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BOOK OF ABSTRACTS

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KEYNOTE

LECTURES

PORPHYRINS IN DISCRETE METAL-MEDIATED ASSEMBLIES

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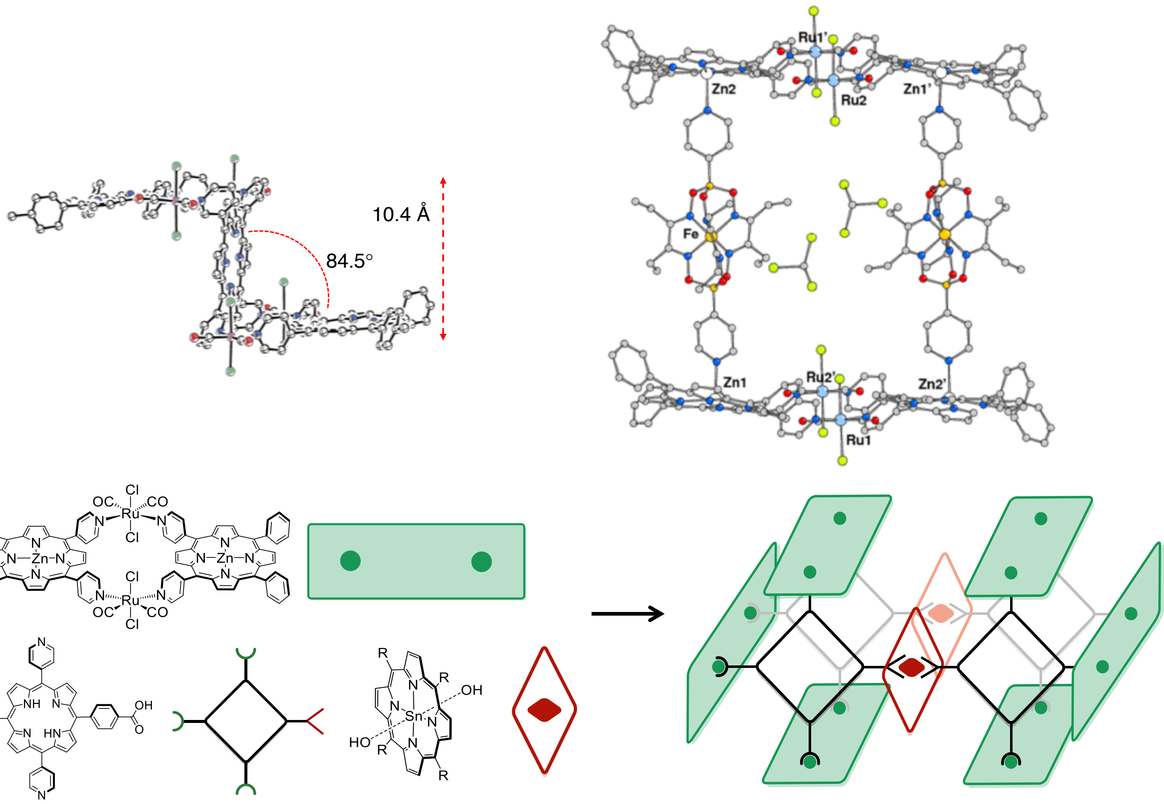
Keywords: Porphyrin, coordination, supramolecular.

(Metallo)porphyrins play a fundamental role in major biochemical enzymatic functions and in natural processes for electron and energy transfer, light harvesting and oxygen transport; in the artificial realm the metal-mediated assembling approach has afforded a variety of spectacular discrete arrays of porphyrins, bringing new functions and applications ranging from molecular recognition and sensing to transport and (photo)catalysis.[1] The vast majority of these arrays are homoleptic systems, with examples containing different type of porphyrins being quite rare. Over the years we have employed the coordination-driven approach for the obtainment of multi-component porphyrin systems, mostly for artificial photosynthesis, with specific focus on the control of the number and relative orientation of the active units.[2] More recently we expanded our interests in the obtainment of heretoleptic architectures, by exploiting both *inert/labile* and *hard/soft* discriminations of coordination bonds.[3] An overview on the strategies and on the most fascinating past and recent examples will be presented (see also Figure below).



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COMPUTATIONAL MODELLING OF COOPERATIVE SMALL MOLECULE ACTIVATION BY APOLAR / WEAKLY POLAR BONDS

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Keywords: small molecule activation; apolar/weakly polar bonds; coinage metal-aluminyls; computational protocol; bond/reactivity relationship

Small molecule activation processes are central in chemical research and cooperativity is a valuable tool for the fine-tuning of their efficiency. In this contribution, recent and remarkable examples in which homogeneous activation processes are mediated by apolar E-E or weakly polar M-M' bonds are illustrated. [1,2] Experimental breakthroughs are analysed from a computational perspective, which highlights how a judicious and non-trivial usage of selected computational tools not only allows to rationalize the observed reactivity but also to infer general principles for activation processes. The application of a simple yet unbiased computational protocol that can easily provide a consistent picture of the relationship between bond nature/polarity and reactivity and ultimately lead to experiments driven "by design", is showcased using highly relevant coinage metal-aluminyl compounds as case studies. [3,4]

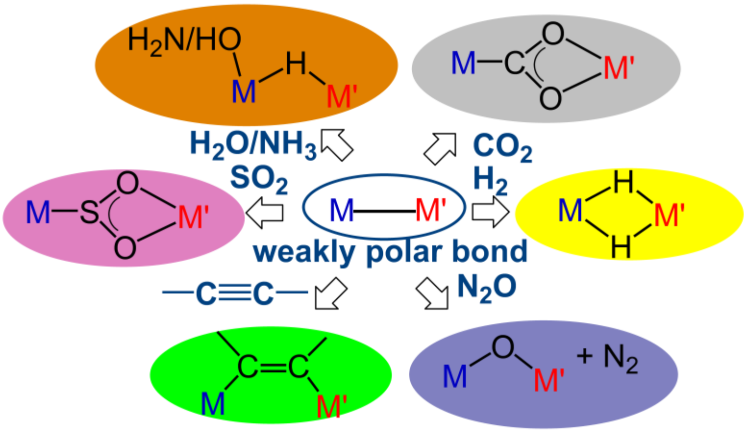

Figure 1 Small molecules reactivity with heterobimetallic M-M' (M = Cu, Ag, Au; M' = Al) compounds featuring a weakly polar bond.

