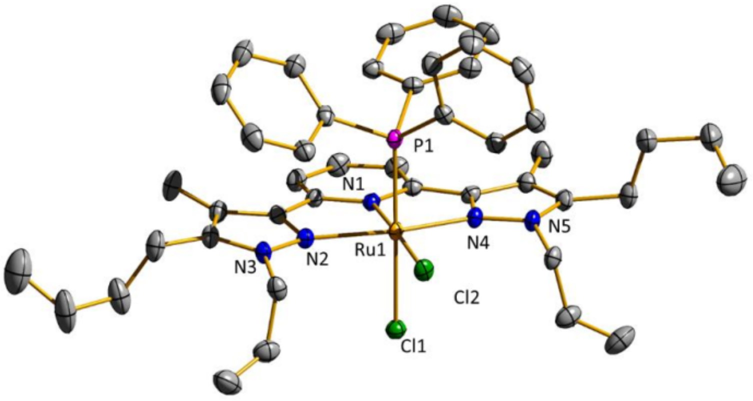
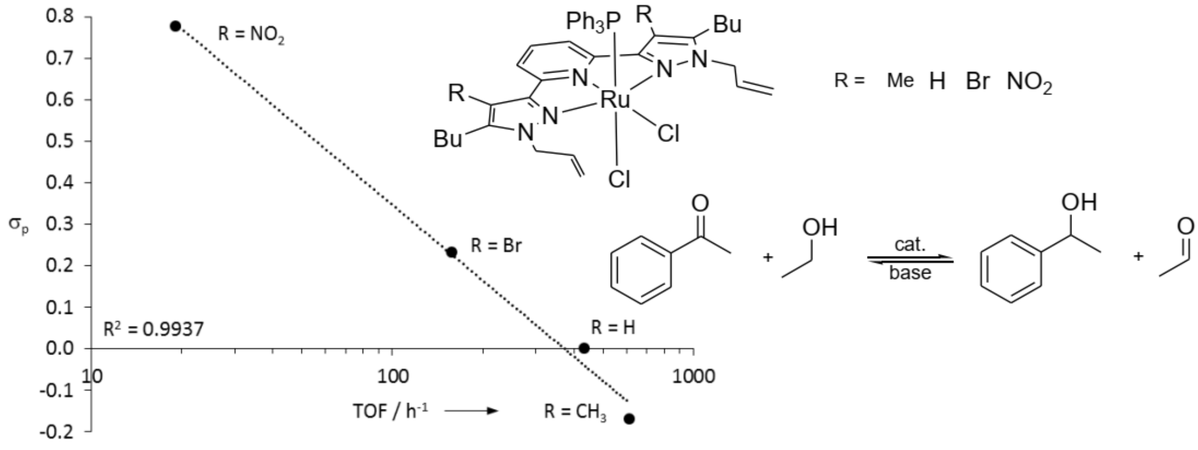
Since the properties of chemical compounds follow their structure, the quantitative description of structure-reactivity relationships is of fundamental importance in chemistry.

The presentation reports a detailed study of the electronic influence of backbone substituents of 2,6-di(pyrazol-3-yl)pyridine-type ligands on the catalytic performance of a particular class of ruthenium(II) complexes (molecular structure: see below). We correlate the Hammett parameters of the substituents with spectroscopic data of the ruthenium complexes and with reactivity data obtained from the catalytic transfer hydrogenation of carbonyl compounds with ethanol as the hydrogen source. This, in combination with DFT calculations, allows a detailed insight into the mechanism of this transformation and also allows the prediction of the catalytic activity of yet unknown members of this class of ruthenium complexes.[1,2]





This work was supported by the EU-INTERREG project BIOVAL.

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OC34 New Triazamacrocycle-Based Chelates for Potential Ga^{3+} Radiopharmaceuticals

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David Esteban-Gómez,[5] Carlos Platas-Iglesias,[5] Gyula Tircsó,[3] Eszter Boros,[2]
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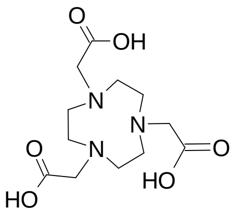
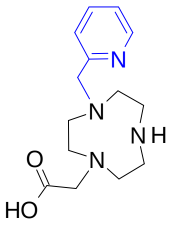
Ga^{3+} is a metallic cation of interest in nuclear medicine with two radioisotopes that possess nuclear properties well-suited for radiopharmaceutical applications: ^{68}Ga, a β$^+$ emitter used in PET (Positron Emission Tomography), and ^{67}Ga, a γ-emitter for SPECT (Single-Photon-Emission Computed Tomography) together with Auger electron emission.[1]

For safe *in vivo* applications, these radionuclides have to be encapsulated in chelators and the resulting chelates need to present high thermodynamic stability and kinetic inertness. Cyclic polyamines are well-known for their capacity to furnish complexes that can meet these conditions. As example, H$_3$**nota** is considered as one current golden standard chelator for Ga^{3+} because of the interesting thermodynamic stability of the neutral [Ga(nota)] chelate.[2] Improvement of these physicochemical characteristics and developments of the usual chelates for the *in vivo* applications are permanently an important issue in a personalised medicine evolution point of view explaining that research about new cyclic polyamine chelates remains a highly active sector.

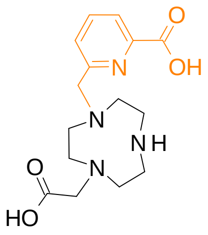
In this perspective, two new nota derivatives, namely H**noapy** and H$_2$**noapa**, have been synthesised, using regiospecific N-functionalisation method of the tacn platform. Their Ga^{3+} complexation has been performed, their thermodynamic properties studied and compared to those of H$_3$**nota**. Radiolabeling with ^{67}Ga has been explored and stability of the radiolabeled chelates has been carried out by competition with human serum transferrin.[3] These different results will be presented.



H$_3$**nota**



H**noapy**



H$_2$**noapa**

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OC35 Plasmonic Au-Nanocatalysts Based on Porphyrins for the N-Dealkylation of Amines

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Metallic nanoparticles (NPs) have many useful properties, in particular some NPs have unique optical qualities while interacting with light known as surface plasmon resonance (SPR). The localized surface plasmon resonance (LSPR) phenomenon refers to the collective electron oscillations in metal nanomaterials upon light excitation. This generates a thin zone (a few nm) of influence around the nanomaterial where physical and chemical processes are spectacularly enhanced.[1] Catalysis is widely used to accelerate reactions and reduce waste in synthetic chemistry. While diverse catalysts exist for enhancing organic reactions, some still demand high energy and lengthy reaction times for decent conversions. In this frame, we thus explore how LSPR can enhance challenging catalytic reactions. In our strategy we associate an efficient known molecular catalyst with LSPR to develop new plasmonic nanocatalysts. This consists in grafting the molecular catalyst onto metal nanostructures, thereby immersing the catalysts within the LSPR sphere of influence. This subjects them to the advantageous effects of LSPR, consequently boosting their catalytic activity (faster kinetics and reduced energy consumption).[2,3] Among the numerous possible catalytic reactions, we focus in this contribution on the N-dealkylation of amines, which is particularly interesting for the decontamination of opioids-polluted water. This process is catalyzed by Co-porphyrin, well-known tetrapyrrolic N-ligand.[4,5] The catalytic conditions however require high temperatures. The aim of this work is thus to prepare a metal porphyrin catalyst bearing a thiolated anchoring group to be grafted onto LSPR gold nanoparticles to provide a plasmon-based catalyst for the room temperature N-dealkylation of amines.

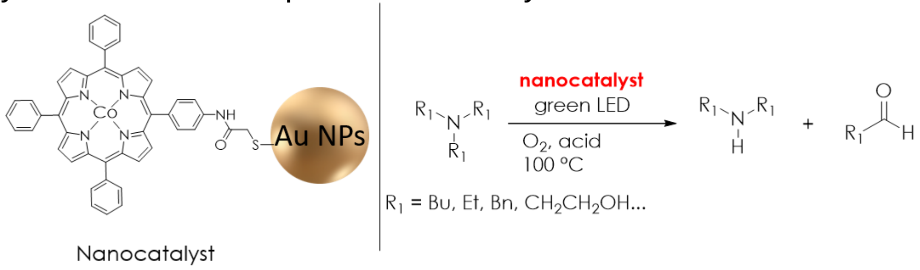

Figure 1. Structure of the nanocatalyst synthesized in this work (left) for plasmon mediated molecular catalysis (right)

This work was supported by the EUR LUMOMAT project and the Investments for the Future program ANR-18-EURE-0012

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OC36 Probing Uranyl Reduction Chemistry with a Tripodal Pyrrole-Imine Ligand

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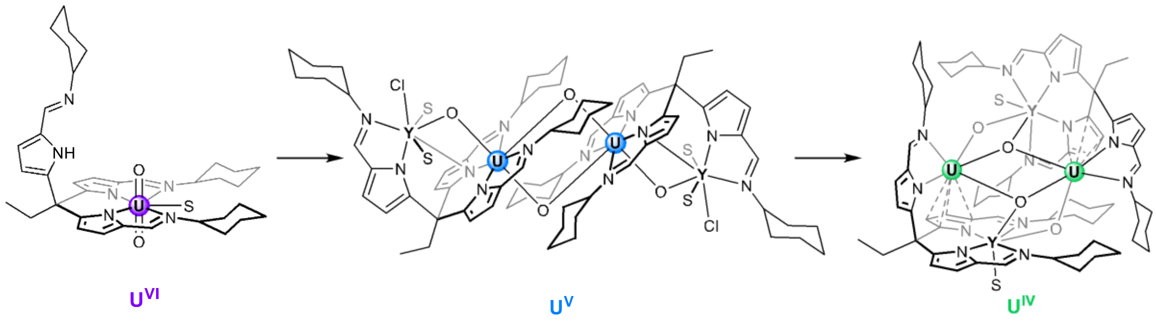
As the least radioactive and most readily available actinyl ion ($[AnO_2]^{n+}$) the uranyl dication $[UO_2]^{2+}$ is by far the most studied. It is the most thermodynamically stable form of uranium found in the environment and is a soluble and problematic environmental contaminant from nuclear waste. It exhibits U-O bonds that are particularly strong making the uranyl oxo groups chemically inert and difficult to functionalise.

The single-electron reduction of $[U^{VI}O_2]^{2+}$ to the monocation $[U^{V}O_2]^{+}$ is achieved by microbes under anaerobic conditions, but is unstable in aqueous conditions and disproportionates to U(VI) and U(IV) species.[1, 2] This disproportionation process is thought to proceed through interaction of the oxo groups on adjacent uranyls, with this cation-cation interaction (CCI) allowing electron transfer between the metals. These CCIs are also seen in heavier actinyls, that are components of nuclear waste, and have the potential to disrupt separation processes such as PUREX.[3]

Here we present a flexible tripodal pyrrole-imine ligand that facilitates the controlled and sequential single-electron reduction of the uranyl dication from the U(VI) oxidation state to U(V), and further to U(IV).This ligand architecture allows us to probe both metathesis reactions of the U(V) CCI complex to form new hetero-tetrametallic uranyl(V) complexes that are stable to disproportionation, and also the mechanism of uranyl reduction, a process that is important in understanding its environmental remediation.



This work was supported by The University of Edinburgh EaStCHEM School of Chemistry and the UK Engineering and Physical Sciences Research Council (EPSRC).

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OC37 Self-Assembling Supramolecular Dendrimers Bearing N-Ligand Terminals for Biomedical Applications

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Nitrogen Ligands play important roles in coordination chemistry, bioactive compounds and materials, as well as non-covalent interactions and supramolecular assemblies. In our effort to explore self-assembling supramolecular dendrimer nanosystems for biomedical applications, we have developed a series of amphiphilic dendrimers bearing various N-ligands such as amines, guanidines, carbohydrates, NOTA and DOTA cages.[1] These dendrimers self-assemble into nanomicelles and readily interact with nucleic acids, proteins and lipids via H-bond and electrostatic interactions, exhibiting excellent performance for drug and nucleic acid delivery[2] as well as antimicrobial activity[3]. The dendrimers bearing NOTA and DOTA cages are able to chelate with the metal ions for tumor imaging using positron emission tomography and magnetic resonance imaging, outperforming the clinical references.[4] We will highlight these results to showcase the versatile applications of N-ligands coupled with dendrimer nanotechnology in biomedical applications.

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OC38 Re-purposing the Reactivity of Metalloporphyrins

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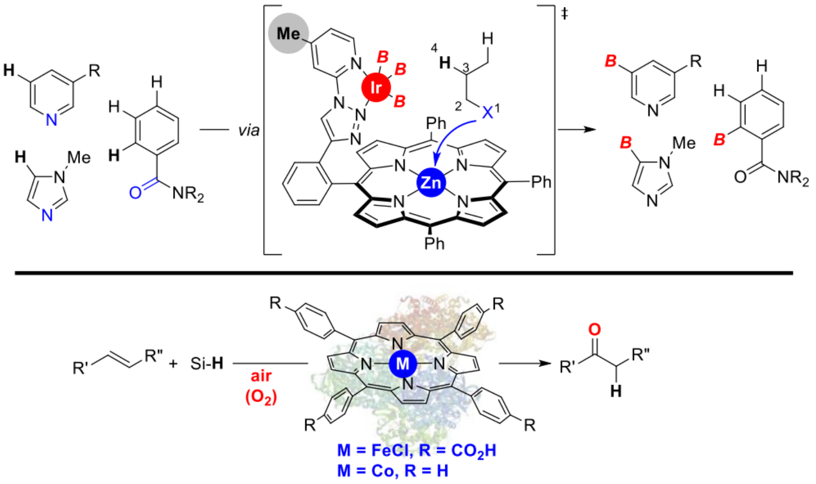
Inspired by the hydroxylase activity of cytochromes P-450, exploiting the metal embedded in metalloporphyrins for catalysis has led to unique breakthroughs.**[1]** On the other hand, metalloporphyrins, typically those derived from zinc, are known to engage in weak coordination chemistry with polar organic compounds, usually nitrogen- containing ones.**[2]** We have exploited this behaviour by engineering catalytically productive iridium active sites in the periphery of the porphyrin whilst the embedded zinc centre serves for substrate-binding *via* remote Zn•••N or Zn•••O=C interactions.**[3]**

The precise distance between the active site and the substrate binding site dictates the selective C-H functionalization for challenging substrates.**[3]** The enzyme-like behaviour of these supramolecular catalysts will be discussed.**[3]** Lastly, the oxidase behaviour of iron- and cobalt-porphyrin catalysts for the industrially-relevant Wacker-type oxidation of olefins into ketones will be shown,**[4]** which is important for replacing the scarce, expensive and toxic palladium catalysts.**[5]** The oxidation reactions, which involve a complex mechanistic scenario, occur at ambient pressure and temperature with high activity and Markovnikov-selectivity in the presence of an hydrosilane.**[4]**



This work was supported by the Agence Nationale de la Recherche (ANR-JCJC), Région Bretagne, Collège de France (PAUSE), CNRS and University of Rennes.

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OC39 SERS Based Bioscreening Platform for Selective Detection of β-Amyloid Peptide

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This study aims to exploit the selective screening of β-Amyloid peptide (Aβ$_{1-42}$) to purine substituted ligand and create SERS hotspot around the host purine ligand by physical binding of plasmonic nanoparticles. Surface energy difference of ligand and nanoparticles was utilized to bring them in contact and analyte was attached to the ligand by π-π stacking between the molecular structures of ligand.[1] This mechanism of bringing analyte and nanoparticles in close vicinity was utilized to generate the effective hotspot for the selectively attached analyte on the ligand molecule.[2] An engineered microfluidic device embedded with the purine ligand was developed to provide effective screening of the biomarker and reduce the noise of additional components present in the simulated real sample. Limit of detection (LoD), Enhancement Factor (EF) and Relative standard deviation (RSD) evaluated in the microfluidic device was reported to be 5.6×10^{-13}, 2×10^{10} and 3.1% respectively. Fabricated device provided selective hotspot generation for target analyte Aβ$_{1-42}$, with highly sensitive, SERS detection in a simulated cerebrospinal fluid (CSF).[3] It was found that ligand interacts more prominently with Aβ$_{1-42}$ and thus corresponding peaks were obtained in SERS spectrum more prominently than any other biomarker. Repeatability and reproducibility of the device was demonstrated to be under limit. Present study opens a new domain of research to synthesize the molecules for specific screening of the biomarkers in a complex detection mixture sample for target applications.

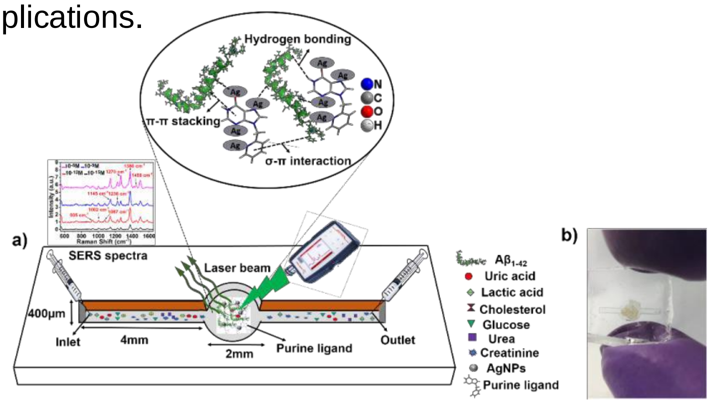

Figure 1.a) Schematic diagram of the detection process in the device using selective screening of the complex detection mixture and b) Fabricated device.

This work was supported by Abdul Kalam Innovation National Fellowship (INAE-SERB).

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OC40 Binuclear Copper(I) Complexes for Near-Infrared Light-Emitting Electrochemical Cells

L. Ballerini,[1] A. Jouaiti,[2] H.-L. Shen,[3] R. Viel,[1] F. Polo,[4] N. Kyritsakas,[5] S. Haacke,[1]
Y- T. Huang,[6] C.-W. Lu,[6] C. Gourlaouen,[7] H-C. Su,[3] and M. Mauro*[1]

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[3] Institute of Lighting and Energy Photonics, National Yang Ming Chiao Tung University Tainan 71150 (Taiwan).
[4] DMSN, Ca' Foscari University of Venice, Venezia (IT).
[5] Fédération de chimie Le Bel − FR2010, Université de Strasbourg & CNRS
[6] Department of Applied Chemistry, Providence Univ. Taichung 43301 (Taiwan).
[7] Laboratoire de Chimie Quantique, Institut de Chimie de Strasbourg UMR7177, Université de Strasbourg & CNRS, 67008 Strasbourg (France).
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Photoactive complexes based on earth-abundant metal are currently the subject of intensive research that is mainly driven by their appealing applications in the field of photocatalysis, solar energy conversion and light emitting devices. In particular, Cu(I)- based emitters are considered as an attractive alternative to those containing rarer and more expensive metals for the development of electro-luminescent materials. However, due to the much smaller spin orbit coupling (SOC) effect exerted by copper ion compared to Ir and Pt, it results that luminescent Cu(I) complexes typically possess slower radiative rate constants and longer-lived excited states.[1] This is a severe drawback that needs to be tackled for their suitable application in efficient solid-state light-emitting devices. Furthermore, Cu(I) complexes typically display emission spectra covering the blueish-green to orange region, while designing compounds that efficiently emits beyond 700 nm from deep-red to near-infrared (NIR) region is still highly challenging.[2,3] This is in spite of the fact that NIR emitters are very appealing for the fabrication of light-emitting devices for night vision display and optical telecommunication technology as well as biological imaging agents. Herein, a novel class of six cationic bimetallic copper(I) complexes with general formula $(Cu(P^\wedge P)(N^\wedge N–N^\wedge N)Cu(P^\wedge P)]^{2+}$, where N^N–N^N is a *bis*-chelating scaffold based on the thiazolo[5,4-*d*]thiazole unit is presented. The emission maxima in CH_2Cl_2 solution span over almost 100 nm between 700 and 800 nm and X-ray analysis reveals two interligand p-p stacking interactions yielding a doubly locked structure that disfavours flattening of the tetrahedral coordination around the Cu(I) centre in the excited state and keeps enhanced NIR luminescence. These complexes features lead to the successfully fabrication of the fist examples of stable NIR light-emitting electrochemical cells (LECs) based on Cu(I) complexes that display electroluminescence maximum up to *ca.* 780 nm and peak external quantum efficiency (EQE) of 0.43%.[4]

This work was supported by the ANR project ChirON "ANR-21-CE29- 0015"

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OC41 Highly Stable Coniage Metal α,α-Dimine Catalysis that Incorporates Carbon Dioxide Into Alkyne Frameworks

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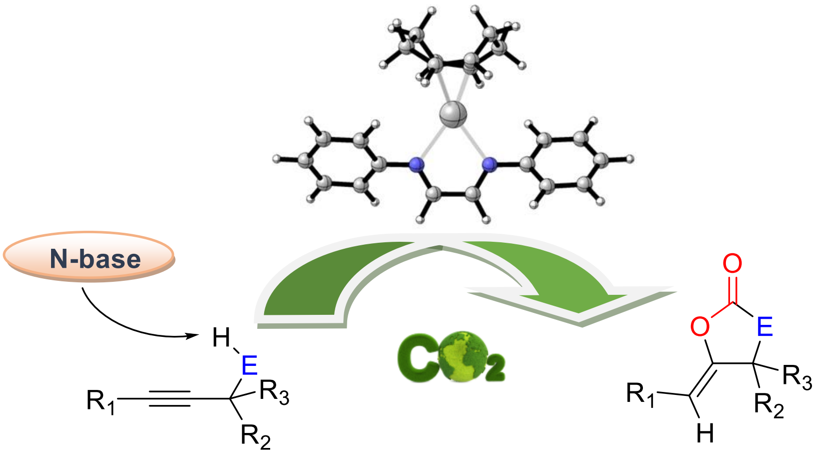
Carbon dioxide is a potentially valuable and highly accessible C-1 platform feedstock; however, the application of this ubiquitous gas in industrial processes is comparably limited due to thermodynamic restraints and general inertness towards C-activation. This work addresses the development of novel room-temperature and air-stable cationic coinage metal ions supported by N,N'-chelating α,α-diimines, that demonstrate high degrees of alkynophilicity. These complexes are highly efficient in incorporating CO_2 into organic alkynes frameworks,[1,2] affording cyclic carbonates and carbamates under mild conditions. The unusually high stability of these pre-catalysts was accomplished by employing a co-ligand; η^2:η^2-chelating *cis*-cyclo-octadiene which has strong stabilising effects as predicted through DFT calculations. The ability of these novel α,α-diimines Cu, Ag and Au complexes to catalyse the incorporation of CO_2 into a propargylic alcohols/amines and the subsequent cyclisation was evaluated using a variety of terminal and internal alkynes substrates in the presence of the base DBU. All reactions were performed at 25 °C under 1 to 6 bars of CO_2 pressure, affording the corresponding α-alkylidene cyclic products, which are employed as precursors for drugs and polymers. The scalability of the reaction has been proven using flow chemistry affording quantitative yields with half the catalyst loading, and only 3 equivalents of CO_2; the residence time being approximately 30 minutes. Two potential novel reaction pathways were fully modelled with DFT/solvent corrections, which is further supported by experimental characterisation of the reaction intermediates.