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From rationalization of metal-catalyzed process mechanism to AI-assisted reaction yield prediction

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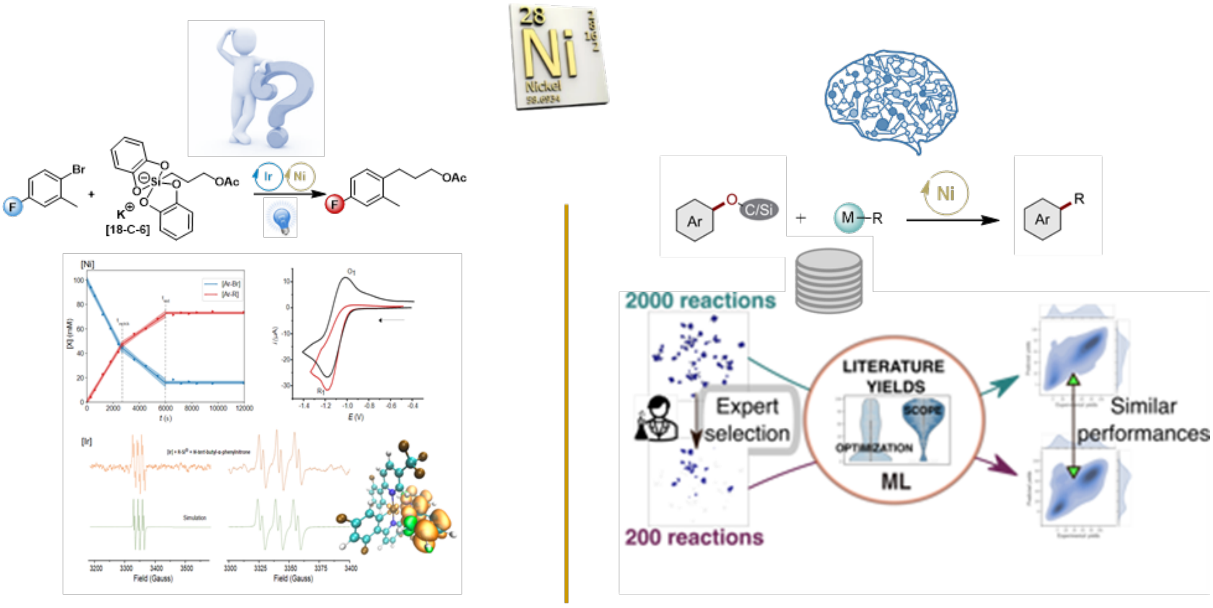
Keywords: Nickel; Mechanism, Kinetics, Machine Learning, Yield Prediction

Text: Metal-catalyzed processes are key tools for the efficient preparation of fine chemicals. Despite the many great advances reached in this field of research over the past two decades, the requisite optimization step is often laborious and frequently entails the blind screening of different reaction parameters. For this reason, a more rational approach is of outmost importance, in which in-depth mechanistic studies are inclined to guide the synthetic chemist. Combining physical organic analyses, micro-modeling kinetics and DFT calculations, we unveiled key aspects of the photoredox- and nickel-catalyzed cross-coupling of aryl bromides and silicates.[1] In parallel, we recently started a research program aiming at predicting reaction yields in the context of the nickel-catalyzed activation of C-O bonds of phenol ethers. Based on manually extracted literature data and including chemical knowledge, we demonstrated that a dataset including no more than a hundred reactions is sufficient to train a machine learning model. This work allowed us to propose guidelines to build an efficient small-size training dataset.[2]



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[1] Combining Microkinetics and Mechanistic Studies of the dual catalyzed C_{sp^3}-C_{sp^2} Coupling of Alkyl *bis*-Catecholato Silicates with Aryl Bromides: Evidence of Two Kinetic Regimes. Jaouadi, K.; Abdellaoui M.; Levernier, E.; Payard, P. A.; Derat, E.; Le Saux, T.; Ollivier, C.; Torelli, S.; Jullien, L.; Plasson, R.; Fensterbank, L.; Grimaud, L. *Chem. Eur. J.* **2023**, e202301780.

[2] Machine Learning Yield Prediction from NiCOlit, a Small-Size Literature Dataset of Nickel Catalyzed C-O Couplings. Schleinitz, J.; Langevin, M.; Smail, Y.; Wehnert, B.; Grimaud, L.; Vuilleumier, R. *J. Am. Chem. Soc.*, **2022**, *144*, 14722.

WATER EXCHANGE IN PARAMAGNETIC METAL COMPLEXES AND MRI DIAGNOSTIC PROBES

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Keywords: paramagnetic chelates, MRI contrast agents, water exchange, relaxometry, lanthanides

Text: In clinical MRI, contrast agents (CAs) commonly comprise complexes involving the Gd(III) ion with multidentate poly-aminocarboxylic ligands, both acyclic and macrocyclic. These complexes enhance image definition and facilitate more efficient imaging procedures.[1] They possess inner-sphere water molecules in rapid exchange with the bulk, capable of catalysing the longitudinal and transverse relaxation times (T_1 and T_2, respectively) of bulk water, thereby modifying its NMR signal intensity.[2] The rate of water exchange (k_{ex}) stands out as a pivotal parameter significantly influencing the effectiveness of CAs in MRI. In Gd complexes, k_{ex} is affected by several key factors:

1. **Coordination Chemistry:** The chemical structure of the Gd complex and the nature of ligands coordinating with Gd ions play a significant role.
2. **Steric Effects:** The size and shape of the ligands surrounding the Gd ion affect the accessibility of water molecules. Bulky ligands can hinder water molecules from accessing the coordination sites, leading to slower water exchange rates.
3. **Electronic Effects:** The electronic properties of ligands and the Gd ion influence the rate of water exchange. Electron-donating ligands can enhance water exchange rates, while electron-withdrawing ligands might slow down the exchange process.
4. **Overall electrical charge**: Generally, the exchange rate tends to decrease when passing from anionic to cationic complexes
5. **Hydration Number:** Complexes exhibiting higher hydration numbers tend to demonstrate faster water exchange rates, attributed to the presence of more labile water molecules.

Comprehending and controlling these factors enable chemists to design Gd(III) complexes with optimized water exchange rates, thereby improving the efficiency and efficacy of contrast agents utilized in MRI procedures. These effects will be discussed with reference to notable examples investigated in our laboratory. Additionally, recent findings concerning Mn(II) and Fe(III) complexes, an emerging category of diagnostic probes, will be briefly outlined.[3]

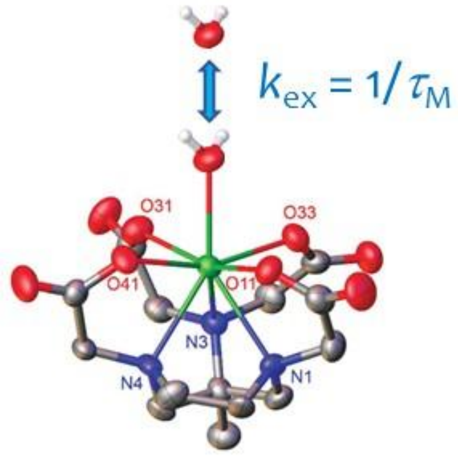

Figure 1. Water exchange process in a macrocyclic Gd(III) complex.

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Proton relays in molecular electrocatalysis: how do they allow for bidirectional/reversible behavior?

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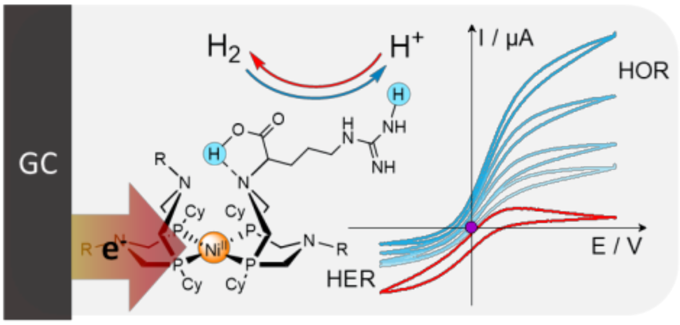
Catalysis in hydrogenases only requires Earth-abundant metal centers, the reactivity of which is enhanced thanks to the presence of basic sites acting as proton relays[1] at their vicinity. Such active sites have been used as an inspiration to design new synthetic catalysts for H_2 evolution[2-4] and oxidation.[5-6] Specifically, catalytic platforms with installed proton relays display bidirectional[7] and, in rare cases, reversible catalysis.[5-6] In this presentation we will show how a detailed molecular electrochemistry study can help understanding and quantifying the role of the protons relays related to these remarkable behaviors.[8]



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TOWARD EXPLOITABLE IRON-SENSISTIZED SOLAR CELLS?

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Keywords: DSSCs; Iron-carbenes; DFT; TDDFT; dye-TiO_2 interfaces

Solar energy harvesting and conversion represent a compelling scientific, technological and societal to move away from the exploitation of fossil fuels. In this context, Dye-sensitized solar cells (DSSCs) are viable and cheap alternatives to conventional silicon-based cells with advantages in terms of transparency and efficiency in indoor conditions.[1] Ruthenium and polypyridine complexes holds the golden standard in this field, as they possess ideal characteristics such as long-lasting metal-ligand charge transfer (MLCT) states and efficient charge separation, limiting recombination at the dye-TiO_2 interface. However, ruthenium is a rare and expensive metal, and the development of more sustainable energy devices based on earth-abundant metals is now a must. A quick glance at the periodic table reveals iron as a potential good candidate. However, striking photophysical differences exist between ruthenium(II) polypyridyl complexes and their Fe(II) analogues, the latter suffering from short-lived MLCT states resulting of their ultra-fast relaxation into metal-centered (MC) states. [2] Pyridyl-N-heterocyclic carbenes (pyridylNHC) brought a strong σ-donor character required to promote a higher ligand field splitting of the iron d orbitals, resulting in a destabilization of the MC states over the MLCT manifold with slowdown of the excited state deactivation providing iron(II) complexes with tens of picoseconds lifetimes making them more promising for applications in DSSCs. [3,4] In this contribution I will present our recent advances in the development and characterization of iron-sensitized solar cells with a focus on the computationally driven design of efficient sensitizers going from homoleptic to heteroleptic complexes (bearing different anchoring groups) and on electrolyte contents.[] Our synergistic computational and experimental approach led to the best photocurrent and efficiency ever reported for an iron sensitized solar cell (2% PCE and 9 mA/cm^{2,} Figure 1) using a co-sensitization process.

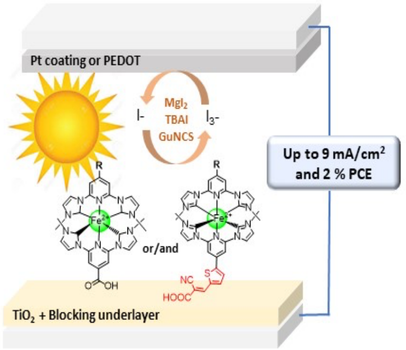

Figure 1. Pictorial representation of a co-sensitized Iron-DSSC showing record photovoltaic efficiencies.

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Metal Halide Perovskites: Synthetic and Structural Design Towards Photonic Applications

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Keywords: perovskites; light emission, low-dimensional semiconductors.

Text: Metal halide perovskites are emerging as an excellent class of materials for applications in photonics, light emitting devices and lasers. In particular, layered perovskites have been proposed as promising platforms to improve the luminescence efficiency, grant increased environmental stability, block ionic diffusion, and relax geometrical constraints giving access to a wider range of lead-free compositions.

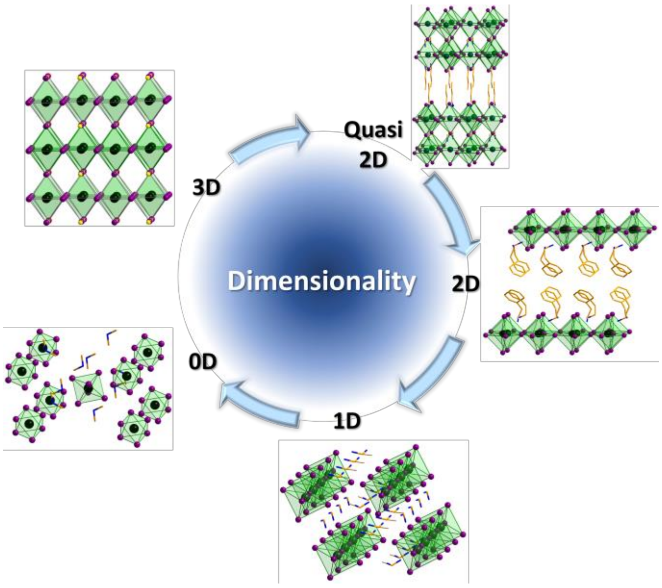

Figure 1 Dimensionality tuning in metal halide perovskite semiconductors

In this presentation, I will discuss how their exceptional chemical versatility (Fig. 1) allows to tune their optoelectronic properties by modulating the chemical composition and structural properties in materials with different dimensionalities.[1,2] The use of optoelectronically active templating cations as well as of inorganic dopants further push the boundaries to create functional perovskites with unprecedented luminescence efficiency and tunability.[3,4] Finally, I will discuss the excellent optoelectronic properties of tin-based perovskites and the impact of the templating organic cation on the structural rigidity, defectivity and photostability, which are critical parameters to enable efficient radiative recombination, amplified spontaneous emission and lasing in perovskites.[5-7] Overall, our findings provide fundamental synthetic guidelines to improve both coherent and incoherent emission properties of metal halide perovskites to enable their effective exploitation in photonic devices.

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Coordination Chemistry for Medicinal Applications

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Keywords: Bioinorganic Chemistry; Bioorganometallic Chemistry; Cancer; Metals in Medicine; Photodynamic Therapy

Text: Metal complexes are currently playing a tremendous role in medicine.[1] For example, the platinum complex cisplatin and its derivatives oxaliplatin and carboplatin are employed in more than 50% of the treatment regimes for patients suffering from cancer!