E= O or NH R_1= H or aryl R_2 and R_3= alkyl or aryl

This work was supported by SSPC, SFI /Science Foundation Ireland) Research Centre for Pharmaceutical Research (Pharm5) and ICHEC for access to high-level computational resources.

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FLASH TALKS

FT 1-8

June 5th, morning session

Margerie Loze

FT1 Grafted Metal-Organic Frameworks with Cobalt Corroles for Carbone Monoxide Detection

M. P.Kroitor

FT2 Ruthenium Phthalocyanines with Orthogonal Substituents Bearing (1R,2S,5R)-Menthoxy Groups as Prototype of Chiral Catalysts

Karolína Salvadori

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M.Sc. Lars Denker

FT4 Amido-imidazolin-2-imine Ligands: Stronger Than β-Diketiminates

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FT6 Interactions of a Quinoline-Squaraine D-A-D triad with Exfoliated Graphene.

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FT8 Expending the Family of Cobalt Tetraaza-Macrocyclic Complexes to Further Enhance HER and CO_2RR Performances

OF9-17

June 5th, afternoon session

Marija Bakija

FT9 Group 11 Transition Metal Complexes of Chiral Monodentate Oxazoline Ligands

Siwen ZHAO

FT10 Making C-N Bonds from Carbon Monoxide and Nitrite Co-Electroreduction

Paulo Jorge Marques Cordeiro Junior

FT11 Cobalt Tetraaza Macrocycle Complexes for Enhanced CO_2 Reduction: From Organic Solvent to Aqueous Carbonate Buffer

Heriniaina Randriamiharisoa

FT12 Symmetric Pyridyl-Diaminotriazine and Pyridyl-Carboxylic Acid as Ligands for Coordination Chemistry:
Synthesis, Characterization, and Potential Applications

Seán J. Byrne

FT13 Disturbing Aromaticity: A Novel Pyrrole Amine Phosphenium ion

Karolina Urbanska

FT14 Tetrapyrroles doped with rigid aliphatic hydrocarbons

Tatiana Munteanu

FT15 From Coupling Principle to π-d Conjugation: Investigating Diamino-Benzoquinonediimine Ligands

Zilong L

FT16 Versatile Homogeneous Catalysts for Hydrogen Storage and Reduction Reactions

Upala dasmahapatra

FT17 Immidazolium based ionic liquid supported copper catalyst for the synthesis of various N-heterocycles

FT1 Grafted Metal-Organic Frameworks with Cobalt Corroles for Carbone Monoxide Detection

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Virginie Blondeau-Patissier[2] and Laurie André [2]

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Keywords: Metal-Organic Frameworks, Cobalt corroles, grafting, CO adsorption

Summary: Carbon monoxide (CO) is an odorless and colorless gas that cannot be detected by humans without the use of a specific sensor. CO is responsible for serious and potentially fatal intoxications every year. It is imperative to develop new technologies capable of detecting this imperceptible and deadly gas at low concentrations before it reaches harmful levels.[1] In this work, our approach is to exploit the high selectivity of cobalt corroles for CO and to support them with porous crystalline materials in order to avoid corroles π-stacking and to improve the access of CO to the cobalt complexes. Indeed, corroles are tetrapyrrole macrocycles of the porphyrinoid family that, when metaled with cobalt, are capable of CO sorption with high selectivity for CO over common interferents such as nitrogen and dioxygen.[2] Here we consider Metal-Organic Frameworks (MOFs) as suitable porous materials to host the métallocorroles due to their well-known high porosity and superior tunability. In particular, it is possible to take advantage of the natural vacancies present in a porphyrin- based MOF such as the PCN-222 (Fig. 1a) which can then be used to graft cobalt corroles on the MOF cluster. This way, the active molecule for detection is strongly anchored by coordination to the zirconium oxide cluster and hangs inside the MOF pores, allowing free access to the cobalt metal center (Fig. 1b). In this study, the synthesis of the designed cobalt corroles grafted on porphyrin-based MOFs have been analyzed and compared with respect to their crystallinity, morphology, and specific surface area thanks to XRD, SEM images, ^{1}H NMR, and BET analysis.

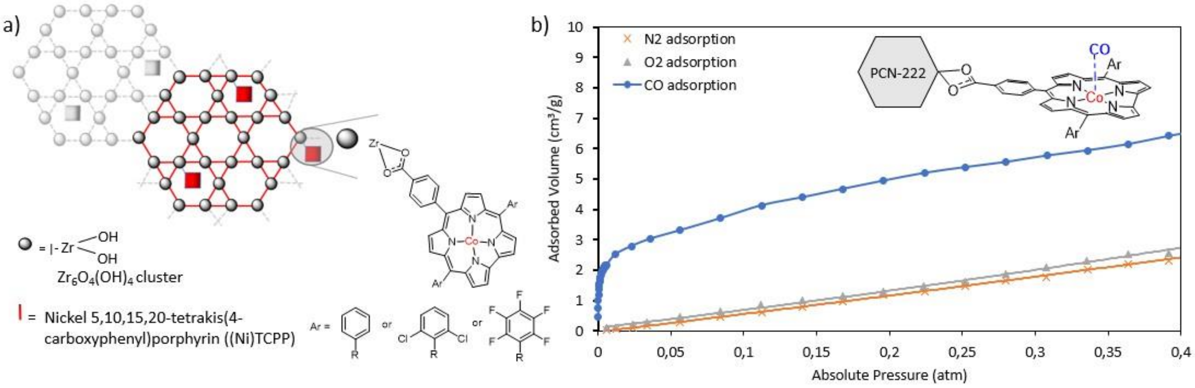

Fig. 1: a) Structure of a cobalt corrole grafted on PCN-222, b) N_2, O_2 and CO adsorptions of the grafting material

Acknowledgements: This work was supported by the CNRS (UMR UB-CNRS 6302, the "Université de Bourgogne Franche-Comté (UBFC)", and the "Conseil Régional de Bourgogne" (ICE PhD thesis). The French Research Agency (ANR) is acknowledged for financial support (ANR-22-CE42-0016-02).

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FT2 Ruthenium Phthalocyanines with Orthogonal Substituents Bearing (1R,2S,5R)-Menthoxy Groups as Prototype of Chiral Catalysts

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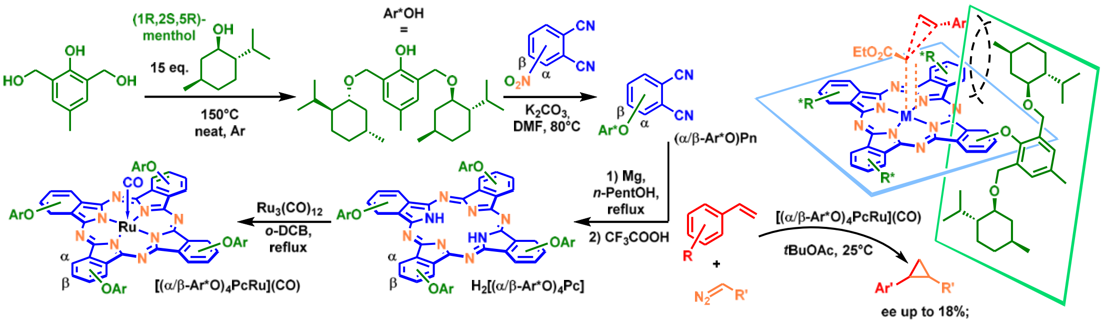
Metal complexes of phthalocyanines (MPc) show significant catalytic activity in a wide range of catalytic reactions.[1] Although phthalocyanines with chiral substituents have been described,[2] MPc have not been unexplored in enantioselective catalysis since chiral groups are typically situated far from the metal site in the macrocyclic plane that prevents a chiral induction.

We present here a novel approach to the synthesis of phthalocyanines with picket- fence architecture with bulky chiral substituents arranged orthogonally to the plane of the macrocycle that creates a chiral environment around the metal site. Natural (1R,2S,5R)-menthol was chosen as the chiral inductor, which interacted with 2,6-bis- (hydroxymethyl)-p-cresol to give the phenol **Ar*OH**. X-ray analysis of the phthalonitrile precursors confirmed the orthogonality of the phthalonitrile rings to the aryloxy-group.

The [**(α/β-Ar*O)$_4$PcRu](CO)** complexes were prepared by the reaction of the metal free phthalocyanines **H$_2$[(α/β-Ar*O)$_4$Pc]** with Ru$_3$(CO)$_{12}$.[3] Using the reaction of styrene with ethyl diazoacetate (EDA) as a benchmark reaction, it was found that peripherally substituted ruthenium phthalocyaninate **[(β-Ar*O)$_4$PcRu](CO)** showed virtually no asymmetric induction, whereas the complex **[(α-Ar*O)$_4$PcRu](CO)** allowed the cis- isomer of the cyclopropanation product to be obtained with ee = 18%, highlighting the importance of introducing substituents in non-peripheral positions.[4]



The development of a second generation of chiral phthalocyanine complexes with improved catalytic properties is in great progress in our laboratories.

This work was supported by the CNRS (International Emerging Action 2022), RFBR (project №21-53-15004) and RSF (project №23-73-01126).

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FT3 Linkage of Urea-Binding Site with Azacalixarene Scaffolds

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Anion recognition, elimination, and sensing are attractive research topics important in biological and environmental issues. Consequently, the formation of reversible host-guest complexes between ligands and negatively charged species represents one of the most important objectives in modern supramolecular chemistry. Moreover, the above-noted objects also encroach on the development of new separation procedures, catalysis, or trace analysis.[1]

Inspired by nature, supramolecular chemists have synthesized various compounds with high values of binding constants to target anions. However, the coordination of basic anions (including phosphates and carboxylates) is continuously a challenge, mainly due to their strong pH dependence, and relatively high values of their solvation energies. Therefore, in our work, we focused on the synthesis of sensory groups based on urea structural motifs, which are known for suitable complexation ability towards both phosphates and carboxylates. Those motifs were introduced to the periphery of azacalix[4]arene macrocycle[2] to take advantages offered by their linkage. Firstly, it has been proven that those systems show remarkable selectivity and efficiency towards monobasic phosphate even in HB competitive solvent (DMSO). Here, the azacalix[4]arene skeleton preorganized the binding motifs, offering cooperative binding action during complexation. Secondly, the anchorage of binding sites to macrocyclic carrier improves ways of their recycling, which is desirable for economic and ecological reasons. The compounds were successfully regenerated by employing nanofiltration.[3]

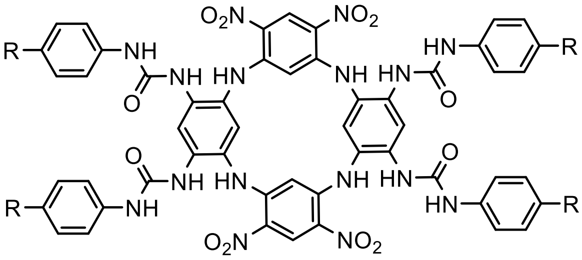

Fig. 1: General structure of urea-based receptors build on azacalix[4]arene.

This work was supported by Specific university research A2_FCHI_2024_025.

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FT4 Amido-imidazolin-2-imine Ligands: Stronger Than *β*-Diketiminates

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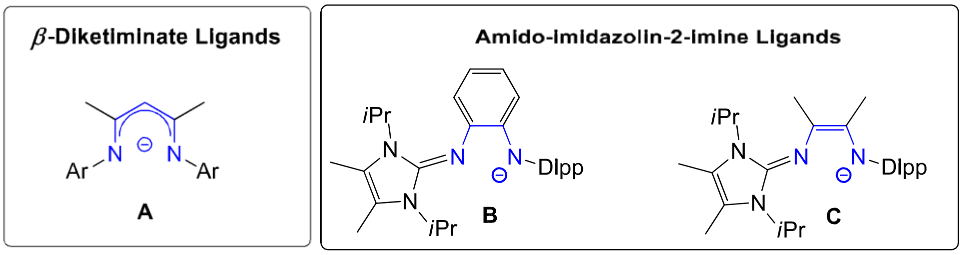
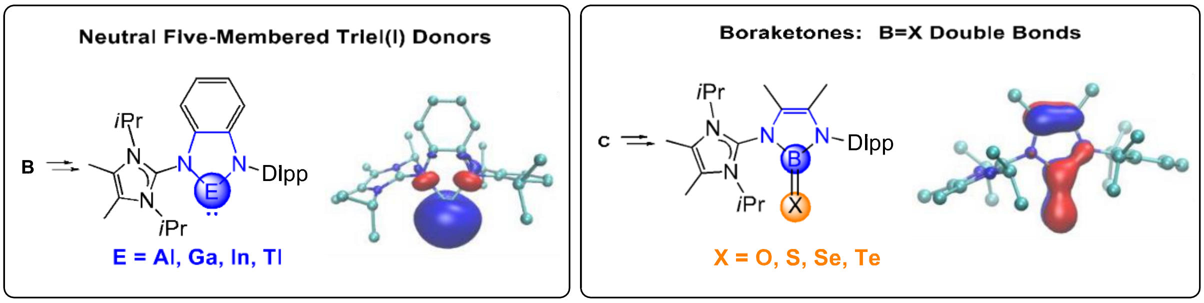
β-Diketiminates (**A**, NacNac) are a well-known class of monoanionic *N,N´*-biden- tate ligands, which have been widely exploited to stabilize six-membered chelates of main group and transition elements with high reactivity and low coordination number.[1]
In contrast, suitable ligands for five-membered element cycles were not available until very recently, despite the obvious elevated stability of five vs. six-membered planar rings. We introduce the new ligand class of monoanionic amido-imidazolin-2-imines (**B** and **C**, AmIm), which give rise to highly stable five-membered ring scaffolds upon coordination and, by extension, improved *π*-donation towards the complexed element.



In approaches to demonstrate the benefits of amido-imidazolin-2-imines we present the synthesis of five-membered triel(I) compounds, which are stronger σ-donor ligands than the related *β*-diketiminate analogues.[2] Further examples include the isolation of a complete series of boraketones with structurally authenticated B=X bonds (X= O, S, Se, Te), which proved to be elusive in the past and could only be obtained with the new ligand system,[3] as well as the synthesis of iminoboranes with isolated B=NR bonds.[4]



This work was supported by the organizations „Fonds der Chemischen Industrie“ (FCI), “Deutsche Forschungsgemeinschaft“ (DFG) and „Heinrich-Böll-Stiftung“

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FT5 Reversing Acetylcholinesterase Organophosphate Poisoning by Zeolitic Imidazolate Framework Structural Degradation

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Organophosphate (OP) toxicity is related to inhibition of acetylcholinesterase (AChE) activity which plays a key role in neurotransmission process.[1] In this work, we report the ability of different zinc zeolitic imidazolate frameworks (ZIFs) to behave as antidotes of organophosphate poisoning. The Zn-L coordination bond (L= purine, benzimidazole, imidazole, 2-methylimidazole) is sensitive to the G-type nerve agent model compound[2] diisopropylfluorophosphate (DIFP) leading to P-X (X= F, Cl) bond breakdown into nontoxic diisopropylphosphate (DIP). P-X hydrolysis is accompanied by ZIF structural degradation (Zn-imidazolate hydrolysis), with concomitant release of the imidazolate linkers and zinc ions. The nucleophilic attack to the OP@AChE adduct by the delivered imidazolate derivatives gives rise to the recovery of enzymatic function (Figure 1). P-F bond breakdown and AChE reactivation are dependent on imidazolate linker nucleophilicity, framework topology and particle size. The best performance is obtained for 18 nm nanoparticles of Zn(2-methylimidazolate)$_2$ (sod ZIF-8) exhibiting DIFP degradation half-life of 2.6 min and full recovery of AChE activity within 1 h. Moreover, 18 nm sod ZIF-8 nanoparticles are not neurotoxic, as proven by in vitro neuroblastoma cell culture viability tests.

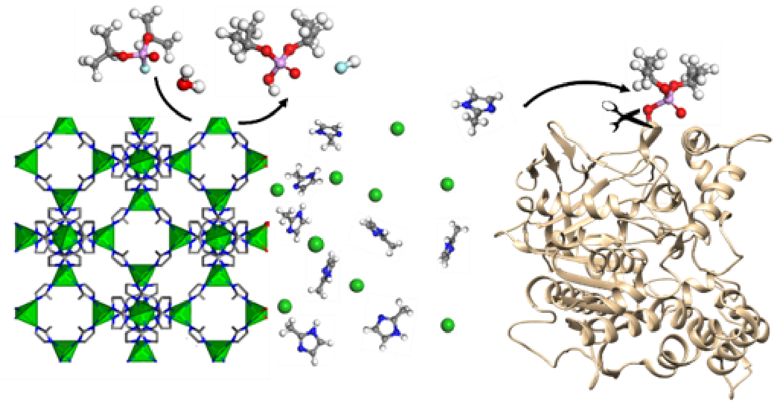

Figure 1. ZIF-8 structural degradation leads to both nerve agent simulant diisopropylphosphate (DIFP) hydrolytic degradation into diisopropylphosphate (DIP) and imidazolate triggered acetylcholinesterase (AChE) reactivation.

This work was supported by Spanish MCIN/ AEI /10.13039/501100011033 (Project PID2020-113608RB-I00; TED2021-129886B-C41

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FT6 Interactions of a Quinoline-Squaraine D-A-D triad with Exfoliated Graphene.

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Squaraine dyes have shown particular promise as a class of dyes exhibiting ultrastrong absorption properties that routinely cover a large part of the visible spectrum and even extend to the near-IR region.[1,2,3] On the other hand, the behavior of squaraine-based dyes in solution or thin films is subject to severe aggregation phenomena.[4] Therefore, detailed knowledge of the squaraine dye interactions in homogenic aggregates and with other species can be of importance for the design of new materials of desired properties.

In this study, a triad comprised of quinoline, squaraine and pyrene chromophores is synthesized and characterized. The resulting chromophore follows a Donor-Acceptor-Donor D-A-D architecture and exhibits very desirable optical characteristics for optoelectronic applications such as solar cells. The chromophores have been studied using steady state absorption and emission spectroscopy. To study the interaction of the light harvester with a well-known electron accepting material, exfoliated graphene nanoparticles are introduced in dilute solutions of the triad and the subsequent formation of H-type and J-aggregates is examined. Picosecond time-resolved fluorescence was used to try and probe the behavior of the observed interactions, while electrochemistry was used to rationalize the thermodynamically favorable pathways for energy or charge transfer in such complex nanoensembles.

This work was supported by the Research Council of Norway, (RCN) through the ACT programme (Accelerating CCS Technologies, Horizon2020 Project No 294766) and through support to the Norwegian Micro- and Nano-Fabrication Facility, NorFab, project number 295864. NTNU Nano is also acknowledged for support via the NTNU Nano Impact Fund and its Enabling Technologies programme (project No 81771713).

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FT7 Electrocatalysis with Bimetallic Complexes Supported by Pyridyldiimine Macrocyclic Ligands

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The cooperative reactivity of two metal centres has long been studied in enzyme active sites, such as the CODH family. Accordingly, bimetallic complexes have recently garnered attention for their potential to show new reaction pathways, and ligands which can support two metals in close proximity are thus very attractive.[1]

NNN–pyridyldiimine (PDI) ligands are common in both proton reduction and CO_2 reduction electrocatalysis.[2] We postulated that the analogous bimetallic compounds would likewise display interesting reactivity for this important, environmentally relevant reaction. We therefore selected macrocyclic bis-PDI ligands, prepared by Schiff base template synthesis around an alkaline earth metal.[3]

In this work, we compare a series of four earth abundant homobimetallic complexes **$[M]_2$** (M = Co, Ni, Fe, Cu). The redox and electrochemical properties of the complexes were studied under homogeneous conditions and it was found that these catalysts displayed good reactivity towards the CO_2 reduction reaction. Furthermore, the macrocyclic ligands were modified in order to append a polyaromatic pyrene group. This allowed the bimetallic complexes to be immobilized onto a carbon electrode through π-π stacking interactions and the behaviour of the homogeneous systems was then compared with the immobilized counterpart.