Over the last years, our research group focused its attention on the development of novel metal complexes as imaging and therapeutic agents against cancer and parasitic diseases.[2-10] During this talk, we will present our latest results, including in vivo results, on these topics.

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Schiff bases of the BIAN family and their metal complexes: recent advances from our group

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Keywords: Shiff bases; Nitrogen Ligands, Palladium complexes

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. After a brief historical introduction, the talk will focus on recent and unpublished achievements in our group. In particular, some results will be described related to the use of a reduced form of the BIAN compounds, Ar-BIANH$_2$.[1,2] Such compounds can be obtained by reduction of the corresponding Ar-BIAN compounds by several techniques (NaBH$_4$, H$_2$NNH$_2$/Pd, Na/MeOH, electrochemistry…) and, albeit air sensitive, can be conveniently stored in an dinitrogen atmosphere for years. As one notable example, 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. Other ligands, e.g. olefins, can also be bound, but in their absence 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).

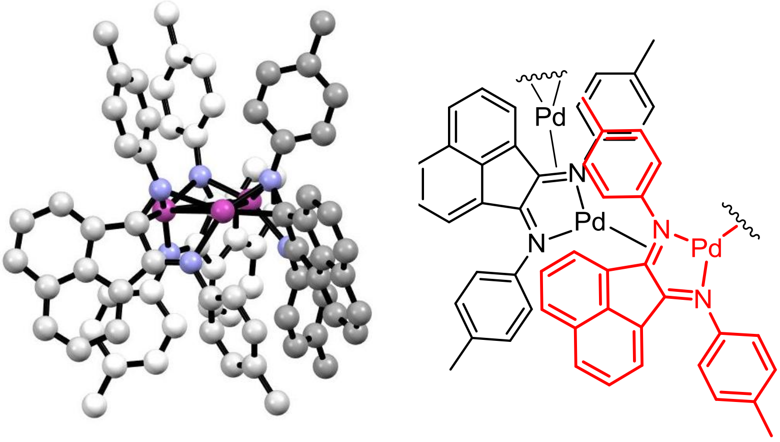

Figure 1 X-Ray structure of trimeric [Pd(4-MeC$_6$H$_4$-BIAN)]$_3$ and its partial bonding scheme.

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.

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Tuning active site properties in de novo designed metalloenzymes.

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Keywords: Bioinorganic chemistry; metalloenzymes; di-nuclear metal sites; activity; de novo design.

Metal ions are ubiquitous in nature and are essential for numerous biological processes. In particular, metalloenzymes are capable of catalyzing a remarkable array of reactions, and a given metal ion can be used in a number of oxidative, reductive, and hydrolytic transformations in different enzymes.[1]
Nature mastered coordination chemistry in such a way that a single metal-based cofactor could access to a wide range of reactivities.[1] Metalloprotein activity arises from a strong partnership between the metal cofactor and protein matrix: the metal brings a modicum of nondiscriminate chemical reactivity, while the protein stabilizes it in solution and directs its reactivity toward a unique and distinct path. The protein matrix directly tunes the metal ion properties by selecting the nature of the first coordination sphere. Further, the protein environment provides a variety of different interactions (e.g., hydrogen bonds, hydrophobic and ionic interactions) in the second coordination sphere.[2]
Bioinorganic chemists tackled the challenge to unravel the mechanisms that allow the protein matrix to modulate the catalytic activity of metal-containing cofactors, through the development of artificial systems. In the last decades, we have witnessed an explosion of protein design strategies leading to artificial metalloproteins, whose performances replicate and, in some exciting cases, overcome the performance of the natural counterparts.[3-6]
While our groups have designed a number of proteins that bind porphyrins[5] and iron-sulfur centers,[7] this lecture will focus primarily on artificial four-helix bundles, housing a diiron or dicopper cofactor, which catalyze a variety of O_2-dependent reactions.[6,8] We first developed the Due Ferri (DF) family of artificial four-helix bundles, housing a diiron site, in which the tertiary structure and catalytic site were both elaborated from first principles.

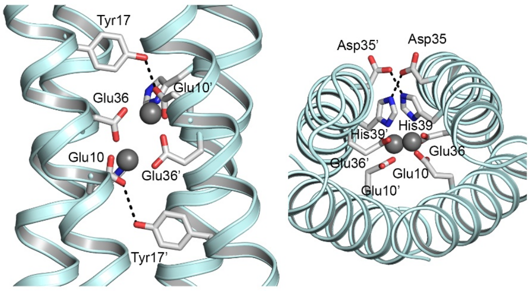

Figure 1 DF1 dimetal site and H-bond second-shell interactions in the X-ray structure of di-Zn^{2+}-DF1 (PDB-ID 1ec5).

An iterative process of design and characterization allowed us to add additional complexity in a stepwise manner to achieve increasingly sophisticated catalytic functions. The simple four-helix bundle scaffold was then manipulated to engineer a Type 3 copper-binding site (DR1).

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COOPERATIVE HETEROBIMETALLIC REACTIVITY: FROM MOLECULES TO CATALYTIC MATERIALS

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Keywords: Heterobimetallics; Surface OrganoMetallic Chemistry; CO2; catalysis

Text: One of the current frontiers in organometallic catalysis is to study the combined action of two metal centers to promote novel modes of reactivity, where the two metal centers act in synergy, in order to access a chemistry not possible with monometallic species. The association of electron-rich late metal centers (such as Ir, Cu, Au), with Lewis acidic metals (such as Al, Hf, Ta, U) is particularly interesting to create polarized metal-metal pairs presenting original electronic structures,[1-4] and thus potentially novel reactivity. Recently, we have shown that these heterobimetallic complexes are able to activate small molecules such as carbon dioxide (Fig. 1a)[3] as well as C-H bonds (Fig. 1b)[5–6] in a concerted way on both metal centers, which explains why these bimetallic systems have a catalytic activity largely superior to their monometallic analogues. Using a Surface OrganoMetallic Chemistry (SOMC) approach, these heterobimetallic complexes are used to prepare original and well-defined heterogeneized catalysts[5-8] highly active and selective in hydrogen isotope exchange (HIE) reactions. In this presentation we will describe our latest results in this area of research, in particular recent efforts to replace iridium by more sustainable metals.