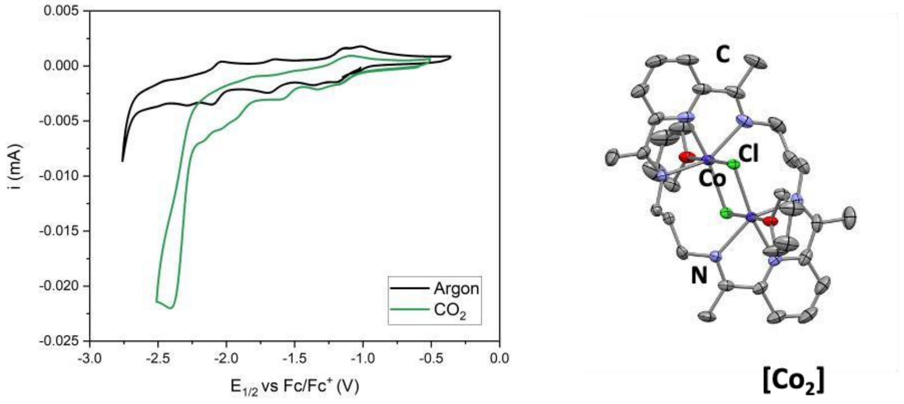

Figure 1. Cyclic voltammogram of the bimetallic cobalt complex **$[Co]_2$** under argon and
CO_2 *(left)*; solid state structure of **$[Co]_2$** *(right)*

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FT8 Expending the Family of Cobalt Tetraaza-Macrocyclic Complexes to Further Enhance HER and CO_2RR Performances

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Laurine Robert,[1] Florian Molton,[1] Fabrice Thomas,[1] Cyrille Costentin,[1] Jérôme
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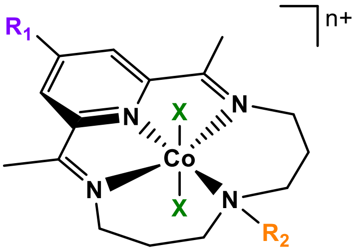
As the demand for more efficient and environmentally friendly energy solutions grows to address current environmental challenges, the development of efficient catalysts for Hydrogen Evolution Reaction (HER) and/or CO_2 Reduction Reaction (CO_2RR) has become essential. Among the various systems proposed for this purpose, cobalt catalysts featuring tetraaza-macrocyclic ligands, particularly those with pyridyl-diimine patterns (CoCR14) first isolated in the 1969,[1] show considerable promises. Despite being only recently applied in both electro- and photo-catalytic HER[2] and CO_2RR[3] in homogeneous solutions, these catalysts exhibit remarkable efficiencies, with CoCR14 recognized as one of the most effective and stable catalysts in aqueous solutions for HER.[4] To enhance catalytic efficiency and tailor the selectivity of this system, our team aims to expand this family of catalysts by incorporating different functional groups at the ligand's periphery, as it has only be done rarely but showed remarkable effect.[5] This presentation will focus on the preparation of several CoCR14 complexes, introducing various electron-withdrawing/donating moieties at the *para* position of the pyridine to modulate the complex's redox properties. Additionally, we will look into the introduction of branching groups at the secondary amine position, potentially serving as proton relays to facilitate H_2 formation. The effects of these modifications will be investigated through spectro-electrochemistry, providing insights into the electro-/photo-catalytic performances of these catalysts.



X = Cl, MeCN

R_1 = Electron-withdrawing/donating groups

R_2 = Proton relay

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FT9 Group 11 Transition Metal Complexes of Chiral Monodentate Oxazoline Ligands

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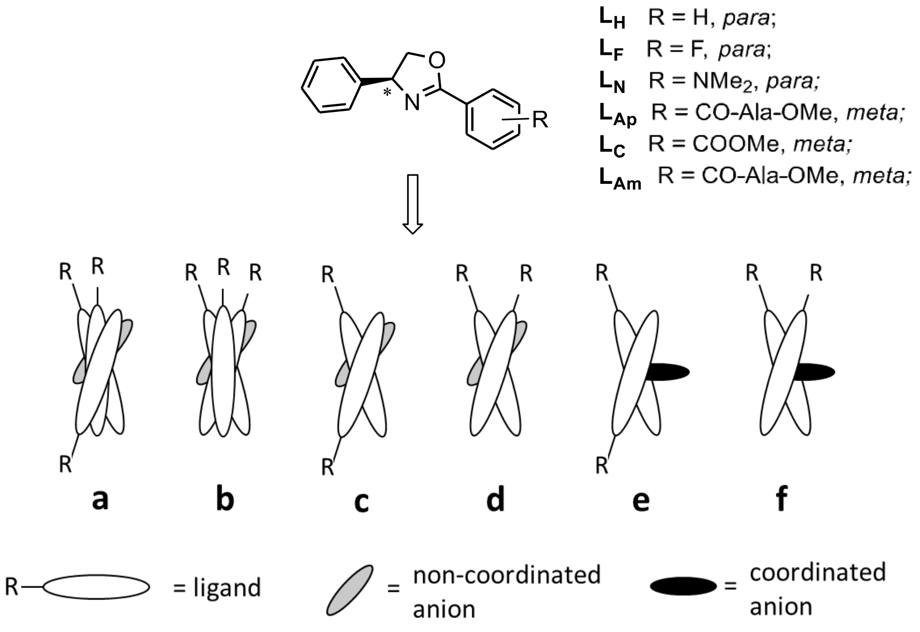
Although application of oxazoline derivatives largely relates to bidentate ligands in catalysis[1] and polymer synthesis,[2] published research concerning transition metal complex structures of monodentate oxazolines amounts to less than 50 crystal structures, among which zinc(II) halide complexes are the most abundant.[3] Following our group's previous work where the choice of metal cations and respective anions affected the structure of the resulting metal complex,[4] compounds with monovalent late transition metals and model monodentate oxazoline ligands are reported herein. In particular, the comparison of obtained SC XRD structures of copper(I) and silver(I) complexes with 2,(4S)-diphenyl oxazoline ligands bearing an electron withdrawing, a neutral (hydrogen) or an electron donating substituent of various chemical character and lengths in the para or meta position of the 2-phenyl group will be presented. These compounds were additionally characterized using NMR, ESI-MS, ESI-HRMS and PD XRD diffraction, as well as DFT computational studies.



Scheme. Types of transition metal complex structures obtained by SC XRD.

This work was supported by CSF doctoral scholarship to Marija Bakija (DOK-2021-02-7366) and Cage Cat (IP-2022-10-8456).

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FT10 Making C-N Bonds from Carbon Monoxide and Nitrite Co-Electroreduction

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The electroreduction of CO_2/CO has been extensively studied due to its promising potential for renewable energy storage and the sustainable production of chemical products and fuels, the so-called solar fuels. It potentially offers a sustainable and an efficient pathway to synthesize crucial compounds and contribute to a circular economy, using CO_2 as feedstock. Moreover, beyond the spectrum of simple carbon species, there is a growing demand for the synthesis of nitrogen-containing compounds. Recently, electrochemically make C-N coupling reactions have attracted wide attention in light of their simplicity, affordability and environmental sustainability. However, despite these advantages, the practical application of these reactions has been hindered by a lack of comprehensive mechanistic understanding and inadequate selectivity in C-N coupling product formation.

In our study, we addressed these challenges by employing CO and NO_2 as reactants for the formation of C-N bonds, utilizing cobalt phthalocyanine immobilized on multi-walled carbon nanotubes as molecular electrocatalysts. Through meticulous optimization of key factors such as the concentration of NO_2 and the pH of the electrolyte, we achieved high yields and selectivity towards two primary C-N coupling products: methylamine (CH_3NH_2) and formaldoxime (CH_2NOH). Our findings provide valuable insights for the rational synthesis of C-N coupling products and present an effective way for producing diverse value-added organonitrogen-containing compounds, including acetamide, amino acids, etc...

This work was supported by CSC for fellowship, CNRS and Université Paris Cité for instrumental facilities.

FT11 Cobalt Tetraaza Macrocycle Complexes for Enhanced CO_2 Reduction: From Organic Solvent to Aqueous Carbonate Buffer

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The development of molecular catalysts for CO_2 reduction is an important frontier in sustainable chemistry, offering a promising avenue for the conversion of CO_2 into value-added chemical compounds. Recently, cobalt tetraaza macrocycle complexes with pyridyldiimine moieties have received considerable attention in this area. Notable contributions have been made by Peters, Frei, Head-Gordon and collaborators.[1,2] They have demonstrated interesting catalytic performances in the reduction of CO_2 and, by means of infrared spectroscopy, have revealed the formation of an intermediate adduct ($[Co^{I}N_4H]^+$-CO_2), which shows a stable interaction between CO_2 and the ligand NH, an important factor for the conversion of CO_2.[2] Considering the potential application of such complexes in catalysis in aqueous medium, their limited solubility in water represents a significant challenge. To overcome this, we propose the introduction of a linking group, such as pyrene, to facilitate their grafting onto multiwall carbon nanotubes (MWCNTs) (Figure 1). Electrochemical evaluations of the **C2** and **C3** complexes (Figure 1) for CO_2 reduction in acetonitrile, under homogeneous conditions, yielded results consistent with previous reports - demonstrating selectivity towards CO with modest Faradaic efficiency. However, the electrocatalytic performance of these complexes is significantly enhanced upon immobilization on MWCNTs in an aqueous carbonate buffer. The complexes exhibit excellent stability, with CO selectivity exceeding 97%, and turnover numbers (TON) and turnover frequencies (TOF) reaching values up to 10^4 and over $1.2\ s^{-1}$, respectively[3].

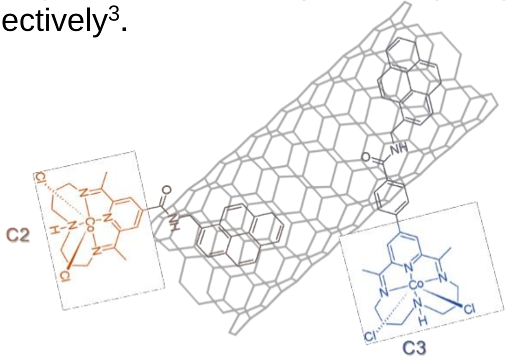

Figure 1. Co-tetraaza complexes, C2 and C3, immobilized in MWCNT.

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FT12 Symmetric Pyridyl-Diaminotriazine and Pyridyl-Carboxylic Acid as Ligands for Coordination Chemistry: Synthesis, Characterization, and Potential Applications

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Pyridyl-diaminotriazine and pyridyl-carboxylic acid ligands were obtained in good yields, by a simple synthetic route via cyanopyridyl intermediates, without using a metal catalyst.[1] It is well known that cyano compounds are one of the most commonly used intermediates in organic synthesis due to the property of cyano moiety to be easily transformed into different functional groups such as carboxylic acids, amines, amidines, tetrazoles, aldehydes, and diaminotriazine.[2,3] All these derivatives are employed as ligands in coordination chemistry.[4,5] Utilizing solvothermal and slow diffusion techniques, new coordination compounds based on pyridyl-diaminotriazine and pyridyl-carboxylic acid ligands with transition (Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}) and rare earth (Nd^{3+}, Eu^{3+}, Tb^{3+}) metal ions were effectively obtained, ranging from individual coordination complexes to coordination polymers. The compounds are elucidated by different analytical technics, including Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR), ultraviolet-visible spectroscopy (UV-Vis), single crystal X-ray diffraction (SCXRD), powder X-ray diffraction (PXRD), and thermogravimetric analysis (TGA). The characterization of the compounds showcases their variety, flexibility, thermal stability, and fascinating topologies.

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FT13 Disturbing Aromaticity: A Novel Pyrrole Amine Phosphenium ion

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The concept of aromaticity has undergone significant development since Kekulé[1], Hückel[2], and Möbius.[3] The terminology is broad and confusing, including anti-, hetero-, homo-, and homohetero-aromatic compounds, leading to many unique theories and misconceptions on the subject. The consistent finding in all theories is that aromatic compounds contain a diamagnetic current above the ring, and antiaromatic compounds contain a paramagnetic current. Pyrroles are heteroaromatic compounds with an acidic NH, making them ideal ligands for main-group catalysis with potential unique properties. However, their use as ligands in main-group catalysis has been underutilized. Disrupting the diamagnetic current by placing a low valent p-block Lewis acid with the symmetry to interact with the pyrroles aromatic π-the system should enhance the acidity of the molecule, thereby promoting substrate activation.

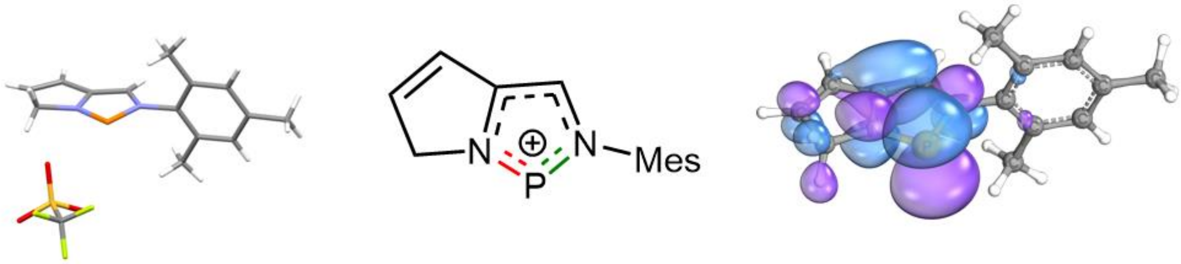

Figure 1.1. Showing X-ray crystal structure of novel phosphenium triflate (left), structure of bicyclic ring showing aromatic delocalization (center), LUMO of novel phosphenium ion showing aromatic M.O's of the ring (right)

This work reports the characterization of novel pyrrole pincer ligands and their respective phosphine chlorides by X-ray diffraction and NMR spectroscopy. Chloride abstraction from the phosphine leads to an unknown 1,5-proton transfer from the methylene group to the 5′-position of the pyrrole ring, rearranging to form a new 5-membered aromatic ring. The novel phosphenium triflate was inserted into a strained alkene system by an oxidative addition to quadricyclane to form a pyrrole iminium ion by 1,2-proton transfer.

This work was supported by funding from University College Dublin and the Royal Society of Chemistry.

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FT14 Tetrapyrroles Doped with Rigid Aliphatic Hydrocarbons

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Bicyclo[1.1.1]pentane (BCP, Figure 1A) is a representant of rigid non-conjugating hydrocarbons, a group of compounds characterized by highly strained three dimensional skeletons. Due to its molecular size and shape, this rigid aliphatic compound serves as an isostere to internal alkyne and 1,4-disubstituted benzene structural motifs,[1] and finds wide-ranging biomedical applications. However, the poor tolerance of the BCP and cubane towards functional group interconversion and certain transition metal-catalyzed processes hamper the development of functional molecules and materials involving this polycyclic motif.[2] We have recently reported synthetic advances towards the functionalization of rigid aliphatic hydrocarbons.[3] We are now focusing on extending the synthetic toolkit targeting rigid aliphatic hydrocarbons in order to facilitate their incorporation in complex molecular architectures and take advantage of their unique properties and 3D non-covalent interactions.[4]

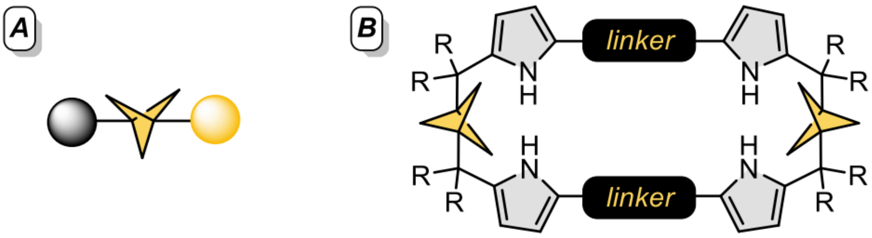

Figure 1. 1,3-disubstituted bicyclo[1.1.1]pentane (A) and a schematic representation of BCP-containing macrocycles (B).

Here we present an incorporation of BCP as a 3D saturated motif in functional tetrapyrroles (Figure 1B), including calix[*n*]pyrrole derivatives[5] and multi-chromophore arrays. The synthesis, structure, properties, and supramolecular interactions of these BCP-containing functional molecules will be discussed.

This work was supported by Science Foundation Ireland (Award 21/FFP-A/9469).

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FT15 From Coupling Principle to π-d Conjugation: Investigating Diamino- Benzoquinonediimine Ligands

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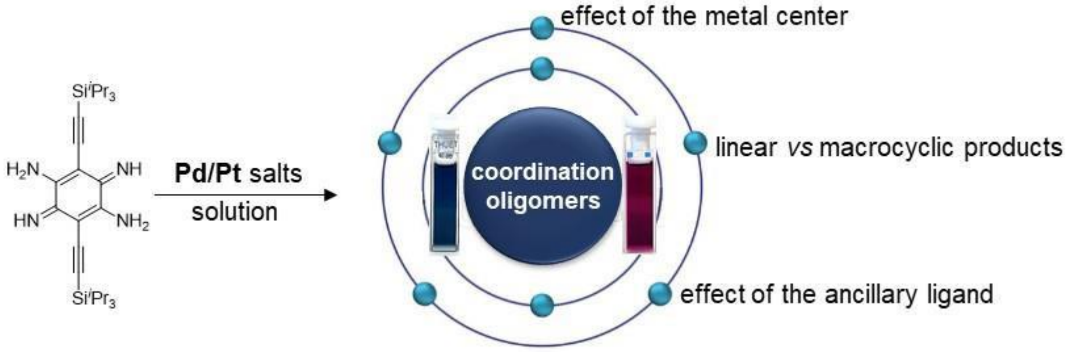
The development of near-infrared (NIR) dyes is at the heart of many of today's scientific challenges, given their high potential for applications in optoelectronics and biophotonics.[1-2] As part of the toolbox, coordination chemistry starts to gain territory due to innovative and unexplored potential, allowing to benefit from non-innocent ligands to build planar and extended architectures.[3-4] In this context, 2,5-diamino-1,4- benzoquinonediimine (BQDI) stands as versatile ditopic, bis-bidentate ligand for the preparation of coordination complexes with catalytic, optical or magnetic properties.[5]

The study of the BQDI alone brings to light curious results related to the chemistry of polymethine dyes,[6] while its metalation allows the isolation of stable mono-, di- or polynuclear oligomers with absorption up to the NIR region due to the extension of the π-d conjugation.[5,8] The N-substitution of BQDI plays an important role on the coordination properties of this building block but can notably be detrimental (steric effect) for the electronic delocalization between the metal centers.[3,7] Consequently, our present investigations takes the process one step further, by introducing C-substituents on the ligand and delving into the complexation mechanism and the optical properties of unprecedented palladium and platinum coordination oligomers.



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FT16 Versatile Homogeneous Catalysts for Hydrogen Storage and Reduction Reactions

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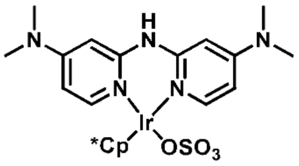
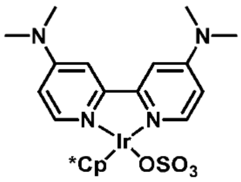
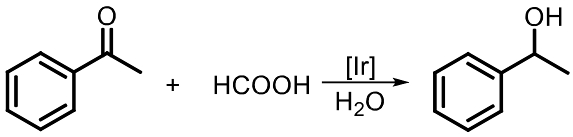
In recent years, nitrogen ligands have played an increasingly important role in organometallic chemistry and homogeneous catalysis. Compared with phosphorus ligands, nitrogen ligands are air-stable and they are relatively easy to synthesize. With the inevitable depletion of fossil resources and the need for sustainable energy sources, formic acid, one of the energy carriers accessible from renewable resources[1], has been extensively studied for hydrogen storage and release. There have been many reports of homogeneous transition metal catalysts capable of dehydrogenating formic acid, but the vast majority requires exogenous bases to achieve high activity.[2,3] The stability of the catalysts under acidic conditions is also one of the issues that need to be considered. Our research group designed and synthesized modified homogeneous dipyridylamine and bispyridine iridium complex, and achieved highly active in the dehydrogenation of formic acid and the hydrogenation of aldehydes and ketones without base.[4,5]





$$HCOOH \xrightarrow[H_2O]{[Ir]} H_2 + CO_2$$



This work was supported by the Chinese Scholarship Council

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FT17 Immidazolium based ionic liquid supported copper catalyst for the synthesis of various *N*-heterocycles

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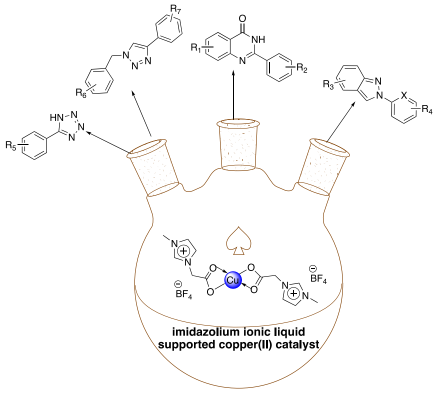
A novel and robust ionic liquid-supported copper(II) catalyst has been developed and explored for the efficient synthesis of various biologically active *N*-heterocycles [1,2,3] such as 5-substituted-1*H*-tetrazoles,[4] 1,4-disubstituted 1,2,3-triazoles,[5] 2*H*-indazoles,[6] 2-substituted quinazolinones under microwave irradiation. The ionic liquid-supported catalyst facilitated the efficient isolation of *N*-heterocycles with high purity by simple extraction with organic solvent. Recovered ionic liquid-supported copper(II) catalyst could be recycled for three times for the synthesis of tetrazole products with high purity. The catalyst is thermally stable, green, easy to prepare, and devoid of any drawback associated with homogeneous catalysts. These synthetic protocol offers a very clean, convenient, and microwave-assisted environment-friendly method for the efficient synthesis of different *N*-heterocycles with high yield. These nitrogen-containing molecules have noted robustness facilitating their applications in coordination chemistry, in the photographic industry, pharmaceutical industry.



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POSTERS

P1 Chemoselective direct reductive amination of aldehydes to primary amines catalyzed by water-soluble catalysts based on nitrogen ligand

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Amines are important precursors to a wide variety of organic substrates including biologically active compounds such as agrochemicals and pharmaceuticals. Direct reductive amination (DRA) of aldehydes and ketones is a commonly used method to prepare amines. The reactions are mostly accomplished by at least stoichiometric amounts of hydride reducing agents. However, safety hazards associated with these reducing agents and their toxic by-products, and the probable contamination of the products after work-up are the major problems of such processes. Direct reductive amination of aldehydes and ketones is also performed by hydrogenation methods since its use is attractive from economical and ecological viewpoints. Although a plethora of heterogeneous hydrogenation methods are known for reductive amination, fewer catalytic homogeneous methods have been developed,[1-4] and the use of ammonia as the aminating substrate is even scarce.[5-6] One of the most important problems of these catalytic hydrogenations is the control of the chemoselectivity. Frequently, secondary and tertiary amines as well as Schiff bases are formed, in addition to primary amines, and the purification of reaction mixtures are usually difficult. Consequently, chemoselective synthesis of primary amines with good yields is subject of tremendous investigations. Furthermore, the separation of the catalysts from the reaction products and their quantitative recovery in active form are cumbersome, in the case of homogeneous processes.

We reported a process for the synthesis of secondary and tertiary amines by direct reductive amination of aldehydes with primary and secondary amines using Palladium water-soluble catalyst.[7] In this presentation we wish to report simple and convenient procedures for homogeneous direct reductive amination of aldehydes to the corresponding primary amines in a very selective manner using ammonia and water- soluble catalysts based on nitrogen ligand.