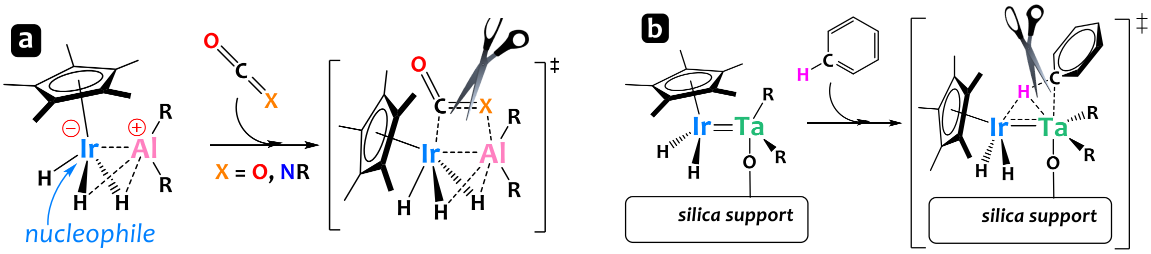

Figure 1 Reactivity of heterobimetallic complexes for the activation of CO_2 or C-H bonds by original cooperative mechanisms across the two metals.

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Development of a Non-Innocent platforms for Metal-Ligand Cooperative catalysis with group 10 metals

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Keywords: Ligand design; Pincer complexes, Non-innocent ligands, Metal-Ligand Cooperation

Over the last decade, cooperative effects in transition metal catalysis have attracted increasing interest from the scientific community. Thanks to the synergy between two different catalytic sites, extraordinary improvements in efficiency and selectivity can be achieved. In this context, metal/ligand cooperation (MLC), in which one of the ligands participates actively to the activations of the substrates, can be highlighted [1]. In this domain, pincer complexes of transition metals play an important role. One of the most representative models was reported by Milstein [1], based on an aromatization/dearomatization process of a pyridine-based pincer ligand.

Although group 10 metals are widely used in catalysis, they are much less studied in MLC than metals of group 8 and 9 [2]. Indeed, the two active sites are further away in the square planar geometry of d 8 complexes of group 10 metals. In this context, our group has reported a series of Pd and Pt pincer complexes bearing a non-innocent indenediide ligand featuring an electron rich backbone [3]. Remarkable results have been obtained in catalytic cyclisation processes involving C-O/C-N & C-C bonds formation thanks to Metal-Ligand Cooperation.

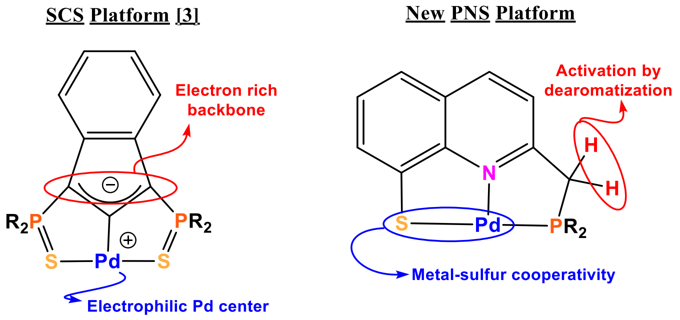

Figure 1 Indenediide and

To further develop MLC with group 10 metals, we are now working on a new platform deriving from the quinoline moiety that can combine two types of non-innocent behavior. The activation can occur either via aromatization/dearomatization of the quinoline moiety or may involve the sulfur atom as described by Ohki & Oestreich [4]. Thanks to these two modes of cooperativity, X-H/E-H bond of opposite polarity can be activated.

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ORAL

COMMUNICATIONS

Heterogenization of biodegradable hematin onto Colour Catcher® for the halogen-free cycloaddition of CO_2 to three-membered rings

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Keywords: carbon dioxide; porphyrin; heterogenization; oxazolidinones; DFT study.

In response to the pressing "CO_2 problem," which is responsible for environmental and societal issues linked to climate change and global warming, a coordinated global initiative is currently underway. This initiative is primarily focused on reducing carbon dioxide emissions, shifting to cleaner and sustainable energy sources, and harnessing the potential of CO_2 as a valuable resource for product manufacturing. In this contest, significant emphasis has been placed on processes involving the capture of carbon dioxide followed by its conversion into valuable products. Among the various synthetic approaches that utilize CO_2 as a key raw material, the cycloaddition of CO_2 to three-membered rings, such as epoxides and aziridines, emerges as a highly efficient method for producing cyclic carbonates and oxazolidin-2-ones with 100% of atom economy. Several catalytic systems have been employed to promote these transformations and porphyrin-based catalysts have proven their high efficiency in catalysing the cycloaddition of CO_2 to both epoxides and aziridines, whether under homogeneous[1] or heterogeneous[2] conditions.

To improve the catalyst biocompatibility and the process's sustainability, we investigated the activity of naturally derived and biocompatible iron porphyrins in promoting the CO_2 cycloaddition to three-membered rings. Thus, hemin (**1**) and its derivatives Fe(OMe)protoporphyrin IX (**2**) and sodium salt of hematin (**3**) were employed under homogeneous conditions to mediate the synthesis of both cyclic carbonates and oxazolidin-2-ones. Cyclic carbonates were achieved in higher yields, up to 100%, by employing the binary system consisting in complex **2** and TBACl (tetrabutyl ammonium chloride) as co-catalyst. Surprisingly, the synthesis of oxazolidin-2-ones proceeded effectively even in the absence of any co-catalyst, yielding desired products in yields up to 95% and A/B ratios up to 99:1 and offering a more convenient and environmentally friendly approach due to the absence of halogen-based co-catalysts.

Moreover, the successful heterogenization of hematin onto Colour Catcher® sheets, a cellulose-based support with full biodegradability, led the formation of **3@CC**. This robust material proved to be a highly efficient, recyclable and environmentally friendly heterogeneous catalyst capable of promoting the halogen-free synthesis of oxazolidin-2-ones in yields of up to 91% and A/B ratios up to 99:1. The versatility of the reaction was finally confirmed by testing various substrates and the reaction mechanism was elucidated through DFT calculations.

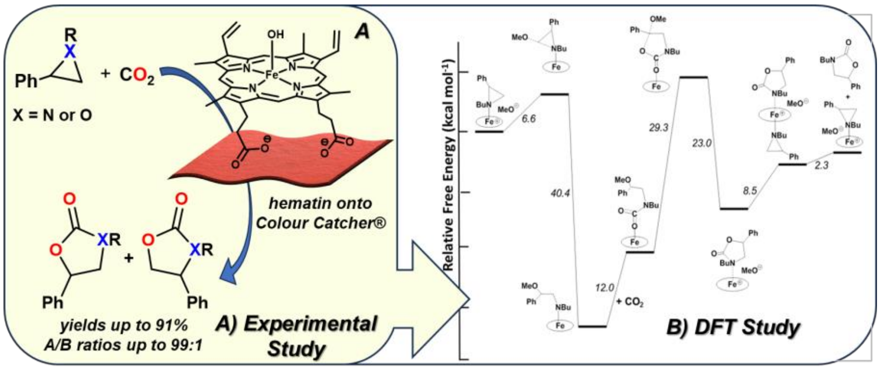

Figure 1 CO_2 cycloaddition promoted by heterogenized hematin (experimental (A) and DFT (B) studies)

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BEYOND CO_2 ACTIVATION: SHEDDING LIGHT ON N_2O ELECTRO-REDUCTION CATALYZED BY A LOW-VALENT IRON PORPHYRIN

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Keywords: N_2O reduction; Catalysis; Electrochemistry; Iron porphyrin

Text: In addition to its euphoric and anaesthetic properties, nitrous oxide (N_2O) is known for its significant impact on the environment. The increase of atmospheric N_2O since the start of the industrial era has contributed to greenhouse gas emission, with a greater global warming potential than carbon dioxide (CO_2), as well as ozone layer depletion.[1] Therefore, N_2O activation is of key interest to help mitigate environmental issues. However, its high chemical inertness makes it challenging.[2]

For this purpose, the electrochemical reduction of N_2O into dinitrogen (N_2) using molecular catalysts is a promising approach. Taking inspiration from the widely studied iron porphyrin catalysts for CO_2 electroreduction into carbon monoxide (CO),[3] recent work from the group has revealed the interesting catalytic activity of the low-valent iron tetraphenylporphyrin. Electrochemically generated, it can selectively reduce N_2O into N_2, but the mechanism involved has not yet been investigated.

The objective of this work is to explore the mechanism involved in the N-O bond activation and compare it with that of the C-O bond activation, using electrochemical and spectroelectrochemical tools. Particular attention is paid to determine the active form of the catalyst as well as the role of the acidic co-substrate.

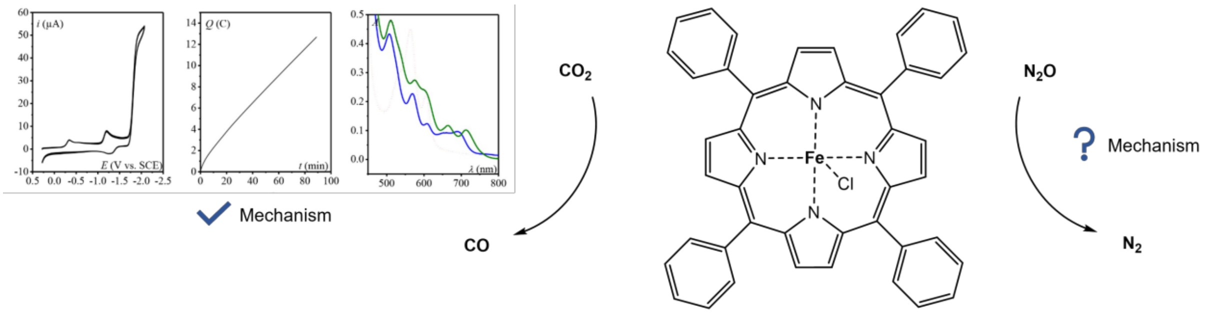

Figure 1 Extension and comparison of the catalytic activity of the iron tetraphenylporphyrin in the electroreduction of N_2O into N_2.[3]

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Exploring chirality transfer and coordination geometry distortion in lead- and tin-based chiral hybrid perovskites

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Keywords: Coordination geometry distortion; chirality; chiroptical properties; perovskites; DFT.

Hybrid organic–inorganic perovskites (HOIPs) have emerged as excellent materials for solar cell applications. Indeed, their extreme tunability and facile synthesis have opened the door to many new applications. Chiral HOIPs are attracting great interest as promising frameworks for chiroptoelectronics as well as spintronics applications. The chiroptical properties observed in chiral HOIPs can be explained understanding the chirality transfer from the chiral organic molecules to the achiral organic octahedra. A key element of the chirality transfer mechanism involves the distortion of the coordination geometry of the inorganic octahedra induced by the presence of chiral ligands. The specific process through which a chiral bias is generated from a chiral organic ligand to the inorganic coordination geometry of the lattice has, until now, remained unclear, [1]

In this study, we propose a tailored simulation workflow based on Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TD-DFT)[2] to theoretically explore the chirality transfer mechanism inducing chirality generation and coordination geometry distortion. To this aim, we investigate the chiroptical response of lead- and tin-based 2D chiral perovskites, specifically 2D R- and S-$(MBA^+)_2PbI_4$[3] and R- and S-$(MBA^+)_2SnI_4$[4]. We delve into the most impactful factors influencing their Circular Dichroism (CD) signals through ab-initio molecular dynamics simulations and the analysis of the density of electronic states (DOSs). Our findings reveal that the relevant chiroptical features are linked to a chirality transfer event driven by a metal–ligand overlap of electronic levels. This effect is more evident for tin-based chiral perovskites showing higher excitonic coupling. The high electronic coupling between the chiral ligands and the tin octahedra can be ascribed to the radically different assembling of the chiral ligands encapsulated in the tin perovskite, resulting in a highly distorted coordination and the formation of CH–π interactions with a distance value of 3.2 Å, not formed in a lead-based system.

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METALLOMIMETIC C–F ACTIVATION CATALYSIS BY SIMPLE PHOSPHINES

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Keywords: fluorine; phosphines; hydrodefluorination; metal-free catalysis; metallomimetism

Metallomimetic main group reactivity has gained interest in recent years. Beyond fundamental interest, it promises sustainable alternatives to the low-abundant, expensive and toxic precious metals. Their ability to undergo reversible 2-e$^-$ redox processes, such as oxidative addition (OA) and reductive elimination (RE) is advantageous for catalysis. Similarly facile redox cycling is rare in the main group.[1] The larger differences in stability between different oxidation states of main group species results in either rapid OA or RE, but a challenging reverse process renders catalysis difficult. Among the main group, the pnictogens (Pn) stand out as they allow access to stable species in different oxidation states, making them ideal candidates for metallomimetism. The introduction of geometrical constraint around the Pn atom, as a key design concept, moves them away from their preferred pyramidal to more planar geometries, changes orbital energies and thus, reactivity. Catalytic hydrodefluorination (HDF) and related C–F functionalization processes are key reactions in which main-group systems have been employed. Recently, some research groups have demonstrated that Pn systems can promote HDF.[2–4] Importantly, the 3 key processes of OA, transmetallation (TM), and RE reminiscent of transition-metal chemistry were evidenced, demonstrating that main-group systems can mimic the key elementary steps of transition-metal catalysis. In this presentation we will show that complex ligand architectures were not necessary for redox-cycling in HDF using Pn catalysts: indeed, we have shown that a simple catalytic system combining commercially available alkyl phosphines and silanes performs the HDF reaction on a range of perfluorinated arenes (see Figure 1).[5]