We are grateful to FESR of Université de Moncton for financial support of this research.

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P2 Synthesis of Amine-Bridged Bis(phenolate) Aluminum Complexes and Their Catalytic Performance for the Polymerization of Trimethylene Carbonate

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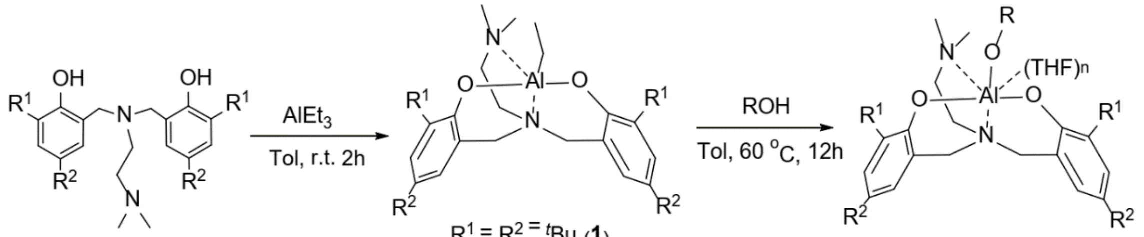
Aliphatic polycarbonates (PCs) are highly valued biomaterials because of their low toxicity, biodegradability and biocompatibility,[1] which are expected to be used in pharmaceutical and medical applications, such as drug delivery systems and tissue engineering scaffolds.[2] It has been reported that the ring-opening polymerization (ROP) of trimethylene carbonate (TMC) is a convenient method for the preparation of PCs, and a lot of metal complexes supported by N-containing ligands are found to be efficient catalysts for this polymerization.[3] In order to further explore and develop the potential of amine-bridged bis(phenolate) aluminum complexes for polymerization catalysis, to gain insight into the relative relationship between the structure and catalytic properties of this series of aluminum complexes. We synthesized and structurally characterized a various of aluminum derivatives and elucidated their application in the ROP of trimethylene carbonate. The results showed that the nature of the ancillary ligands and the coordination environment around the aluminum center have a significant effect on the polymerization activity of TMC, and the amine-bridged bis(phenolate) aluminum complexes exhibit good activity in the polymerization of TMC.



$R^1 = R^2 = {}^t\mathrm{Bu}$ (**1**)
$R^1 = R^2 = CH_3$ (**2**)
$R^1 = R^2 =$ Cumyl (**3**)
$R^1 = R^2 =$ Cl (**4**)

R = CH_2Ph, n = 0, $R^1 = R^2 = {}^t\mathrm{Bu}$ (**5**), CH_3 (**6**)
R = CH_2Ph, n = 1, $R^1 = R^2 =$ Cl (**7**)
R = CH_2CF_3, n = 0, $R^1 = R^2 =$ Cumyl (**8**)
R = CH_2Ph, n = 0, $R^1 = {}^t\mathrm{Bu}$, $R^2 =$ OMe (**9**)

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P3 1D to 2D Covalent Coordination Polymers at Synthetized at Surfaces

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On-surface synthesis under ultra-high vacuum allows to control matter at the atomic level, with important implications for the design of new 1D/2D materials with remarkable electronic, magnetic or catalytic properties [1]. Our objective is to synthesize covalent single layer of 1D coordination polymers by on-surface polymerization reactions. These polymers are very stable thanks to the robustness of the covalent bonds involved and offer the advantage to preserve the functionality of the molecule in the self-assembly. Through this approach, we obtained different 2D polymers but due to the non-reversible character of the covalent bond, self-healing is prevented leading to the formation of polymers with limited size (few tens of nanometers). We show that extended materials can be obtained from a controlled co-deposition process of suitably set of parameters. In particular, co-deposition of quinonoid zwitterion molecules with iron atoms on a Ag(111) surface form covalent metal ligand coordination network of unprecedented micrometer sizes. This work opens up the field of on-surface chemistry for the construction of large covalent metal organic coordination networks materials in a single layer regime [2].

This work was supported by Region Paca under contract 2D ElectroPol…

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P4 Luminescent Oxygen Sensor Based on Platinum(II)-Decorated DNA

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Different metal ions have been introduced into nucleic acids using metal-mediated base pairs[1] to generate bioconjugates with fascinating applications in DNA-mediated charge transfer and in nano- and sensor technology (including SNP sensors).[2]

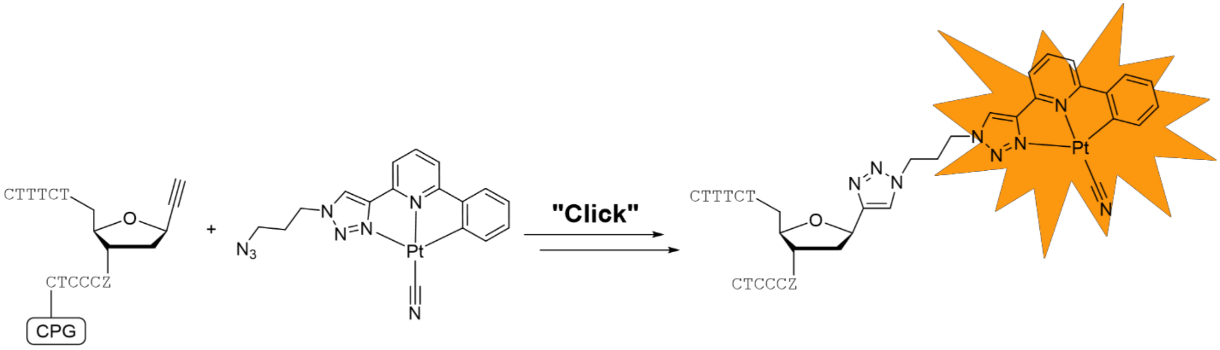
However, applications with potential biological relevance are still absent, most likely because of the scarcity of suitable metal ions in the intracellular microenvironment and the lability of many coordinate bonds. To tackle this challenge, we have developed an organometallic platinum(II) complex with robust phosphorescence. It is composed of a tridentate C^N^N ligand and an ancillary monodentate ligand while its phosphorescence is essentially independent of the identity of the ancillary ligand.[3]

Provided that a suitable substitution pattern is obtained, such complexes can be applied as DNA groove binders[4] which can potentially be introduced into eukaryotic cells to act as cellular sensors.

Most recently, we were able to covalently link the phosphorescent platinum(II) complex to a series of DNA oligonucleotides.[5] Interestingly, when two platinum complexes were introduced into the oligonucleotide in adjacent positions, the phosphorescence lifetimes turned out to be strongly dioxygen-dependent. In particular, emission bands were observed that can be assigned to monomers and excimers.

Interestingly, the excimeric emission (625 nm) was found to be significantly less sensitive towards the dioxygen concentration than the monomeric emission (505 nm), which was strongly quenched in the presence of dioxygen.

We propose that such oligonucleotides can serve as lifetime-based (i.e., time-resolved) or ratiometric intensity-based (i.e., wavelength-dependent) $^3O_2$ sensors in aqueous solutions.



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P5 Novel Insights to Reactions of Cyclophosphazenes and Amines

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Phosphazene derivatives have found applications in various areas (biomedicine, photocatalysis, fluorescent sensors, OLEDs)[1] due to their properties, such as chemical stability, solubility in organic solvents, active P-halogen bonds, structural variability and electrical conductivity. In the literature, the most prevalent molecule is a cyclic trimer, hexachlorocyclotriphosphazene. Cyclic tetramer, octachlorocyclotetraphosphazene, has not been as extensively studied due to its limited availability.

We focus on extending the family of amido derivatives of both of these cyclophosphazenes and investigating their properties in solution and in the solid state, with the aim of evaluating their potential use as sensors with multi-stimuli response.

In this contribution, we would like to report preparation of tris[(1,8-diamino)naphthyl]cyclotriphosphazene hydrochloride **1** (Fig. 1). The hydrogen atom in this compound quarternises the imine nitrogen of the ring, forming tubular structures (Fig. 1b). Interestingly, the phosphazene columns interact solely through hydrogen bonds, creating a porous material with cavities of approximately 12 × 16 Å, occupying 52 % of the crystal volume (Fig. 1c). We believe that this substance could be suitable for the adsorption of gases and small molecules, similarly to HOF, COF and MOF materials.

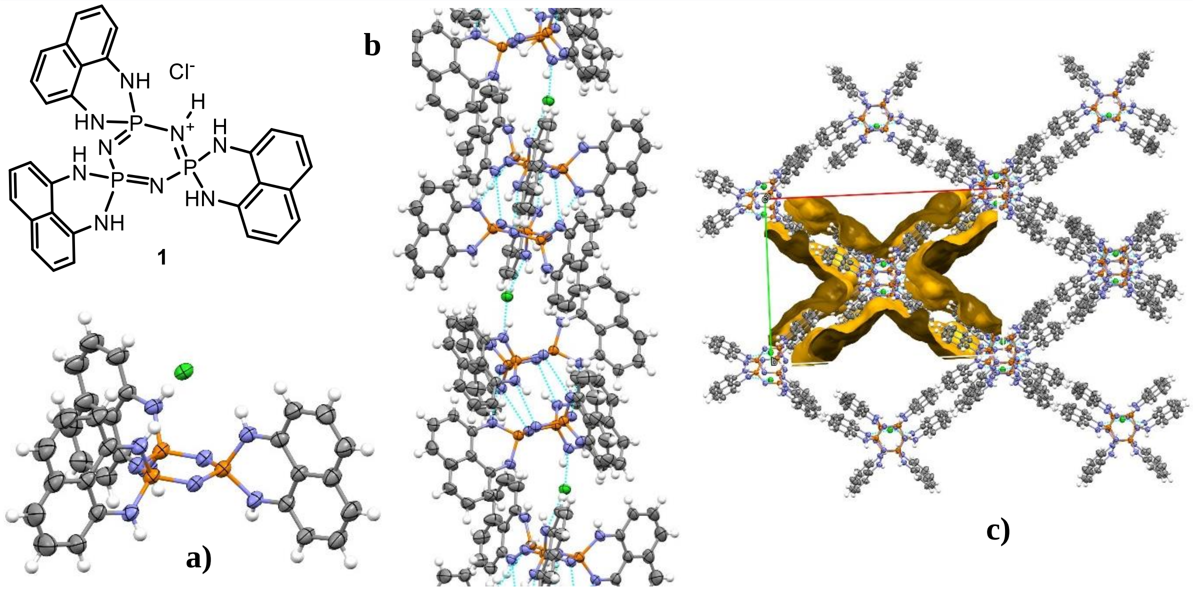

Figure 1: Compound **1**, its crystal structure (a) and crystal packing (b,c).

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P6 Diastereoselective Synthesis of Sulfoxide-Functionalized N-HHC Ru Complexes: An Experimental and Computational Study

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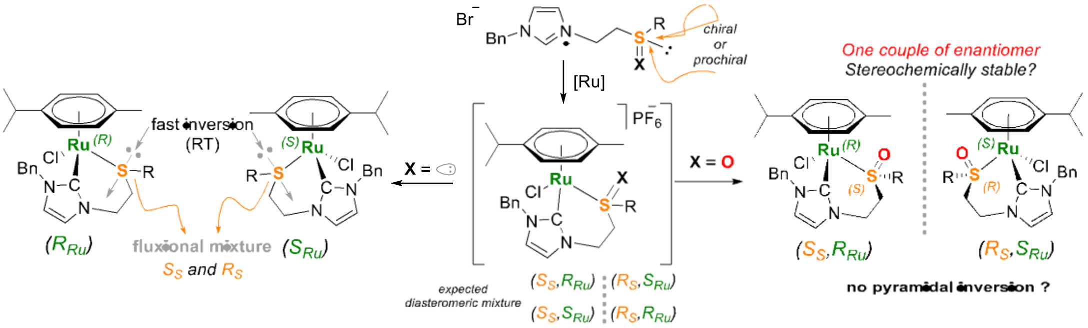
Heterocyclic N carbenes (NHCs) are recognized as good ligands because of their remarkable thermal stability, their strong sigma donation, and of course their easily tunable steric and electronic properties.[1] Although most NHCs are monodentate ligands, the chemistry of bidentate hybrid NHCs carrying an additional Lewis base (often an N, P or O atom) has attracted (over the last 10 years) and continues to attract considerable interest.[2] S-functionalized NHCs remain a less exploited class of ligands,[3] however they have shown their effectiveness as ligands in various metal- catalyzed reactions and more particularly for NHC thioether derivatives.[4]

Our group is interested in the development of ruthenium complexes with sulfur-functionalized NHC ligands. We have shown that despite the prochirality and intrinsic chirality of the sulfur and ruthenium centers respectively (on coordination), in the solid state only a single diastereomer (in the form of an enantiomeric pair) was observed instead of the expected diastereomeric mixture. Despite this, the very rapid inversion of sulfur at room temperature (established by VT-NMR and DFT calculations) indicates a dynamic stereochemical rearrangement in the liquid state.[5]



In order to avoid this type of process and to have better defined and stereochemically stable complexes, we replaced the thioether group with a sulphoxide. The latter is known to have a very high inversion barrier. In this work, a series of cationic Ru complexes were prepared. DFT calculations, VT-NMR and X ray analysis were conducted to demonstrated that there was no favorable stereochemical rearrangement (via sulfur inversion or hemilabile process) at RT. Consequently, the synthesis of these complexes is perfectly diastereoselective.

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P7 Corrole - Based Hemicryptophanes: Towards Confined Heme – Like Catalysts

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Corroles are synthetic porphyrin analogs that only contain three meso carbon atom and display a trianionic N4 metal-binding core. Over the last decades, there has been an impressive boost in corrole chemistry driven by the discovery of straightforward synthetic methodologies leading to this bioinspired macrocycle.[1] Fine tuning of both corrole backbone and its inner core afford a large scope of compounds which can be further studied in a catalysis,[2] material science, medical chemistry etc.[3]

We aimed though to build a cage-like second coordination sphere around the metallocorrole in order to reproduce the hydrophobic cavity found in mettaloenzymes and study its influence on small molecule activation reactions. We focused our attention on the C_3-symmetrical bawl-shaped cyclotriveratrylene cap which provides a rigid hemicryptophane cavity around the metal center, mimicking a heme-based enzymatic structures.[4]

Very recent results on (*i*) synthetic strategies suitable for corrole-based hemicryptophanes preparation, (*ii*) role of the metal center in the cage closure and (*iii*) characterization features, will be enlightened.

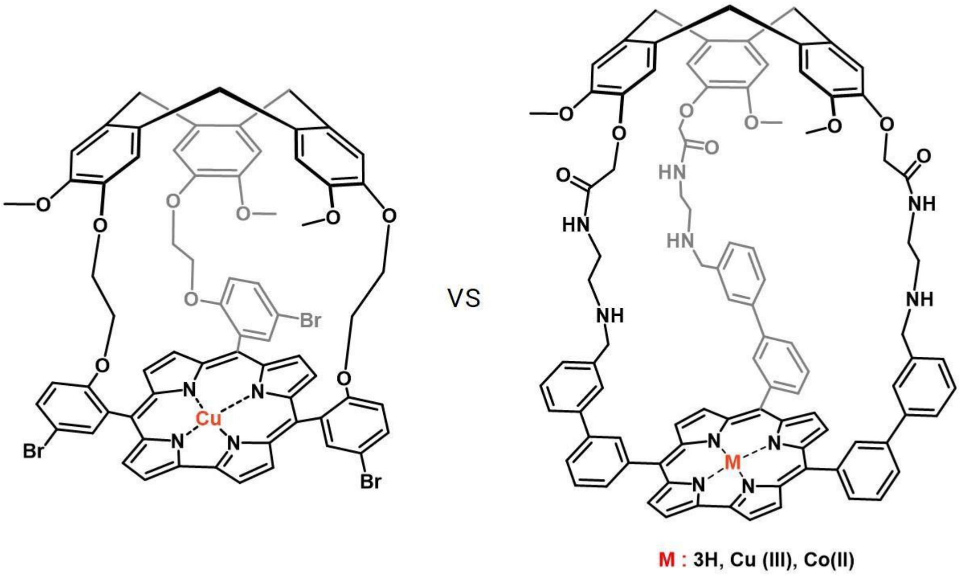

Figure 1: Schematic representation of targeted molecular cages.

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P8 BODIPY-Anthracene Dyads as Versatile Photosensitizers

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Boron dipyrromethene (BODIPY) dyes as highly fluorescent molecules were first synthesized in 1968[1] and have drawn considerable attention as fluorophores. Their photosensitizing capability has led to extensive research aiming to develop new derivatives for diverse applications, including photodynamic therapy (PDT). Therein, the interaction between light, biological matter and a photosensitizing species is utilized to induce cell death which provides an effective therapeutic method to treat diseases such as cancer.

The principle of PDT relies on the formation of triplet excited states, from where reactive oxygen species (ROS) acting as local cytotoxins are generated. Until recently, BODIPY triplet sensitizers depended on the presence of heavy atoms. The introduction of a donor unit, like anthracene, to the BODIPY periphery (Fig. 1) enables the generation of triplet states *via* photoinduced electron transfer (PeT). Moreover, the resulting $^1O_2$ can react with the anthracene moiety to form highly fluorogenic photoproducts.[2] Therefore, these BODIPY dyads can act as both emitters and sensitizers. Lastly, the decay pathway after exciting the molecule into the singlet excited state, i.e., radiative emission *vs*. nonradiative intersystem crossing, can be tuned by the choice of either non-polar or polar solvent medium, respectively.[3]

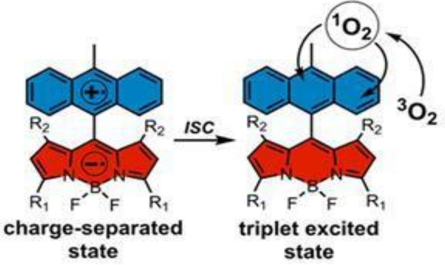

Fig. 1: A representative of the BODIPY-anthracene dyad.

Here we present the synthesis and characterization of BODIPY-anthracene dyads (BADs) with unsymmetrical substitution patterns as functional dyes with switchable intersystem crossing and potential applications in PDT. [4]

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P9 Design and Synthesis of new Hybrid Azole-type Ligands as Potencial Copper Chelators for Cancer Therapeutics

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Small organo-nitrogen molecules continue to occupy a privileged space on the development of crucial areas such as medicinal chemistry. Within the huge number of such organic compounds currently known, there are restricted families that are distinctive, proving to be effective when applied to different problems. Within this limited group we can highlight three heterocyclic compounds namely, tetrazole, thiazole and thiadiazole.These 5-membered ring heterocycles are very important building blocks in organic synthesis and are widely used in coordination chemistry as ligands. Such kind of azoles can coordinate through the N- or S- electron-donating atoms in the ring, acting as multidentate robust units able to participate in distinct coordination modes with metal ions. Besides, in designing ligands, the binding affinity and selectivity towards a specific metal are instrumental features to consider, especially if applications in medicinal chemistry are envisaged. The design of selective ligands for copper has attracted attention is recent years. While this metal is involved in a variety of vital redox processes in the human body, alterations of its normal homeostasis are known to promote toxicity through induced formation of reactive oxygen species (ROS) that may target lipids, proteins or nucleic acids.[1] Cancer cells have high requirements of copper than their normal counterparts, as this metal is essential for angiogenesis and metastasis.[2] The selective capture of copper by chelators in cancer cells represents an optimal therapy to annul or stopping metastasis.[3]

Following our research line on the production of azole-based conjugates,[4] herein we present the synthesis of a series of original hybrid tetrazole-type ligands (pyrimidine-, purine-, 1,2,4-thiadiazole- and triazine-tetrazolyl conjugates) as potential copper chelators that can avidly capture Cu(II) in neoplasms. If, in addition, the redox active copper complexes formed exhibit cytotoxicity, ultimately leading to harmful reactive oxygen species (ROS) in cancer cells, then the copper chelators could inhibit tumor growth by a dual mode of action, acting as powerful tools for cancer chemotherapy.

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P10 Exploration of Synthetic Strategies for the Development of non- Planar Atropisomeric Porphyrins

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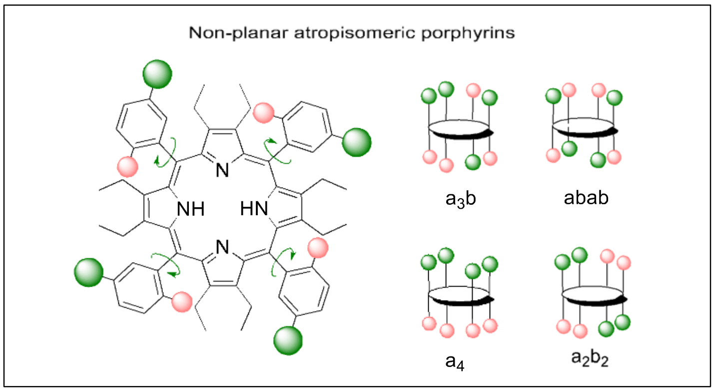
Atropisomers are a subclass of conformers arising from restricted rotation about a C–C single bond, predominantly due to steric hindrance. This phenomena has been exploited in porphyrins for applications ranging from sensing[1] to biomimetic models.[2]
Work has also demonstrated the significance of tetrapyrrole atropisomerism in medicine, reporting the enhanced phototoxicity of the α_4-atropisomer in comparison to the other three atropisomers of Redaporfin©, a pre-clinical bacteriochlorin photosensitizer.[3] Overall, atropisomeric porphyrins offer routes to easily adaptable, yet complex systems due to the wide variety of possible peripheral functionalities, compounded by the multiple environments that each atropisomer can provide, which allows for precise control of the internal and external environments.

Whilst the above examples provide a glimpse into the potential impact of utilizing atropisomerism,[4] studies are still required to fully understand the fundamental mechanisms in tetrapyrrole systems. This work therefore describes the synthesis of a library of non-planar atropisomeric porphyrins with various peripheral functionalities, which has allowed us to comprehend the relationship between structure and atropisomer stability. Hence, by harnessing these observations, it is possible to utilize the appropriate atropisomers as both picket fence receptors and metallocage precursors.



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P11 A convenient solid-phase synthesis method of cyclic amides

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Cyclic amides were a derivatives of peptides and has versitle biological effects. They was also considered as one type of cyclic peptides. Desipite its biological advantages, lack of convenient synthetic method limited their development. Convenient approach apply liquid-phase amidation which was inefficient and are ring-size dependent. Furthermore, inevitable side-products cause the chromatographic purification and damaged the yield. Herein, we reported a solid-phase method to prepare cyclic amide with predicted structures without chromatographic purification. A clickable conjugation strategy by incorporating a new protecting group for glutamic acid and aspartic acid derivatives. These two residues could be activated by developed method[1]. The following intramolecule cyclization afforded the desired cyclic amides with intrinsic free amine.

This work was supported by Kaohsiung Medical University and the national science and technology council, Taiwan

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P12 Enhanced Catalytic Activity of Triply Fused Porphyrin based Fe(III) Complexes Towards Electrochemical CO_2 Reduction

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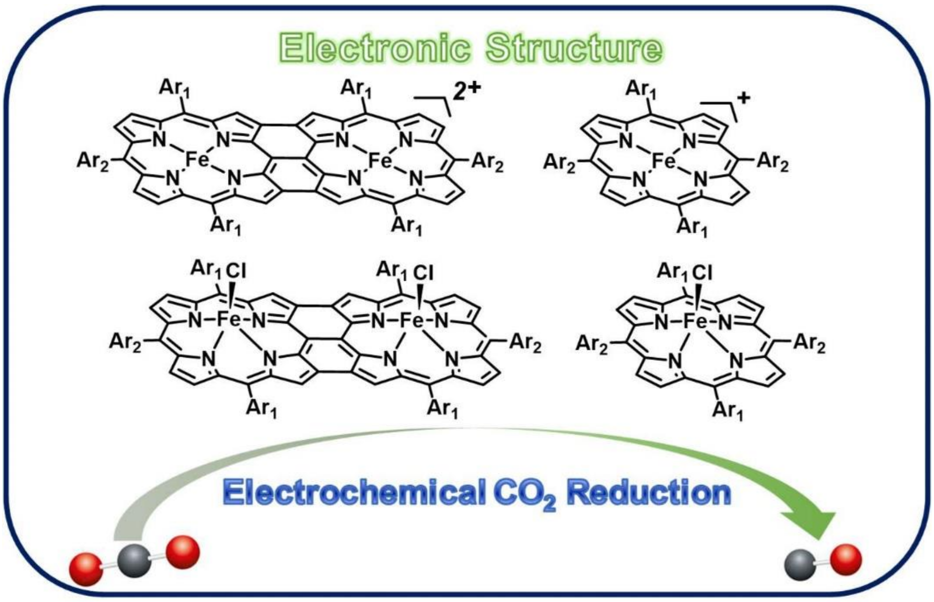
The widespread utilization of fossil fuels, in conjunction with the process of industrialization, has led to a continuous increase in the CO_2 concentration in the Earth's atmosphere over the past century.[1] Scientists, therefore, are currently exploring technological applications to capture and convert CO_2 from the atmosphere into value-added materials.[2] In addressing this environmental concern, our research focuses on the utilization of iron porphyrin complexes as effective catalysts for CO_2 reduction in solution.[3] Within this framework, we have successfully synthesized and analyzed comprehensive electronic structure of a series of tetra and penta-coordinated mono and triply-fused iron(III) porphyrin complexes employing various analytical techniques such as high-field EPR, Mössbauer, magnetic measurements, cyclic voltammetry, and UV-visible and infrared spectroelectrochemistry in solid and/or solution states. The aforementioned complexes have demonstrated excellent activity towards electrocatalytic CO_2 reduction, notably the tetra-coordinated triply-fused porphyrin-based iron complex exhibited a turnover frequency (TOF_{max}) of 95% in DMF medium. These findings significantly contribute to the understanding of iron porphyrin complexes as promising catalysts for mitigating CO_2 levels and offer potential applications in sustainable electrocatalysis.



Acknowledgements: This work was supported by SFB (CRC 1333).

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P13 Taming 2,2’-Biimidazole Ligands in Trivalent Chromium Complexes

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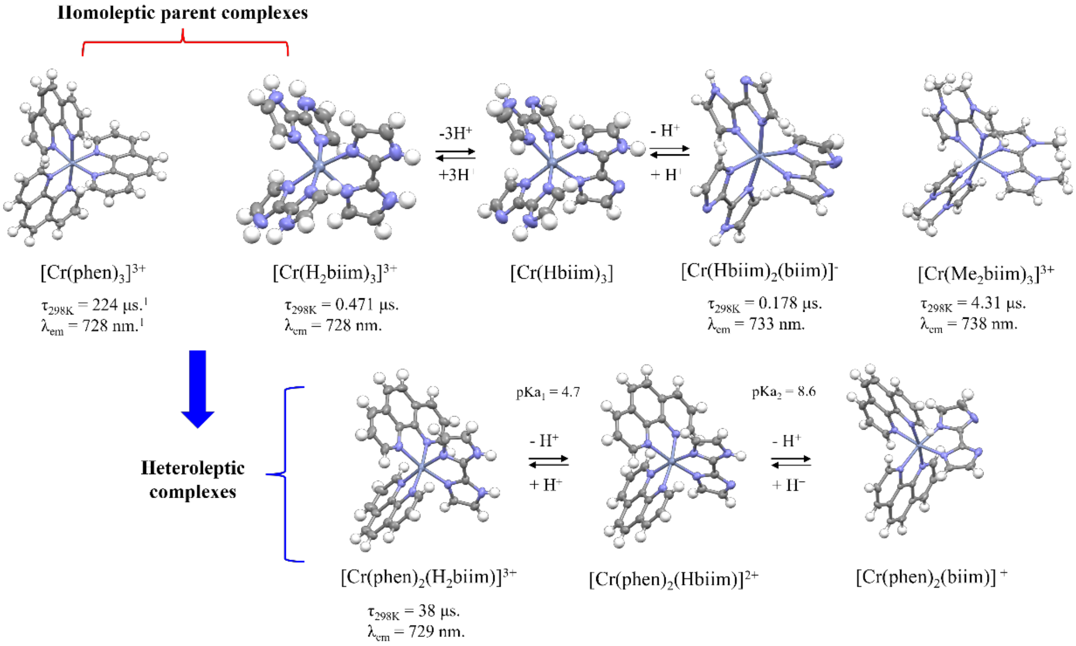
A series of inert homoleptic and heteroleptic [$Cr^{III}N_6$] complexes based on the ligand 2,2’-biimidazole (H_2biim) were synthetized, characterized, and studied. Upon coordination to Cr(III), the H_2biim ligand gains the ability to liberate protons, forming the conjugate bases of the corresponding complexes, containing the deprotonated ligands Hbiim$^-$ or biim^{2-}, which were subsequently isolated and studied. These deprotonated complexes have the potential to be used as building blocks for polymetallic architectures using the “complex as ligand strategy” where the Cr(III) complex acts as the ligand, thanks to the bridging nature of biim^{2-}. In addition, the photophysical properties of the long-lived spin-flip excited states inherent to Cr(III) were investigated. While the homoleptic complex [Cr(H_2biim)$_3$]$^{3+}$ is poorly emissive with a relatively short emission lifetime, substitution of two H_2biim with two 1,10-phenanthroline drastically enhances the emission lifetime, rendering it suitable for energy transfer between metal centers in a polymetallic assembly.



This work was supported by the Swiss National Science Foundation.

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P14 BiPyridyl-Substituted Tetrathiafulvalene-Based MOFs for High Efficient Supercapattery Materials

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The growing demands for powerful and sustainable energy sources continuously promote the development of alternative renewable energy source devices.[1,2] In this work, we report the application of bipyridyl-substituted tetrathiafulvalene-based MOFs for high performance electrodes in supercapatteries. Two isostructural MOFs, formulated as $[M(py\text{-}TTF\text{-}py)(BPDC)]\cdot 2H_2O$ (M = NiII (1), ZnII (2); py-TTF-py = 2,6- bis(4'-pyridyl)TTF; H_2BPDC = biphenyl-4,4'-dicarboxylic acid), are crystallographically characterized. The two MOFs possess a three-dimensional 8-fold interpenetrating diamond-like topology, which is the first example for TTF-based dual-ligand MOFs. Upon iodine treatment, MOFs 1 and 2 are converted into oxidatively doped 1-ox and 2-ox. The electrical conductivity of 1-ox and 2-ox is significantly increased and the specific capacities reach 833.2 and 828.3 C g^{-1} at a specific current of 1 A g^{-1} for 1-ox and 2-ox, respectively. When used as a battery-type positrode to assemble supercapattery, the AC || 1-ox and AC || 2-ox present an energy density of 90.3 and 83.0 Wh kg^{-1} at a power density of 1.18 KW kg^{-1} and great cycling stability with 82% of original capacity and 92% columbic efficiency retention after 10000 cycles. The excellent electrochemical performances of 1-ox and 2-ox illustrate that the construction of unique highly dense and robust structures of MOFs followed by post-synthetic oxidative doping is an effective approach to fabricating MOF-based electrode materials.

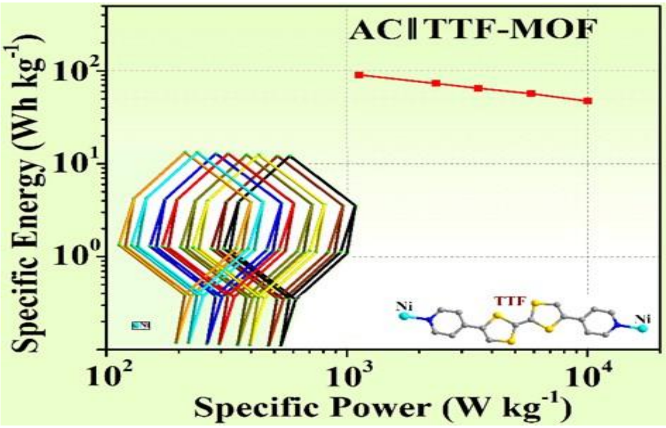

Figure: 3D 8-fold interpenetrating dia-like TTF-based MOFs are synthesized, showing an enhanced conductivity, boosted specific capacity and high specific energy of the supercapattery.

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P15 Synthesis, Spectroscopic and Structural Characterization of [Ru^{II}(arene)Cl]$^+$, [Rh^{III}(cyclopentadienyl)Cl]$^+$ and Pt^{II}Cl$_2$ Derivatives of Bis(indazolyl)methane

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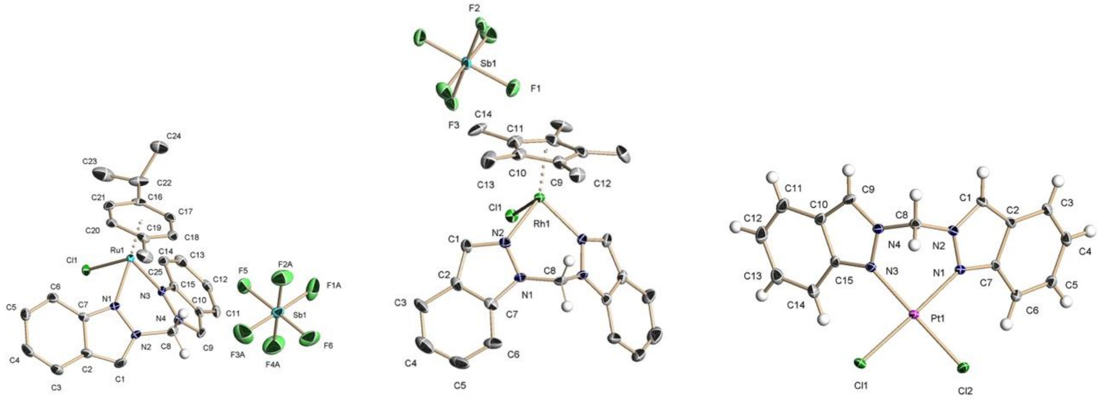
Bis(pyrazolyl)alkanes [R$_2$C(pz^x)$_2$], firstly reported by Trofimenko,[1] continue to receive great attention.[2] Complexes containing these ligands has been widely investigated as potential catalysts in important industrial processes as transfer hydrogenation[3] and C-H-aminations.[4] The neutral bidentate [R$_2$C(pz^x)$_2$] are flexible and chemically stable and able to coordinate any metal of the periodic table.[5] In addition, it is very easy their functionalization and several groups with different steric and electronic properties can be introduced on the heterocyclic rings and on the bridging carbon.[6] We reported here the result concerning the coordination ability and metal chelation aptitude of the three regioisomers of bis(indazolyl)alkanes, i.e di(1H-indazol-1-yl)methane (L*), di(2H-indazol-2-yl)methane (L') and (1H-indazol-1-yl)(2H-indazol-2-yl)methane (L") toward Rh(III), Ru(II) and Pt(II) acceptors. Complexes [Ru(η^6-p-Cym)Cl(L)]SbF$_6$, [Rh(η^5-Cp*)Cl(L)]SbF$_6$ and [PtCl$_2$(L)] (L = L*, L', L") (Figure 1) were synthesized and spectroscopically and structurally characterized.



[Ru(η^6-p-Cym)Cl(L)]SbF$_6$. **[Rh(η^5-Cp*)Cl(L)]SbF$_6$** **[PtCl$_2$(L)]**

Figure 1. Ru, Rh and Pt derivatives of di(2H -indazol-2-yl)methane (L')

This work was supported by Ministry of Economy and Competitiveness, Spain, MP09-FQM-4826 *and Ministry of Science, Innovation and Universities, Spain*, PGC2018-093443.B-100

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P16 The Effect of Ligand Substitution on Long-Lived CPL from Chiral Cr(III) Complexes.

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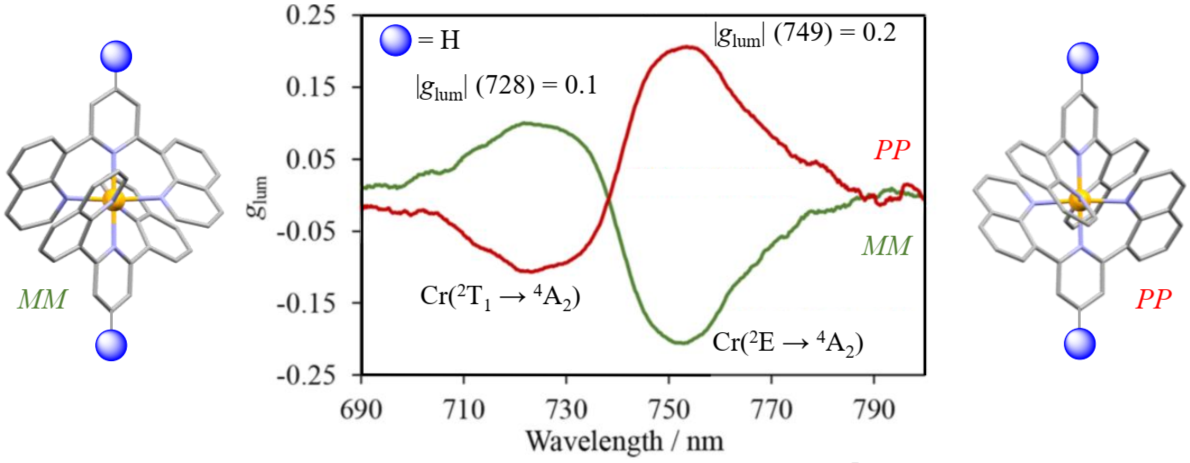
A series of highly emissive inert and chiral Cr(III) complexes displaying positive and negative Circularly Polarized Luminescence (CPL) within the NIR region at room temperature have been prepared and characterized to study the effect of ligand substitution on the photophysical properties, more specifically on the chiroptical properties. The helical homoleptic $[Cr(dqp\text{-}R)_2]^{3+}$ (dqp = 2,6-di(quinolin-8-yl)pyridine; R = H, OCH_3, Br, C≡CH, Ph, ≡-Ph, DMA, ≡-DMA (DMA=*N,N*-dimethylaniline)) complexes were synthesized as racemic mixtures and could be resolved and isolated into their respective *PP* and *MM* enantiomers by chiral stationary phase HPLC. The corresponding enantiomers show two polarized emission bands within the 700-780 nm range corresponding to the characteristic metal-centered $Cr(^2E \rightarrow {}^4A_2)$ and $Cr(^2T_1 \rightarrow {}^4A_2)$ transitions with large g_{lum} ranging from 0.17 to 0.20 for the former transition. The high quantum yields afford important CPL brightness of up to 582 M^{-1}■cm^{-1} (for $[Cr(dqpC{\equiv}CH)_2]^{3+}$), a key point for applications as chiral luminescent probes.



λ_{exc}=390 nm, deaerated CH_3CN (5×10^{-5} M)

Solid-state structures for the MM (green), PP (red) enantiomers, and their respective CPL spectra in solution.

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P17 Electrosynthesis of Pyridinium-Porphyrins as Precursors of Amino-Porphyrins

Asmae Bousfiha,[1] Abdou K. D. Dimé,[2] Julie Echaubard,[1] Mathieu Berthelot,[1]
Amelle
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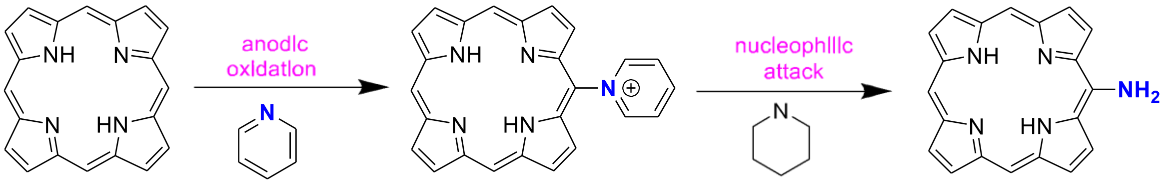
For many decades, porphyrins have attracted considerable attention due to their implication in natural processes (photosynthesis, O_2 transport in blood…) and their recent applications in various research fields such as photovoltaic solar cells, non-linear optical materials, photodynamic therapy and molecular electronics. To finely tune and improve the performance of porphyrin-based materials, peripheral functionalization of the porphyrin ring with judicious (hetero) atoms or molecular fragment(s) is essential. In particular, the introduction of a nitrogen atom directly bonded to the *meso* or *β* position of the porphyrin induces intense alterations of the electronic, optical, and electrochemical properties.

Numerous methods exist to introduce an amine function on porphyrin (reduction of a nitro function,[1] Buchwald-Hartwig coupling with palladium[2] or attack of an azide anion on a brominated porphyrin.[3] However, they remain not always selective and require pre-functionalization of the porphyrin core.

This poster will present our recent electrochemical/chemical two-step one-pot amination of porphyrins based on 1) the regioselective anodic nucleophilic substitution of the porphyrin with pyridinium, 2) the chemical ring-opening of the pyridinium- porphyrin *via* nucleophilic attack of piperidine (Scheme 1).[4]



Scheme: *Oxidative C-N fusion of meso-pyri(mi)din-2-ylthio-porphyrins.*

This work was supported by the ANR (ANR-15-CE29-0018-01, ANR-15-IDEX-03), CNRS, Regional Council of Bourgogne Franche-Comté, Univ. Bourgogne Franche- Comté, FEDER

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P18 Stepwise Oxidative Intermolecular C-C or Intramolecular C-N Couplings of Zn(II) *meso*-Pyridin-2-ylthio-Porphyrins

Fatima Akhssas,[1] Mathieu Berthelot,[1] Abdou K. D. Dimé,[2] Asmae Bousfiha,[1] J. Echaubard,[1] Hélène Cattey,[1] Paul Fleurat-Lessard,[1] Charles H. Devillers[1,*]

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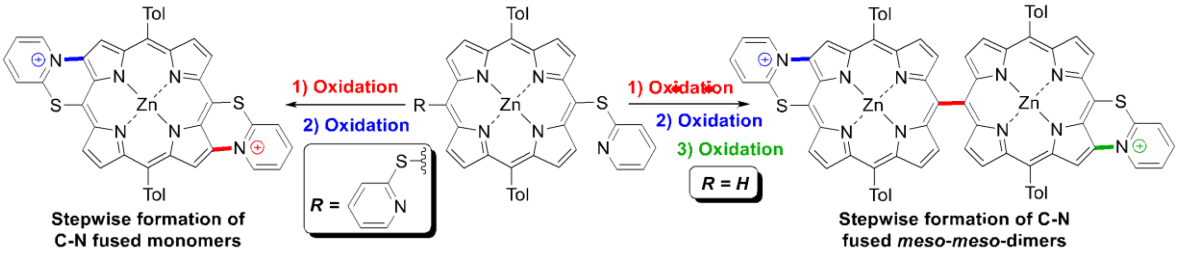
Extending the π-conjugation of aromatic molecules, in particular porphyrinoids, *via* C-C or C-N coupling(s) with peripheral aromatic fragment(s) has been the focus of numerous researches over the last two decades.[1] Indeed, C-C/C-N fusion of one are several hydrocarbon(s) or aromatic heterocycle(s) onto the porphyrin periphery forces the porphyrin core and the substituent to be coplanar, that enhances the electronic communication between both fragments. π-extended porphyrins display important changes in their optical and electrochemical properties such as decrease of the HOMO/LUMO gap, bathochromic shift in their absorption/emission spectra, large absorption and fluorescence in the NIR range.[2] Nowadays, π-extended C-C/C-N linked porphyrins are commonly obtained using toxic and/or expensive chemicals, often under harsh conditions. Due to the extension of the conjugation path, the oxidation potential decreases which may lead to over-oxidation during the fusion process. In this work, the (electro)chemical oxidation of original zinc(II) *meso*-(pyridin-2- ylthio)porphyrins will be presented affording the C-N fused (bis)pyridinium derivatives in a stepwise manner. When one *meso* position remains free, the first oxidative reaction consists in the *meso*,*meso* C-C dimerization. The resulting pyridinium derivatives exhibits important changes in their physico-chemical properties (NMR, UV- vis., CV) as compared to their initial unfused precursors.[3]



Scheme: *Stepwise Oxidative C-N fusion of meso-pyridin-2-ylthio-porphyrins.*

This work was supported by the ANR (ANR-15-CE29-0018-01, ANR-15-IDEX-03), CNRS, Regional Council of Bourgogne Franche-Comté, Univ. Bourgogne Franche- Comté, FEDER

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P19 Homoleptic Complexes of Bis(4-carboxylpyrazol-1-yl)acetic acid: a New Building Unit for MOFs

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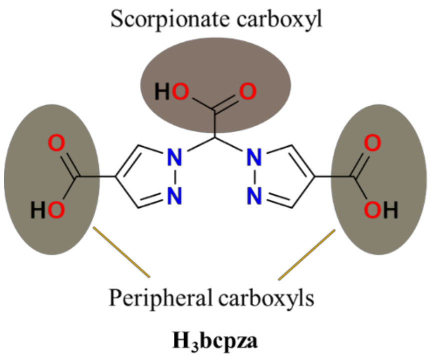
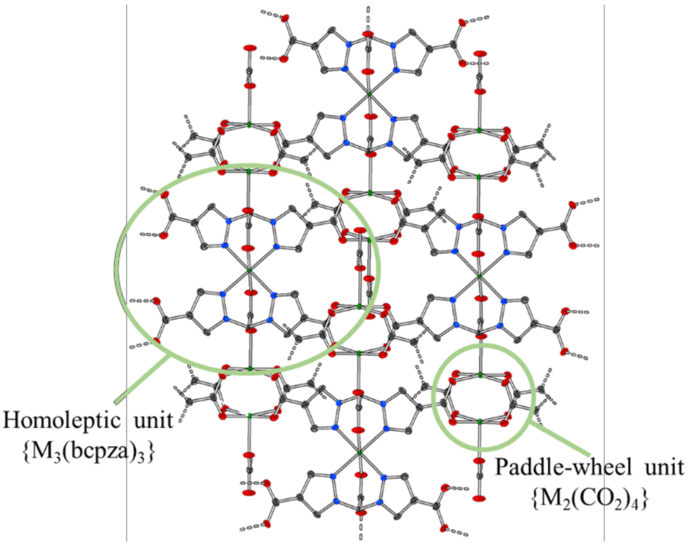
Recently our group reported on a novel bis(4-carboxylpyrazol-1-yl)acetic acid (H_3bcpza) ligand that shows improved water solubility as well as new possibilities in coordination behavior due to the additional peripheral carboxylic acid functionalities on the pyrazoles.[1] Several homoleptic transition metal complexes $[M(L)_2]$ bearing this ligand were synthesized and their molecular structures were resolved by single crystal X-ray structure determination. The coordinational behavior of H_3bcpza was explored further. These homoleptic complexes $[M(L)_2]$ become potential building units for new metal-organic frameworks (MOFs) resulting in microporous materials of the composition $[M_3(\text{bcpza})_2]_n$ x 12 H_2O.[2] The single crystal structure analysis of such a MOF revealed the highly regular structure comprised from essentially two building units: the homoleptic units $\{M(\text{bcpza})_2\}$ and paddle-wheel moieties $\{M_2(CO_2)_4\}$. The stability of such MOF was studied by powder XRD, TGA and BET analyses. Currently the synthesis of similar $[M_3(\text{bcpza})_2]_n$ type MOFs is tested with other divalent transition metals.