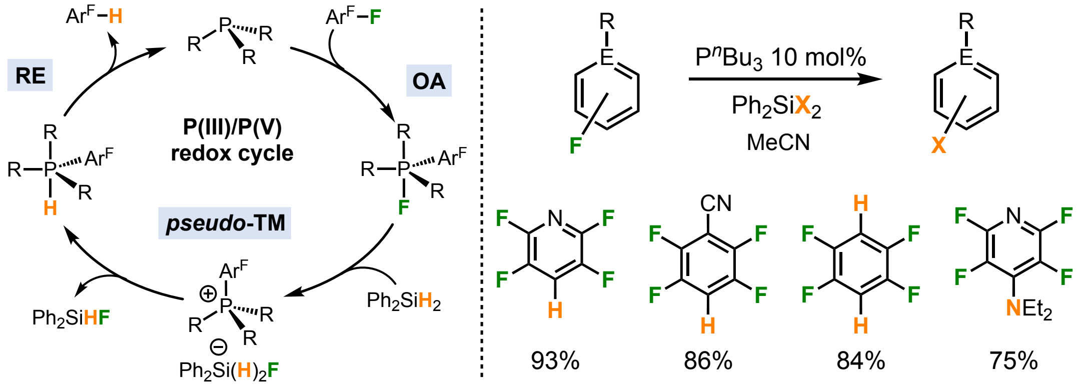

Figure 1 Catalytic HDF by redox-cycling of simple & cheap phosphines

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New trimetallic Fe_2M-thiolate (M = Cu, Ag, Au) complexes: the coinage metal inhibits the reactivity with O_2

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Keywords: bioinspired chemistry, iron-thiolate complexes; ORR; heterotrimetallic complexes.

Since the discovery of the critical role that molecular oxygen plays in oxidative metabolism, chemists have been intrigued by the mechanism via which metalloenzymes activate dioxygen[1].
Iron centers play a key role in dioxygen binding and activation. A growing ubiquitous subclass of metalloenzymes able to trigger this reaction contain non-heme iron centre in their active site, featuring thiolate moieties in their first coordination sphere[2].In this domain, there has been intense interest in studying model complexes that mimic the non-heme iron-thiolate active site to investigate their ability to activate O_2 and form metal-oxo species, which are proposed to be reactive intermediates in these reactions[3].

In this context, the ability of the non-heme iron-thiolate $[Fe_2^{II}(LS)_2]$ ($[Fe_2^S]$) complex (**Figure 1**) to activate O_2, to form iron-oxygen adducts, and to catalyze the oxygen reduction reaction (ORR) had been previously demonstrated[2],[4],[5].
New heterotrimetallic complexes $[Fe_2^{Cu}]^+$, $[Fe_2^{Ag}]^+$ and $[Fe_2^{Au}]^+$ ($[Fe_2^M]^+$, **Figure 1**) related to $[Fe_2^S]$ have been isolated and characterized by single crystal X-ray diffraction, cyclic voltammetry, mass spectrometry and through UV-vis, paramagnetic NMR and zero-field ^{57}Fe Mössbauer spectroscopies. In addition, the reactivity of these complexes with O_2 has been investigated to evaluate the influence of the third metal on electronic and steric properties of the initial $[Fe_2^S]$ complex. Indeed, the presence of the additional metal centre in the heterotrimetallic complexes, in all cases, has been observed to partly inhibit their reactivity with dioxygen if compared to the previously reported diiron counterpart.

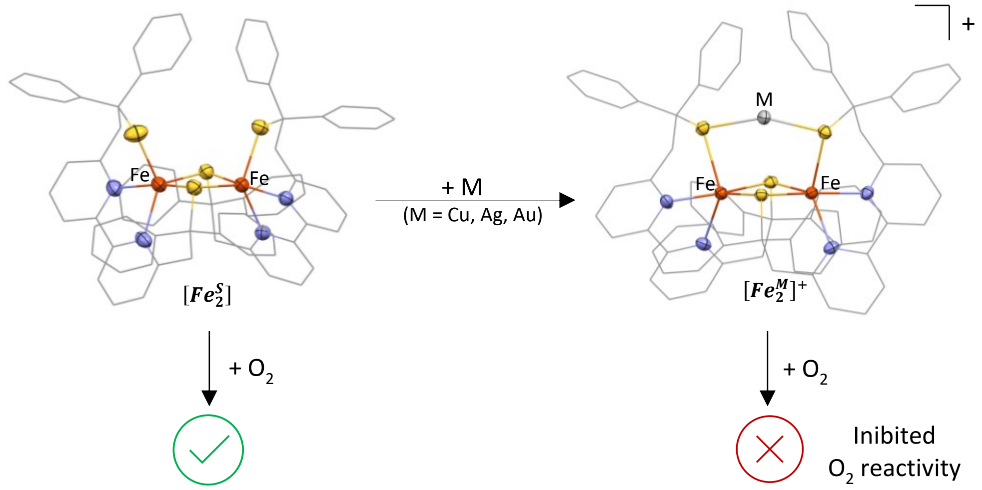

Figure 1: Metal-thiolate $[Fe_2^S]$ and $[Fe_2^M]^+$ complexes, discussed in this study and their reactivity with oxygen.

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Mechanistic Study of the Photochemical Benzene Carbonylation Reaction: Metal-Ligand Cooperation and Light Dependence

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Keywords: Rhodium complexes, Photocatalysis, Metal-Ligand Cooperation, Organometallic Chemistry, Reaction Mechanism.

Photochemical benzene carbonylation mediated by Rh(I) complexes is a challenging process that saw little advancement since the pioneering studies by Goldman *et al.* in 1994.[1] In the meantime, metal-ligand cooperation (MLC) has been investigated as a tool for the catalytic transformation of strong bonds.[2] In 2016, the Milstein group, for example, has shown that a Rh(I) MLC pincer complex (Fig. 1, **Rh-1**) was able to activate the unreactive C-H bond of benzene under irradiation with UV light.[3] The consequent CO insertion in the Rh-C bond allows the formation of an acyl complex that can stoichiometrically release benzaldehyde upon acid treatment.

Here, we chose to re-investigate the mechanism of this intriguing transformation. By combining organometallic synthesis of key intermediates, spectrophotochemical studies and DFT calculations, we were able to propose a putative mechanistic cycle. An in-depth mechanistic investigation allowed to highlight potential bottlenecks of this catalytic cycle, hampering catalytic turnover. By optimizing the reaction conditions accordingly, we were able to show for the first time, that a MLC rhodium pincer complex can promote the catalytic carbonylation of benzene under mild conditions (RT, 390 nm, 1 atm CO).[4] Based on these detailed mechanistic studies, we hope to spark further development in the field of MLC-powered C-H bond functionalization.