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P20 Reactivity of Heterocyclic Rings Embedded in 21-oxa-23-Telluraporphyrin: Furan Breaking and Mending, Tellurophene to Metallacycle Transformation, and Macrocycle Degradation.

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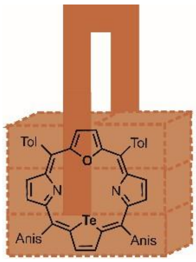
Porphyrin analogues containing oxygen or tellurium atoms instead of the internal nitrogen atoms exhibit unusual reactivity. In the case of tetraoxaporphyrinogen, four oxygen atoms were replaced by selenium or sulphur atoms using H_2Se or H_2S, respectively [1]. For 21,23-dioxaporphyrin, the Achmatowicz rearrangement occurred, in which the furan unit was converted into a 3-pyranone ring [2]. Telluraporphyrins often undergo tellurium-centered reactions, exemplified by chlorination or oxidation of 21-telluraporphyrin [3, 4] and 23-tellura-21-carbaporphyrin [5]. In the reaction of 21,23-ditelluraporphyrin with HCl the extrusion of tellurium atoms occurred, leading to the formation of a porphyrin-annulene hybrid [6]. The tellurophene rings of the 21,23-ditelluraporphyrin and 21-oxa-23-telluraporphyrin **1** can be transformed into metallacyclopentadiene units embedded within the macrocycle using metal salts (Pd, Pt, Rh). Thus, the first *metalla*porphyrins were obtained, 21-oxa-23-rhodaporphyrin, 21-metalla-23-telluraporphyrins, and 21,23-dimetallaporphyrins [7]. Here, we will show the unexpected reactivity of **1** (Figure), in which one furan C-O bond-breaking was promoted by the insertion of a ruthenium ion, and compound **2** was formed. The reaction of **2** with $[RhCl(CO)_2]_2$ recreates the C-O bond and yields 21-oxa-23-rhodaporphyrin [8]. Demetallation of **2** leads to a new macrocycle, 1-oxo-23-tellura-21- vacataporphyrin, which exposed to oxygen undergoes degradation to open-chain **3**.



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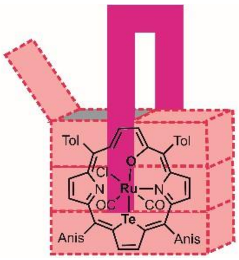

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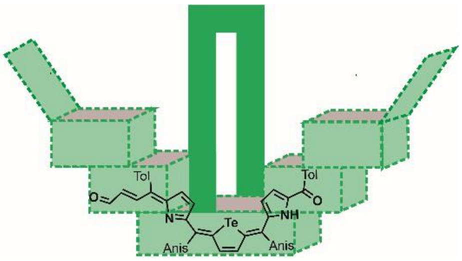

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This work was supported by the National Science Centre (2020/37/B/ST4/00869).

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P21 Optimizing Toluene Oxidation: New Iron(III) C-scorpionate Catalysts and Ligand Influence

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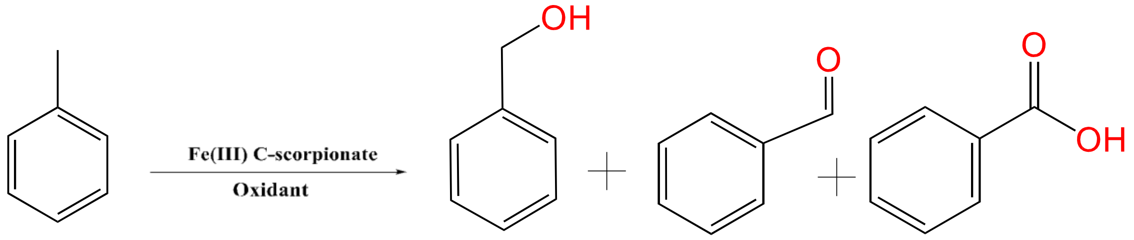
In the present study, iron(III) complexes bearing the C-scorpionate ligand,[1–3] hydro-tris(pyrazolyl)methane ($HC(pz)_3$) were synthesized and their catalytic activity screened for the peroxidative oxidation through conventional heating and alternative methods of toluene following the principles of green chemistry. Benzaldehyde is the main product of the toluene oxidation reaction (Scheme). [1,4] It's obtained industrially by applying harsh conditions (achieving low yields and selectivity) and is an important starting material for dyes, perfumes, and pharmaceutical industries[4]. The new C-scorpionate iron(III) complexes were synthesized using different iron salts ($FeCl_3$, Fe_2SO_4, and $Fe(NO_3)_3$) to study the effect of the anionic ligand on the structure, electrochemistry, and catalytic activity of the complex. Therefore, compounds were characterized by elemental analysis, IR, among other techniques. The catalytic activity of the iron complexes was then tested (with tert-butyl hydroperoxide or hydrogen peroxide) under mild conditions (temperature below 80 ºC, green oxidant, solvent-free or green solvents). The influence of various parameters, such as reaction time, type and amount of catalyst, temperature, and presence of additives, is also evaluated and discussed.



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P22 Can we induce a Moiré effect on Graphene with a supramolecular layer of Zwitterions?

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Imposing a Moiré effect by the superposition of two-dimensional materials has recently emerged as an efficient approach to modify the band structure in van der Waals heterostructures. This Moiré effect, or superlattice, induces a periodic modulation of the electrostatic surface potential, which could lead to materials with strongly correlated electronic states.[1] Until now, these experiments were done on inorganic heterostructures in which the spatial modulation and the amplitude of the electrostatic potential are determined by the lattice parameters of the inorganic 2D layers used. The versatility of these heterostructures allows for the possibility of substituting an inorganic layer with a supramolecular layer composed of dipolar organic molecules. The inherent characteristic of these molecules allows for the modulation of the surface potential amplitude, while the periodicity is determined by the lattice parameters of the supramolecular network.

Our methodology consists in introducing a precise control on the superlattice's structural parameters via chemical synthesis. We have deposited a self-assembled monolayer of the di-Phenyl Zwitterionic Tetraazapentacene (DP-ZTAP)[2] molecules onto a Graphene surface. Following a structural analysis through Scanning Tunneling Microscopy (STM), revealing a tilted adsorption of the molecules, we proceeded to map the Local Contact Potential Difference (LCPD) using Kelvin Probe Force Microscopy (KPFM). This mapping was performed across multiple X, Y and Z coordinates, spanning several elementary meshes of the molecular network, showing a clear and periodic shift of the LCPD at the expected position of the dipole of each molecule. These measurements show, for the first time, the capability to modulate the surface potential on graphene through the incorporation of organic layers.

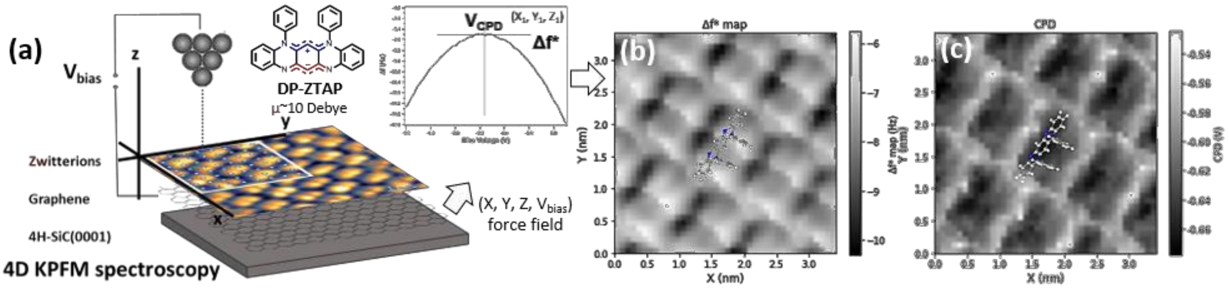

Figure 1:(a) Schematic of the measurement principle. At each tip position, the frequency shift is recorded as function of sample bias voltage. The maximum of the fitted parabola yields V_{CPD} and Δf* for that position. (b) A local spectroscopy map using KPFM was performed on DP-ZTAP molecules, illustrating the variation in oscillation frequency shift at a fixed height. The measurement is conducted across the surface to generate maps of the LCPD as illustrated in (c).

This work was supported by ANR SUPERZIC.

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P23 Benefiting from Supramolecular Stability to Access an Unattainable Complex

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Cationic cyanine-dyes have been connected to ligands for inducing a near infrared antenna effect.[1,2] This design is currently limited to 1:1 metal-to-ligand(dye) ratio, but there is a growing interest in expanding this ratio to enhance the system brightness by increasing the number of antennas surrounding the metallic center. Moreover, the presence of multiple excited sensitizers around the metallic luminophore may open new excitation pathways, thus improving the final luminescence. Attempts to transition from [Er(hfac)$_3$dig], allowing only one ligand exchange, to [Er(CF$_3$SO$_3$)$_3$], proved unsuccessful due to significant cationic repulsion when several dyes approach the cationic center (Figure 1, top). However, a breakthrough results from the use of self- assembly processes for overcoming the latter limitation.[3]

This new strategy offers kinetic stabilization through additional complexation sites, a phenomenon known as supramolecular stability,[4] thereby enabling the acceptance of three positive cyanine dyes around a cationic trivalent lanthanide while maintaining its stability (Figure 1, bottom).

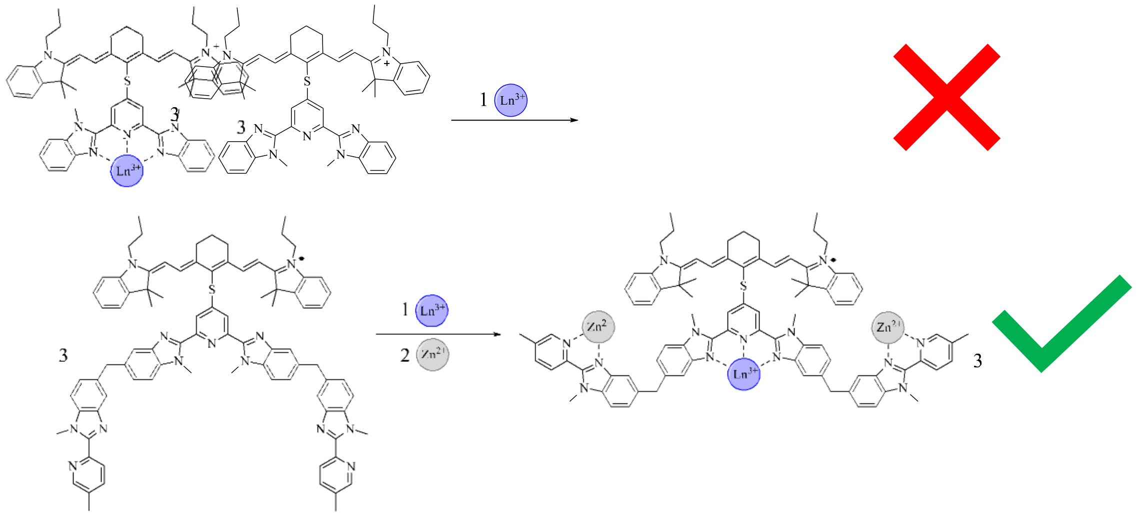

Figure 1. Successive complexation (top) and metallosupramolecular self-assembly (bottom) for the connection of three cationic dyes around a trivalent lanthanide.

This work was supported by the Swiss National Science Foundation.

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P24 Fullerene-Based *N,N*-Chelating Ligands

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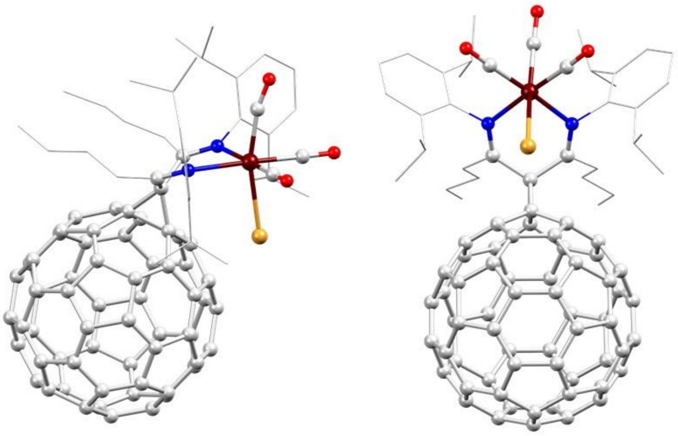
A novel chelating ligand system was obtained *via* Bingel-Hirsch addition of diketones to C_{60}[1-2] and subsequent conversion into imines. These κ^2-*N,N*-bidentate ligands were tested for their coordination behavior to group 6 and 7 transition metals. Due to its capability of generally taking up electrons reversibly, the fullerene seemes an intriguing moiety to create a redox non-innocent backbone in the ligand system. For some group 6 metals, carbonyl complexes bearing redox non-innocent κ^2-*N,N*-bidentate chelate ligands, have been shown to be promising CO_2 reduction catalysts.[3-4] Therefore, the complexes $[M^I(L^{Me/nBu})(CO)_3Br]$ (M = Mn, Re) and $[M^0(L^{Me/nBu})(CO)_4]$ (M = Mo, W) were synthesized and characterized *via* NMR, IR and UV-Vis spectroscopy. Electrochemical studies of the ligand and selected complexes were conducted under inert gas as well as CO_2 atmosphere. DFT calculations confirmed structural stability and furthermore provided some insight into the predicted coordination geometry around the metal centers (see figure below).



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P25 Metal Chelators Based on *N*-alkylamine Azoles for Potential Antifungal Compounds

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Azole drugs are the most used antifungal drug class due to their broad-spectrum activity and bioavailability. They target the biosynthesis of ergosterol as an essential component of fungal cell membranes.[1] Considering the alarming rise in drug resistance of fungal pathogens and the low number of new antifungals under development, it becomes urgent to discover new drugs and novel activity mechanisms. Metal complexes have recently attracted great interest to fight antimicrobial resistance, since these can offer additional activity mechanisms when compared to organic compounds. Indeed, some complexes of various transition metals have been shown to present strong antifungal activity.[2] In a previous work, an azole compound containing a chelating moiety was synthesized and coordinated to copper(II), demonstrating interesting results as an antifungal agent.[3]

Now, we have developed a family of new metal chelators based on *N*-alkylamine azole skeletons appended with a chelating moiety. These azoles were subsequently used to prepare complexes of copper(II), nickel(II), palladium(II) and gallium(III). All compounds were studied regarding their antifungal activity against *Candida albicans* and *Candida glabrata*. Preliminary results show that some of the compounds display antifungal activity against one or both *Candida* species.

This work was supported by FCT - Fundação para a Ciência e a Tecnologia, I.P., through project 2022.04565.PTDC, MOSTMICRO-ITQB R&D Unit (UIDB/04612/2020, UIDP/04612/2020) and LS4FUTURE Associated Laboratory (LA/P/0087/2020).

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P26 Dinuclear Ruthenium Complexes as Electrocatalysts for the Oxidation of Ammonia

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The global climate crisis is the most drastic challenge for our modern civilization. Thus, it is urgent to rethink our ways of energy production. A promising, but yet barely exploited option is the use of ammonia as a fuel, producing unproblematic nitrogen as the only waste product.[1] Our group has contributed to the research field of water oxidation catalysis and has developed a class of highly performing dinuclear ruthenium catalysts based on a robust bis(bipyridyl)pyrazolate ligand backbone.[2,3] In our recent studies, we aim to extend the scope of these catalysts towards the ammonia oxidation reaction. For this purpose, we have successfully modified our existing systems synthetically in order to create a suitable platform to initiate the electrocatalytic formation of dinitrogen from ammonia (Figure 1, left). Detailed electrochemical (Figure 1, right) and spectroscopic studies give promising indications that our system is an active electrocatalyst at low to moderate overpotentials, thus paving the way to a class of ammonia oxidation catalysts with a binuclear substrate binding motive.

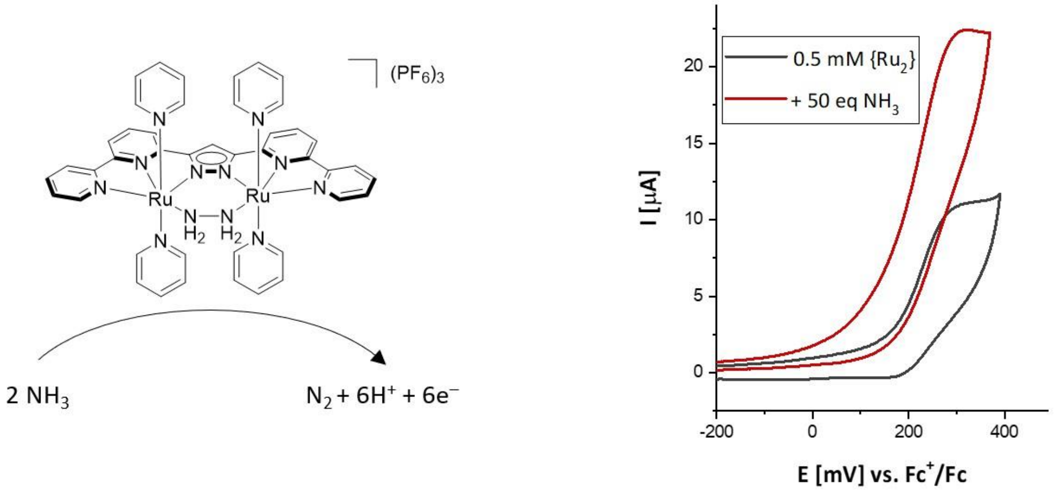

Figure 1: *Ammonia oxidation with a binuclear ruthenium complex as potential catalyst (left) and CV experiment indicating the turnover of ammonia in the presence of the catalyst (right).*

This work was supported by the German Research Foundation (CRC 1073) and the Fonds der Chemischen Industrie.

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P27 Rigid Hydrocarbon Isosteres as Linkers in Porphyrin Dyads for Sensing Applications

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Traditionally, multi-porphyrin arrays are networks of two or more porphyrins connected by rigid linkers like benzene or alkyne groups, resulting in systems with increased electron delocalization. The unique electronic properties of these compounds have led to their application in a variety of materials from molecular wires to light harvesting molecules.[1, 2] However, as these arrays typically consist of conjugated linkers, modulation of the material properties of the arrays has been limited.

Rigid hydrocarbons like bicyclo[1.1.1]pentane (BCP) and cubane have recently gained interest as isosteres for alkynes and benzene units respectively (Figure 1). Isosteres are compounds which act as drop- in replacements for moieties within a molecule, modifying the chemical properties while preserving the physical structure. The replacement of conjugated linkers with non-conjugated linkers, BCP or cubane, in multi-porphyrin arrays maintains rigid connectivity while decreasing conjugation between individual porphyrins. This modification allows for selective modulation of the multi-porphyrin arrays' chemical properties, resulting in the potential for unique optical, electronic, and sensing applications.

Here we present a library of BCP and cubane based linkers for symmetric and non-symmetric porphyrin dyads with different linker lengths and controlled connectivity (Figure 1).[3] The structure, properties, and sensing abilities of both BCP and cubane- linked porphyrin dyads will be discussed.[4]

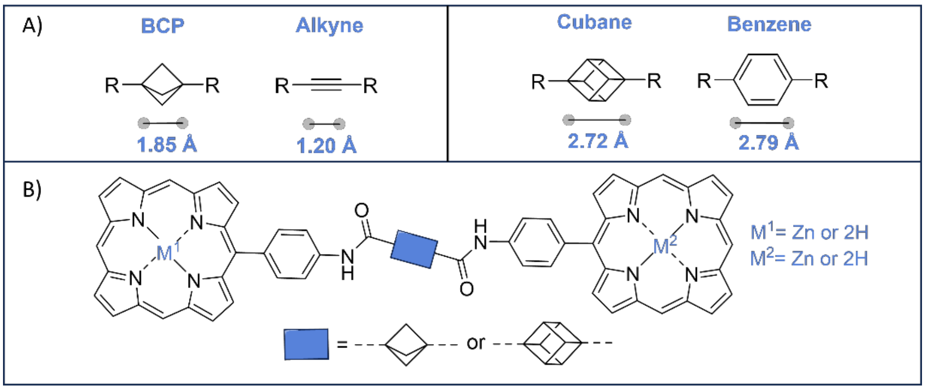

Figure 1A) Examples of rigid aliphatic hydrocarbons as isosteres. B) Model of symmetric and non-symmetric porphyrin dyads synthesized.

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P28 Synthesis and Characterization of a 1,4,7-Triazacyclononane-Based Cu-Complexes Equipped with an Hemicryptophane Cavity.

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Metalloenzymes are impressive molecular entities capable of numerous chemical transformations with excellent selectivity and efficiency under moderate mild conditions. For instance, methane monooxygenases (**MMO**) activate oxygen to reach the highly challenging oxidation of methane to methanol. The reactivity of metalloproteins relies on biologically active metal ions (Cu, Fe, Mn) supported by O, S, or N-donors ligands, confined within the enzyme's cavity.[1]

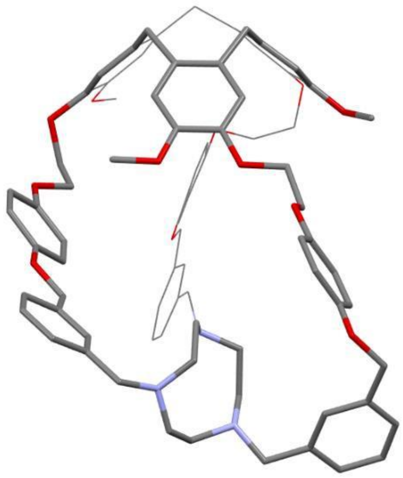

Figure 1 *XRD structure of the* ***TACN****-based ligand* ***Hm-TACN***

Copper centers, which mainly exist in the $Cu^{I/II}$ oxidation states, are used in these systems to bind and activate oxygen *via* the cleavage of the O-O bond. The incorporation of copper has been widely used in enzyme mimicking complexes, but their use is often limited by the formation of binuclear Cu_2O_2 species.[2]

The 1,4,7-triazacyclononane ligand (**TACN**) is a N-donor ligand displaying 3 nitrogen atoms. It was demonstrated by Tolman and coworkers, that open Cu(I) complexes based on the **TACN** ligand activate O_2, yielding Cu_2O_2 species.[1]

However, these open complexes did not reproduce the hydrophobic cavity found in the enzymes. On this basis, the goal of this work is to equip the canonical **TACN** ligand with a hemicryptophane cavity. Hemicryptophanes are organic cage structures, that

have been recently used in our group to develop bioinspired caged catalysts.[3]

So this work aims at preparing and studying the unprecedented **TACN**-based ligand **Hm-TACN** (Figure 1) and corresponding Cu complexes.

This work was supported by the National Research Agency (ANR-22-CE50-0009-01).

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P29 Development of New Building Blocks Based on Phosphonic Acid Corroles for the Preparation of Porous Materials for Gas Detection

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Air quality monitoring has become an important challenge in order to prevent damage to human health and the environment. It is therefore essential to develop sensors that are suitable and sensitive enough to detect dangerous gases, such as CO or NH_3, at low concentrations. For several years, our laboratory has been interested in the development of cobalt corroles that can coordinate selectively and reversibly CO or NH_3.[1] To improve gas access, porous materials, such as Metal Organic Frameworks (MOFs) have attracted our attention due to their high porosity and high tunability. Our idea is to graft cobalt corroles onto MOFS and deposit these materials on SAW (Surface Acoustic Wave) sensors. Until now we have only used corroles functionalized with a carboxylic acid to construct materials. In this work, we propose to develop new corroles bearing phosphonic acid function. We will present the synthesis of these new precursors and also give preliminary results on the grafting of these compounds onto a porphyrin-based MOFs (PCN 222). These new materials have been characterized thanks to the usual analyses (Mass Spectrometry, multinuclear NMR spectroscopy and UV-Visible) but also using BET, XRD, gases adsorption (CO, N_2, O_2 and CO_2).

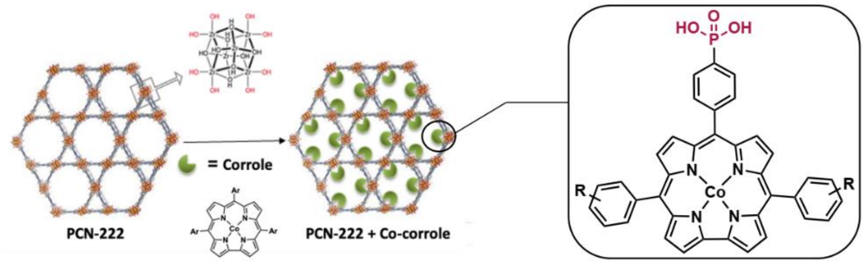

Figure 1.a). Cobalt-corroles grafted into porphyrin-based MOF. b). Structure of phosphonic acid cobalt- corrole, new precursors for porous materials.

This work was supported by the CNRS (UMR UB-CNRS 6302, the "Université de Bourgogne (UB). The French Research Agency (ANR) is acknowledged for financial support (ANR-22-CE42-0016-02).

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P30 Metal Complexes of a New Chelator Derived from Fluconazole with Promising Antifungal Activity

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Antifungal drug resistance occurrence by important fungal pathogens is a growing concern that requires urgent attention in the field of drug discovery, so finding new drugs and novel activity mechanisms has never been so important. Exploring metal complexes as potential antimicrobial drugs is an approach that has been gaining renewed interest given the ability of complexes to access additional activity mechanisms in comparison with organic compounds.[1] To this end, the model triazole drug Fluconazole was recently appended with a range of chelating functions designed to bind copper(II), while the antimicrobial activity of these compounds in the presence of supplemental copper(II) was found to have variable success.[2]

In this work, we set out to develop a new chelator derived from fluconazole by introducing a particular chelating function on the original structure of Fluconazole, aiming to allow for the preparation of different metal complexes. This Fluconazole derivative was then used as a ligand to synthesize complexes with selected metal cations, which were studied regarding their antifungal activity against Candida spp. We are now presenting preliminary results that demonstrate a suitable antifungal activity of these complexes against several Candida species, showing promise for the future development of chelator derivatives of azole drugs.

This work was supported by FCT - Fundação para a Ciência e a Tecnologia, I.P., through project 2022.04565.PTDC, MOSTMICRO-ITQB R&D Unit (UIDB/04612/2020, UIDP/04612/2020) and LS4FUTURE Associated Laboratory (LA/P/0087/2020).

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P31 2D/3D Covalent Organic Frameworks Based on Cobalt Corroles for CO Binding

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Corroles belong to the family of porphyrinoids which is largely used for sensing applications [1]. We have shown that cobalt metallocorroles are able to bind carbon monoxide in the axial position with a high affinity even in the presence of nitrogen and dioxygen, the two main components of the atmosphere [2]. We have recently fabricated sensing devices for low CO detection level (sub-ppm) using cobalt corroles deposited as films on a Surface Acoustic Wave (SAW) device by spray coating [3]. Herein, we will describe the synthesis of new 2D and 3D porous materials belonging to the Covalent Organic Frameworks (COF) family based on cobalt corroles (Figure 1). Their synthesis and selective sorption properties for CO over N_2 and O_2 will be presented.

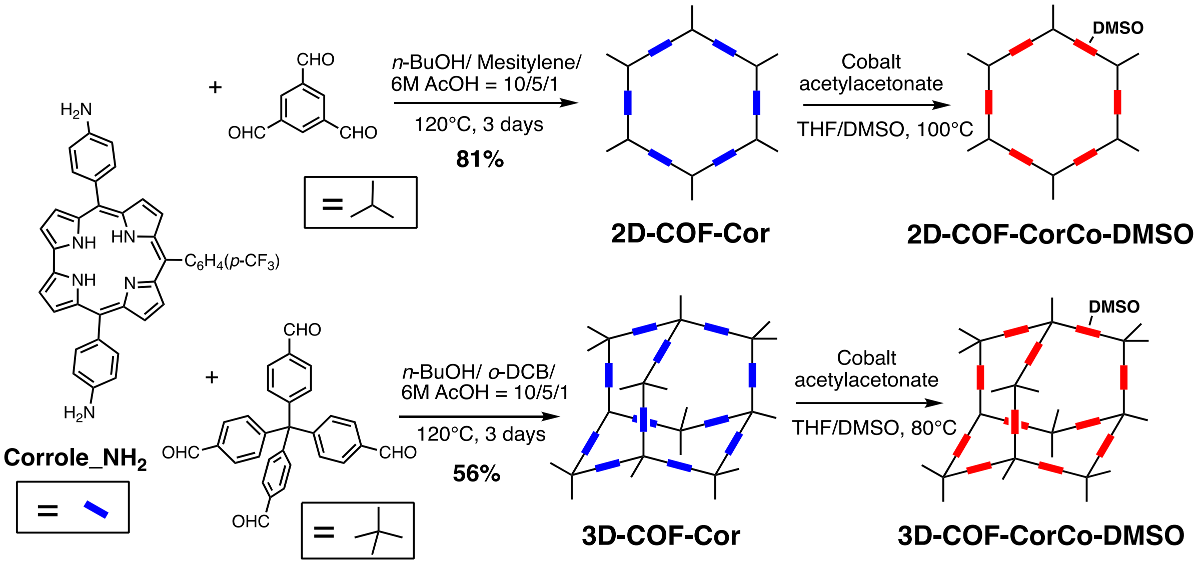

FIG. 1. Synthesis of 2D and 3D COFS

Acknowledgments. *Authors would like to acknowledge the ISITE-BFC (CO2DECIN project), the Université Bourgogne Franche-Comté, the FEDER, the Conseil Régional de Bourgogne (PARI IME SMT8 program) for financial supports, and the French Ministry of Research for the allocation of a PhD grant (JY).*

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P32 Light Induced on-Surface Photoswitch and Polymerization Reaction Studied by Scanning Tunneling Microscope

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Light-reactivities of different photo-sensitive molecules are of great importance for the design of highly controllable "smart materials" applications. Scanning tunneling microscope (STM) is a powerful technique to investigate topographic as well as electronic properties on functional organic molecules down to sub-molecular level.[1-3]

We have recently studied the light induced on-surface photoswitch from Bpy-DAE-bpy (ditopic ligand terminated with bipyridine groups linked through photochromic central diarylethene) or on-surface photo-polymerization from vinyl-OC18 molecules (ditopic ligand consisting of vinylphenyl and two octadecyloxy). Bpy-DAE-bpy and vinyl-OC18 molecules first self-organize on surface then were irradiated by light where the photo-reactivities of these molecules were evidenced by STM, before and after shining light at the solid/liquid interface.

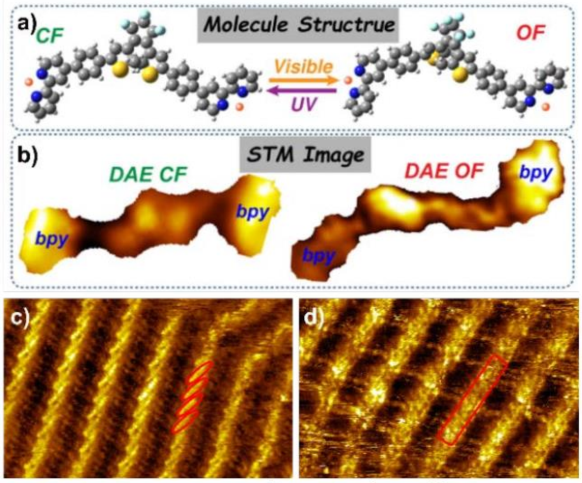

Figure 1 – STM images showing the self-organizations from bpy-DAE-bpy and vinyl-OC18, respectively.

The bpy-DAE-bpy molecules, can reversibly switch between its open-(OF) and closed-form (CF) upon visible and UV light irradiation, respectively.[4] The CF/OF photo- switches are evidenced by the different LUMO density of states (DOS) patterns and are presented in Figure 1a and b, respectively. Density function theory calculation provides a theoretical comprehension to the observed HOMO/LUMO images of the DAE switches.[4] Next, we have investigated UV light induced photochemical [2+2] cyclo-addition of C=C bonds of consecutive vinyl-OC18 .molecules.[5] Monomers can be observed to self-organize on solid/liquid interface before polymerization (Figure 1c). Then, the surface was exposed either to UV light irradiation or thermal annealing. The disjoined triphenyl of vinyl-OC18 monomers can be no more observed, instead, continuous bright wires attributed to linear polymer chains were visible overwhelmingly covering the whole surface (Figure 1d).

These observations demonstrate on-surface photoswitch and on-surface polymerization reaction at a sub-molecular level.

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P33 Electric Field Induced Conductance Switch of Single-Molecule Junctions with Non-Volatile Memory Properties

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The use of single molecules in molecular electronics aims to miniaturize the electronic devices in size and to lower the cost of current nanoelectronics or to develop low power consuming electronics. The building and the conductance measurement of single-molecular junctions (SMJs) is of great interest to obtain resistive switches with high on/off ratio and non-volatile memories. We have recently investigated conductance properties of viologen (VIO) and diarylethene (DAE) based SMJs, which are built by connecting the single molecule (pre-grafted using diazonium electroreduction) between two metal electrodes.[1-4]

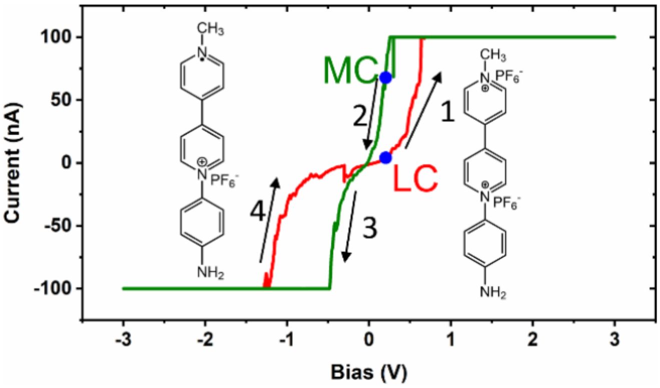

Figure 1 – I(V) curve of Vio-C1 SMJ and corresponding molecule structure.

Viologens are a set of well-known redox- active molecules with different reduced and oxidized states at around -0.4 and -0.8 V (vs. SCE) showing three redox states (V^{2+}, V^{+} and V^{0}) and are model systems to be used as switching building blocks in MJs. In this work, Au-[NH2-VIO-C1-NH2]-Pt SMJ is formed and its conductance states are studied using the STM break junction (STM-bj) method. Two different conductance values f 4×10^{-3} G0 and 3×10^{-4} G0 are recorded, corresponding to V^{+} and V^{2+} states, respectively. Stable SMJs, with a lifetime as long as a minute, are also formed for further I(V) characterization. Most importantly, hysteresis I(V) loops (Figure 1) have been recorded showing the reversible and reproducible conductance switching between the molecule's two redox states, namely V^{+} and V^{2+}.NH_2-DAE-NH_2 is a photochromic molecule that switch between its closed and open forms upon UV and visible light irradiation, showing different conjugated structures.[1] Using the same STM-bj technique, light-induced high conductance (HC)and low conductance (LC) from Au-[NH_2-DAE-NH_2]-Pt SMJs are recorded, corresponding to conductance switching between the molecular CF and OF states, respectively. Cycles of reproducible hysteresis I(V) curves display an electric field-generated SMJ non-volatile memory effect between OF and CF states. The NH_2- [DAE]n-NH_2 (n=1~4) oligomers can be generated to form SMJs with different lengths where length dependent charge transport mechanisms are discussed from the attenuation factors (β values). We observed that the different OF or CF SMJs show different β values and thus transport charge differently.

Overall, we have successfully studied the single molecule non-volatile memory effects from two different Vio-C1- and DAE-based SMJs. The switchable SMJs could be expected to be applied in future molecule electronic devices for data storage.

This work was supported by The Agence Nationale de la Recherche (France ANR-15-CE09 0001-01) and China Scholarship Council.

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P34 Phenanthroline Bonded Eu-Ti Oxo-Clusters for High Luminescent Materials and Films

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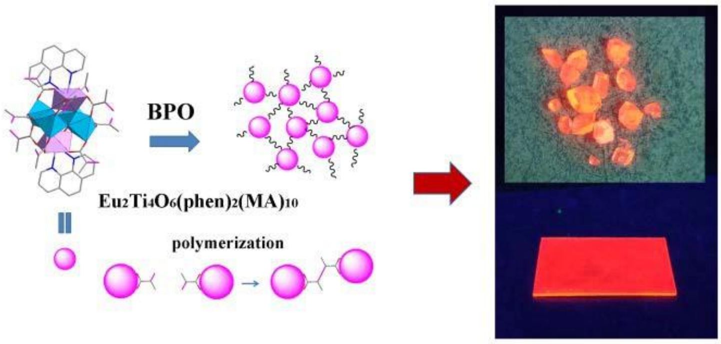
Incorporation of Eu-complexes into various organic or inorganic matrixes is one of the strategies to obtain displaying materials having practical applications. In this work, we report a convenient approach to preparing high luminescent organic–inorganic hybrid materials and films from the europium-titanium oxo-clusters (EuTOCs) having photoactive antenna ligands.[1] Three Eu_2Ti_4 oxo-clusters were synthesized and crystallographically characterized. They are the first reported lanthanide-TOCs coordinated with 1,10-phenanthroline (phen) and 2,2'-bipyridine (bpy) as photoactive ligands, $Eu_2Ti_4O_6(phen)_2(pa)_{10}$ (**1**) (pa = propionate), $Eu_2Ti_4O_6(bpy)_2(pa)_{10}$ (**2**) and $Eu_2Ti_4O_6(phen)_2(MA)_{10}$ (**3**) (MA = methacrylate). Benefited from the photoactive phen and bpy antenna ligands and the rigid cluster structures, these clusters showed bright red luminescence with quantum yield in the range of 60 %—80% and long lifetime up to 3.0 ms. Unlike those physically mixed polymeric materials, the MA coordinated compound **3** can be self-polymerized to form a brilliant luminescent film. The film coated slide was used to develop a fluorescence sensor for biomolecule ascorbic acid (AA). The low detection limit and reusable properties suggest great potential of such EuTOC films in real applications.



A convenient approach to preparing high luminescent organic–inorganic hybrid materials and films from the europium-titanium oxo-clusters (EuTOCs) with photoactive Phenanthroline ligand is reported.

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P35 C-C Bond Formation in a Sterically Demanding Environment

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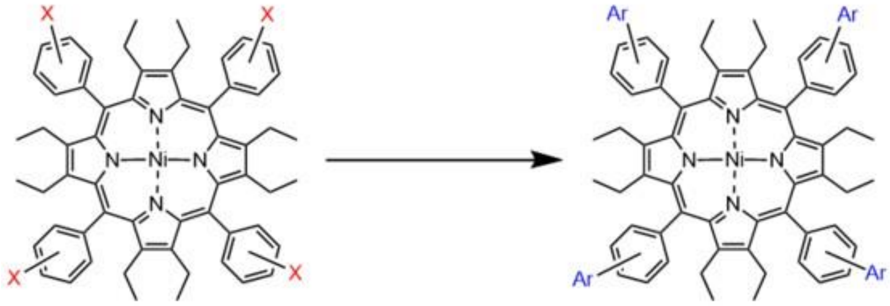
Nonplanar porphyrins are porphyrins which undergo macrocyclic distortion due to steric repulsion in the core of the macrocycle or overloading the periphery of the porphyrin with sterically demanding groups. Dodecasubstituted porphyrins where the periphery of the porphyrin is fully substituted often exhibit saddled conformations. This class of nonplanar porphyrins has been found to be useful in molecular recognition, organo- and photoredox-catalysis.[1] This is a result of the nonplanar framework allowing guest molecules to interact directly with the core.[2] These functions can be enhanced by decorating the porphyrin with functional groups with varying electronic and steric modifications to achieve these functional materials.[3] Unlike their planar counterparts, classic synthetic protocols for C-C bond forming reactions of non-planar porphyrins are underdeveloped. Here we present synthetic advances towards nonplanar dodecasubstituted porphyrin with robust architectures designed as enzyme mimic precursors. The synthetic details of C-C couplings performed in the sterically demanding environment of *ortho*-, *meta*-, and *para*- positions of dodecasubstituted porphyrins will be presented. The methodological advances will open a new door for the functionalization of nonplanar porphyrins and facilitate accessing new molecular shapes and functions.



This work was supported by Science Foundation Ireland (Award 21/FFP- A/9469).

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P36 Molecular Platforms for Multivalent Binding to Membrane Receptors

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Affibody molecules (AfB) are small three-helix bundle protein scaffolds (~ 7 kDa) acting as robust non-immunoglobulin affinity ligands capable of binding to a wide range of proteins.[1] Broadly, AfBs can be considered as nitrogen-containing ligands preorganized for maximizing H-bond/salt bridge interactions with target molecules. The optimized AfBs can be thus used as efficient tools for molecular recognition in bioimaging, diagnostic and therapeutic applications. AfBs were initially developed for targeting the human epidermal growth factor membrane receptors (EGFR, HER2) that are often overexpressed in different carcinomas. AfBs attracted a considerable attention for their ability to bind these tumor markers with nanomolar affinities.

In this context, we have started to develop multivalent molecular platforms for combining several AfBs within the same macromolecule. These constructs exhibit several advantages including high affinity and avidity. In this work, the AfB conjugates (mono-AfB and two di-AfBs) were obtained through a covalent coupling via bispecific linkers based on flexible PEG chains.[2] Advantageously, we have also incorporated a fluorescent motif into the anchoring platform to facilitate optical detection. The synthesized compounds were fully characterized with NMR and mass spectrometry. The binding affinities to purified HER2 receptors were determined with fluorescence anisotropy and biolayer interferometry. Flow cytometry was performed to validate the di-AfBs binding to surface receptors of HER2-overexpressing cells.

This work was supported by the Ligue contre le cancer and the CNRS.

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P37 Advancing Compartmental N-Donor Ligands for Dinuclear Ruthenium Water Oxidation Catalysts

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Water oxidation is a key reaction for sustainable fuel generation in artificial photosynthesis schemes, and dinuclear ruthenium complexes featuring two closely spaced metal ions have emerged as promising molecular catalysts for mediating this challenging $4e^-/4H^+$ transformation.[1] Among them, catalysts based on compartmental ligands with a bridging pyrazolate unit, such as 3,5-bis(pyridyl)pyrazolate (bpp) and 3,5-bis(bipyridyl)pyrazolate (bbp), are particularly prominent and have provided valuable insights into structure-activity correlations.[2,3] These systems exhibit remarkable stability against oxidative degradation and can be functionalized for surface immobilization, making them attractive for rugged and highly active photoanodes.[4] Interestingly, complexes of the $\{(bpp)Ru_2\}$ type were shown to operate via the so-called I2M mechanism with intramolecular coupling of two high-valent Ru=O units for O–O bond formation, whereas complexes of the $\{(bbp)Ru_2\}$ type were shown to undergo water nucleophilic attack (WNA) on one Ru=O unit, the other Ru=O serving as a base. A detailed understanding of the factors governing the preference for the different mechanistic scenarios has remained elusive. To that end we have now developed a novel dinuclear ruthenium complex based on a non-symmetric pyridyl(bipyridyl) pyrazolate (pbp) ligand, which can be viewed as a hybrid of the $\{(bpp)Ru_2\}$ and $\{(bbp)Ru_2\}$ systems. The multi-step synthesis of the pbp ligand and its diruthenium complex as well as water oxidation results will be presented and discussed in comparison with the symmetric bpp and bbp based systems.

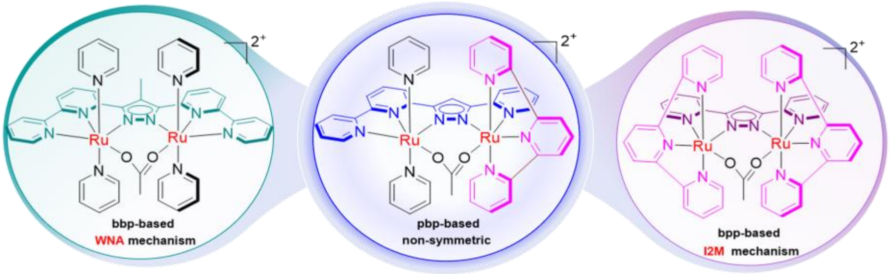

Figure. Schematic representation pyrazolate-based dinuclear Ru-WOCs.

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P38 Synthesis of Titanium(IV) Complexes with $N_2O_2Cl_2$ Coordination Spheres towards Combined Coordination and Radical Polymerizations

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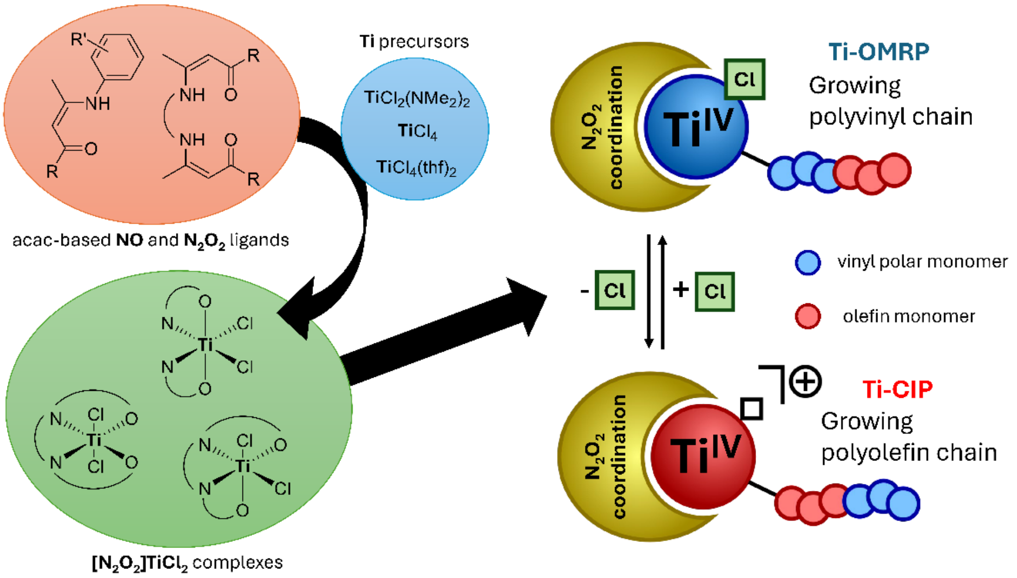
Copolymerization with vinyl polar monomers (VPMs, e.g., acrylates, vinyl esters) can greatly enhance the physical properties of olefin (e.g., ethylene, propylene) polymers. However, this copolymerization is challenging due to differences in reactivity. Thus, this work aims at combining organometallic-mediated radical polymerization (OMRP, efficient at polymerizing VPM)[1] and coordination-insertion polymerization (CIP, efficient at polymerizing olefins).[2]

Neutral titanium(III) complexes, active in radical reactions[3], initiate radical polymerization and are efficient radical traps to control OMRP.[4] Cationic titanium(IV) complexes catalyze living CIP of 1-alkenes.[5] Finding a mechanism to switch between these neutral and cationic forms of titanium would lead to combined CIP-OMRP.

Some Ti^{IV} complexes with $N_2O_2Cl_2$ coordination spheres were identified by DFT calculations as promising candidates for OMRP control, synthesized by direct deprotonation or salt metathesis reactions, and characterized by NMR and scXRD. Polymerization tests are ongoing, with some promising early results.



This work was supported by ANR (project RadiCoord).

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P39 Zn-Phenanthroline-Cucurbit[n]uril Coordination Supramolecular Assembly

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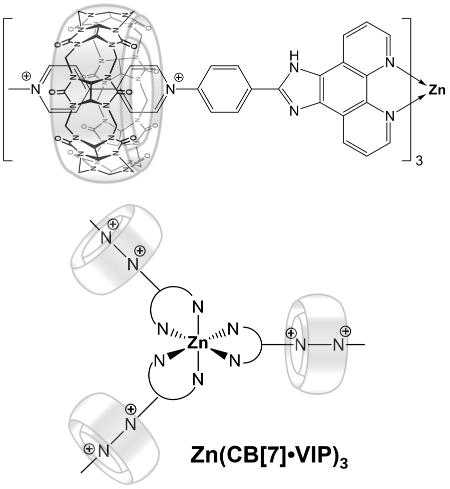
Cucurbit[n]uril CB[n] macrocycles are major elements of the host:guest supramolecular chemistry. However the control of well-defined oligomeric CB[n] assembly remains a high challenge.[1]

In recent articles, we showed that combination of metal-coordination and CB[7] supramolecular chemistry gives access to fascinating properties such as a molecular switch on viologen-phenylene-imidazole VPI axle activated by the silver complexation.[2]

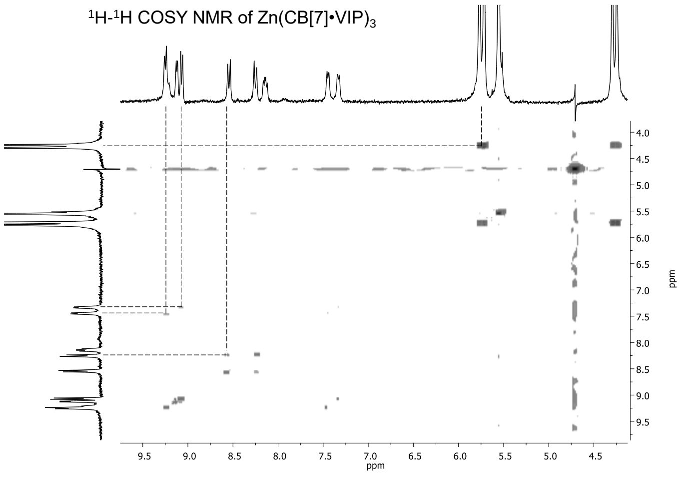
In this contribution we prepared a new guest VIP bearing a viologen function and a 1,10-phenanthroline group using an imidazole spacer.

NMR titration established the hexacoordination of a Zn(II) center via the bidendate complexation of the phenanthroline group, while CB[7] macrocyles occupied the viologen site of the guests.

This strategy combining metal *N*-complexation and supramolecular assembly led to an original Zn(CB[7]•VIP)$_3$ complex.



Zn(CB[7]•VIP)$_3$



^{1}H-^{1}H COSY NMR of Zn(CB[7]•VIP)$_3$

This work was supported by Aix-Marseille University and AMUTech.

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P40 Ammonia Sensors Based on Ni(II) Complexes in Quinoid Chemistry

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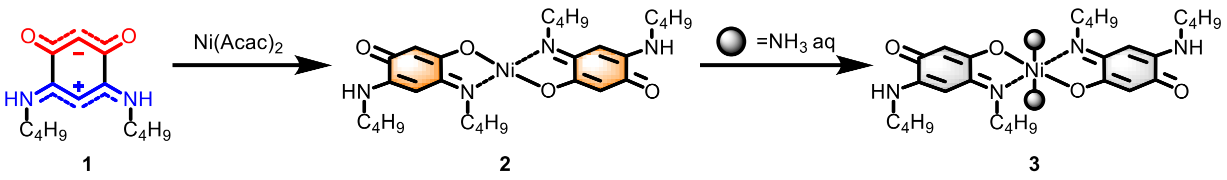
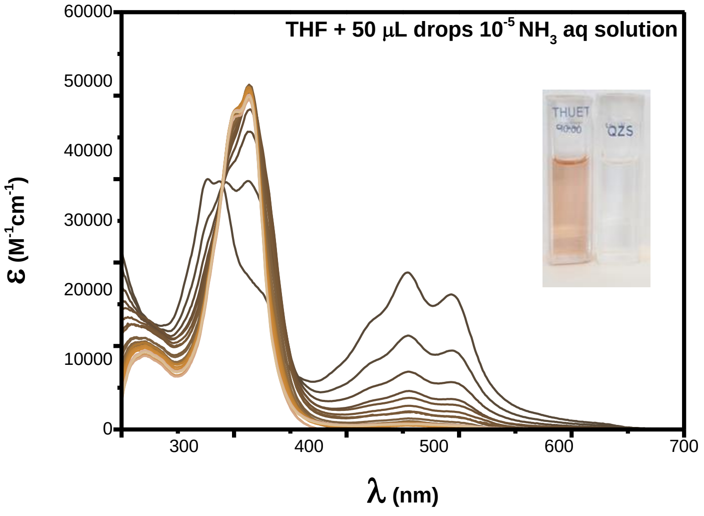
Quinones represent an essential class of molecules that have shown their ability and versatility in various chemistry fields as oxidizing agents,[1] dye and pigments,[2] and pharmaceuticals[3]. Particularly intriguing are the quinones derived from 2,5-dihydroxy-1,4-benzoquinone (DHBQ) for their interesting ability to form zwitterionic diaminobenzoquinonediimines **1**.[4] The latter appeared to be very good ligands in coordination chemistry for the preparation of complexes with a tunable stoichiometry. Recently the demand of efficient ammonia detectors has increased proportionally with the high use in various industrial sectors.[5]

In this context, square planar Ni(II) complexes have attracted a lot of attention due to their capability of switching between low/high spins in solution and/or solid state upon axial coordination.[6]

Herein, following this line, we report the synthesis of Ni(II) metal complexes[7] of type **2** and their potential as ammonia detecting sensors **3**.





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P41 New N_3O quinoidal ligand for the selective formation of trinuclear complexes

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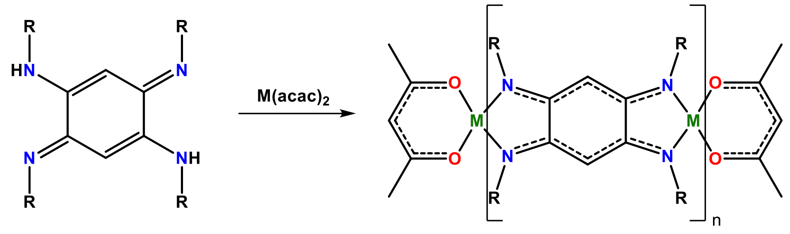
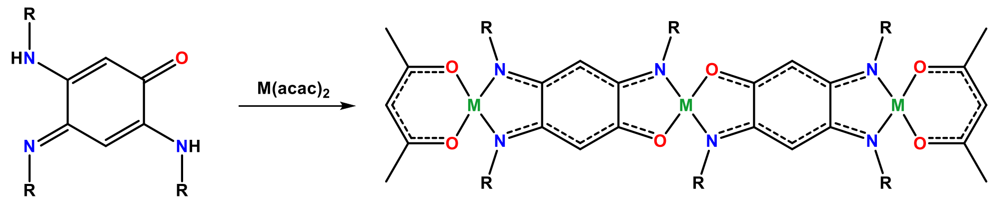
Tremendous interest was given to quinoidal molecules over the past decades thanks to their outstanding fundamental properties, as well as diverse applications in various fields. Among these, 2,5-diamino-1,4-benzoquinonediimines (QDIs) **1** are particularly interesting due to their unusual 12-π electron system distribution that can be considered as two nearly independent 6- π electrons sub-units, chemically linked by two C-C bonds, leading to remarkable optical properties.[1]

Extensive studies on QDIs enlightened their great versatility as ligands towards coordination species with a wide range of metals (M = Fe, Co, Ni, Cu, Zn, Ru, Pd, W, Re, Ir, Pt, Na, Li, B, Sn), exhibiting great technological value.[2] Steric hindrance of tetra-substituted QDIs lead to mono- or dinuclear coumpounds **2** while unsubstituted QDIs give rise to polynuclear species **3** with NIR absorption. However unsubstituted QDIs complexes experience dynamic exchange in solution towards longer insoluble oligomers. [3] Here, we show that substituting one nitrogen heteroatom by an oxygen **4** allow selective formation of unprecedented soluble trinuclear complexes **5** with promising physical properties.



1 : R = or ≠ H

2 : R ≠ H ; n = 1 ; M = Ni, Pd
3 : R = H ; n = 1 – 4 ; M = Ni



4 : R ≠ H

5 : R ≠ H ; M = Ni, Pd

This work was supported by the national research agency (CONDOR project)

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P42 Formation of a cytosine–Ag(I)–cytosine pair in an i-motif structure

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DNA can adopt a variety of triplex and quadruplex structures distinct from the well-known double-helical B-DNA.[1,2] Amongst these, the i-motif represents a quadruplex composed of two parallel-stranded cytosine-rich oligonucleotide duplexes intercalating in an antiparallel fashion. Instead of the canonical Watson-Crick base pairs, hemi-protonated C:CH$^+$ base pairs form a continuous stack in the center of this quadruplex.[2] Given that C–Ag(I)–C base pairs are well established in double-helical DNA and are known to enhance the thermal stability of a duplex,[3] we investigated the possibility that, instead of hemi-protonated C:CH$^+$ base pairs, C–Ag(I)–C base pairs can be formed within an i-motif structure. Towards this end, we applied various derivatives of an i-motif/duplex junction recently reported by Escaja, González *et al*.[4] Our data indicate that a single C–Ag(I)–C pair is formed in an i-motif structure formerly comprising four C:CH$^+$ base pairs. Apparently, only the most accessible C:CH$^+$ pair can be transformed into a C–Ag(I)–C pair.

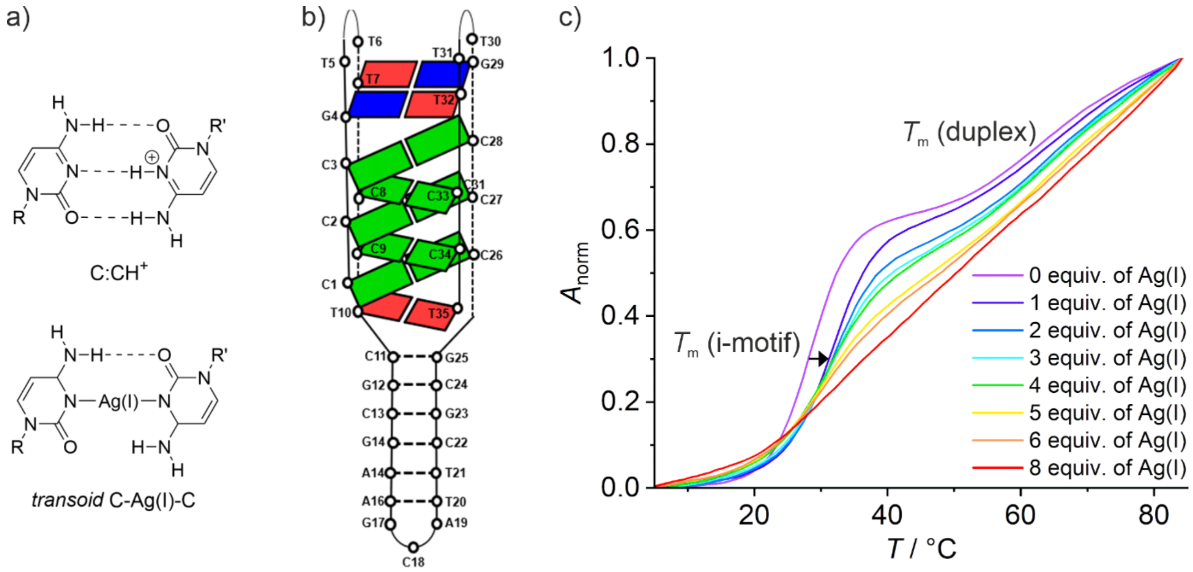

Figure. a) C:CH$^+$ and *transoid* C–Ag(I)–C base pairs. b) Schematic representation of the i-motif/duplex junction. c) Melting curves of the i-motif/duplex junction in the presence of increasing amounts of Ag(I).

This work was supported by the Deutsche Forschungsgemeinschaft.

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AUTHOR INDEX

8th International Conference on N-Ligands

	Monday, June 3rd	*Tuesday, June 4th*	*Wednesday, June 5th*	*Thursday, June 6th*	*Friday, June 7th*
8:30 – 9:15	PL: 45 min KN: 30 min IL: 20 min OC: 15 min Flash: 4 min	Angela CASINI (PL2)	Jeanne CRASSOUS (PL3)	David LEIGH (PL4)	Armando POMBEIRO (PL5)
9:15 – 9:45		Alceo MACCHIONI (KN2)	Simona GALLI (KN4)	Abhik GHOSH (KN8)	Claude PIGUET (KN9)
9:45 – 10:00		Arkadi VIGALOK (OC1)	Josef HAMACEK (OC18)	Sébastien GOEB (OC29)	Clémence QUEFFÉLEC (OC35)
10:00 – 10:15		Cédric COLOMBAN (OC2)	Fabio MARCHETTI (OC19)	Karim ABDEL HADY (OC30)	Tom J. N. OBEY (OC36)
10:15 – 10:30		Fabio RAGAINI (OC3)	Nicolas DESBOIS (OC20)	Alla LEMEUNE (OC31)	Ling PENG (OC37)
10:30 – 11:00		*Coffee break*	*Coffee break*	*Coffee break*	*Coffee break*
11:00 – 11:15		Grzegorz HRECZYCHO (OC4)	Carole DUBOC (KN5)	*Chemistry Europe Lecture* (KN7) Stéphane BELLEMIN LAPONNAZ	Rafael GRAMAGE-DORIA (OC38)
11:15 – 11:30		Stéphane LE GAC (OC5)			Ankita JAISWAL (OC39)
11:30 – 11:50		Macarena POYATOS (IL2)	Jean WEISS (OC21)	Biprajit SARKAR (IL6)	Matthias TAMM (IL7)
11:50 – 12:05		Gilles LEMERCIER (OC6)	Flash talks (8) ABCR (Sponsor)	Ally AUKAULOO (OC32)	Matteo MAURO (OC40)
12:05– 12:20		Piotr PAWLUC (OC7)		Werner THIEL (OC33)	Andrew PHILLIPS (OC41)
12:20– 12:35		Zakaria HALIME (OC8)		Véronique PATINEC (OC34)	Poster Awards & Closing
12:35 – 14:00		*Lunch*	*Lunch*	*Lunch*	*Lunch*
14:00 – 14:30		Violetta PATRONIAK (KN3)	Paolo FALCARO (KN6)	Free time	*Departure*
14:30 – 14:45	Registration	Alexander SOROKIN (OC9)	Yann PELLEGRIN (OC22)		
14:45 – 15:00		Cristina PERONA (OC10)	Charlie McTERNAN (OC23)		
15:00 – 15:15		Olivier CHUZEL (OC11)	Stéphanie DUROT (OC24)		
15:15 – 15:30		A. BAVANDSAVADKOUHI (OC12)	Pavel LHOTAK (OC25)		
15:30 – 15:45		Arno ESTIVAL (OC13)	Mohamed AMEDJKOUH (OC26)		
15:45 – 16:05		GLINDEMANN / LNI (Sponsors)	Elisabetta IENGO (IL4)		
16:05 – 16:35		*Coffee break*	*Coffee break*		
16:35 – 16:55	Welcome (16:45)	Wen-Hua SUN (IL3)	Denis JACQUEMIN (IL5)		
16:55 – 17:10		Charles H. DEVILLERS (OC14)	Ewa PACHOLSKA-DUDZIAK (OC27)		
17:10 – 17:25	Makoto FUJITA (PL1)	Nicolai BURZLAFF (OC15)	Jean-Christophe LACROIX (OC28)		
17:25 – 17:40		Renaud HARDRE (OC16)	Flash talks (9) ADVION INTERCHIM (Sponsor) HEIDOLPH (Sponsor)		
17:40 – 17:55		Chanjuan XI (OC17)			
17:55 – 18:15	Sonja HERRES-PAWLIS (KN1)				
18:15 – 18:25			Poster session Beer mixer		
18:25 – 18:45	Mark GANDELMAN (IL1)			Gala dinner (19:30)	
	Welcome Cocktail (19:00)				