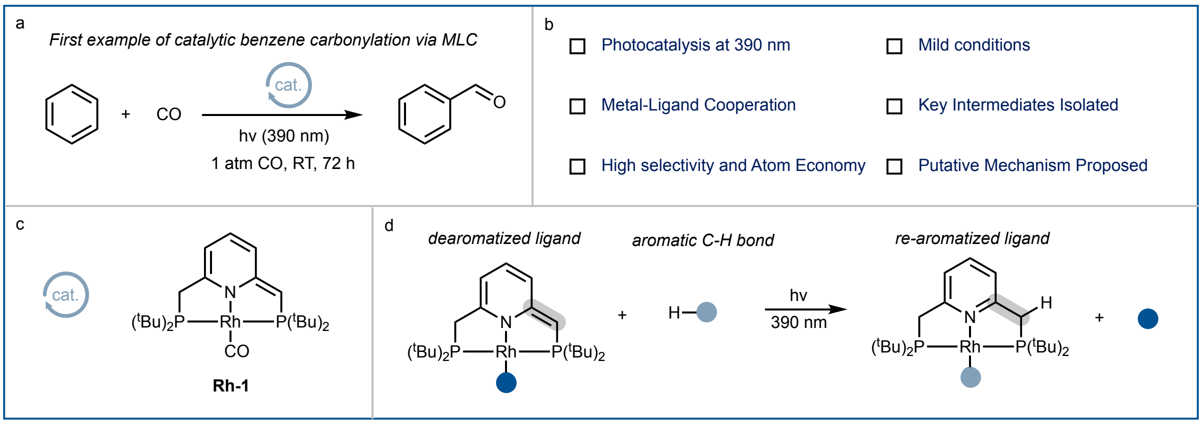

Figure 1. a. Overall scheme of the photochemical benzene carbonylation reaction. b. some highlights of the process. c. structure of the catalyst. d. scheme of the C-H activation via Metal-Ligand Cooperation.

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Study of Magnesium and Calcium Hydride Complexes for CO_2 Reduction and Efficient Catalytic CO_2 Hydroboration

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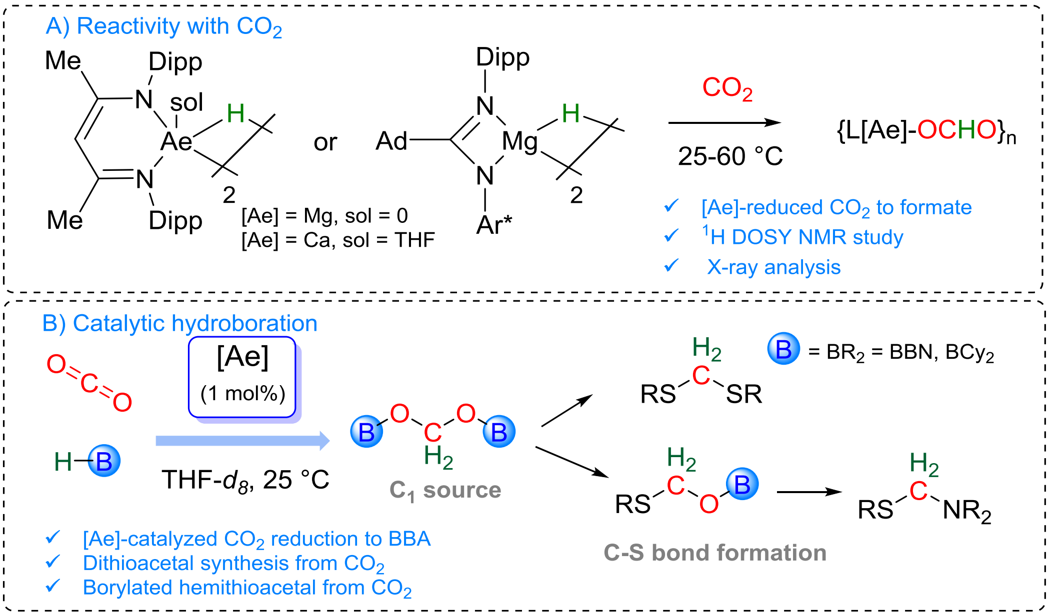
Keywords: alkaline earth metal hydrides; CO_2; hydroboration; $4e^-$ reduction; C-S bond formation

Group 2 metal coordination compounds, especially Mg and Ca complexes, are attractive due to their cost effectiveness and environmentally friendly properties, and their hydrides are recognized as active participants in various catalytic reactions[1]. While CO_2 reduction is of great interest, its transformation remains challenging. This is due to its high thermodynamic and kinetic stability. To overcome the high kinetic barrier of CO_2 reduction, the use of molecular hydride complexes may provide an alternative approach. Thus, in our study, we have investigated the reactivity of a novel amidinate-Mg hydride complex as well as the β-diketiminate-Mg and Ca dihydrides[2-3] towards CO_2 reduction. These hydride complexes were shown to efficiently incorporate CO_2 to form various formate species with different nuclearities. In addition, we investigated their catalytic role in the hydroboration of CO_2 by hydroborane, leading to the selective generation of $4e^-$ reduction products, or bis(boryl)acetal (BBA). This BBA served as a reactive methylene transfer reagent, facilitating the formation of various symmetric and asymmetric acetals in C-S bond formation[4].


A) Reactivity with CO_2

[Ae] = Mg, sol = 0
[Ae] = Ca, sol = THF

✓ [Ae]-reduced CO_2 to formate
✓ ^1H DOSY NMR study
✓ X-ray analysis

B) Catalytic hydroboration

✓ [Ae]-catalyzed CO_2 reduction to BBA
✓ Dithioacetal synthesis from CO_2
✓ Borylated hemithioacetal from CO_2

Figure 1: A) Reaction of Mg and Ca hydride complexes with CO_2, B) The [Ae]-catalyzed hydroboration of CO_2 to BBA and the subsequent C-S bond formation.

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Dual ^{18}F PET/^{19}F MRI imaging enabled by trifluoroborate prosthetic groups on an azamacrocyclic chelator for metallic cations.

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Keywords: Macrocyclic ligands; Metal chelation properties; ^{18}F Radiolabeling; ^{19}F MRI.

Polyazamacrocycles (cyclen, cyclam …) are ubiquitous ligands that possess remarkable coordination properties towards a wide range of cations, from transition metals to lanthanides. In particular, they are cornerstone in medical imaging and radiotherapy, where they chelate cations that would be toxic *in vivo* under their free form to allow their safe injection to patients and excretion. In particular, Dota ligand and its derivatives are approved clinically for administration of MRI contrast agents (with Gd^{3+}), PET probes ($^{68}Ga^{3+}$) or internal β radiotherapy ($^{177}Lu^{3+}$).

In this field, chemical research is now tackling the challenge of multimodality and theranostics with molecular tracers, *i.e.* the implementation of multiple modalities (imaging and/or therapy) on the same architecture, allowing identical biodistributions and improved diagnosis and treatment for patients. In this context, we provide a new class of ligands combining a polyazamacrocyclic ring and a fluorinated moiety to take advantage of both the properties of metal cation in the cavity and the ^{18}F PET and ^{19}F MRI possibilities offered by small trifluoroborate groups ($-BF_3^-$).[1]

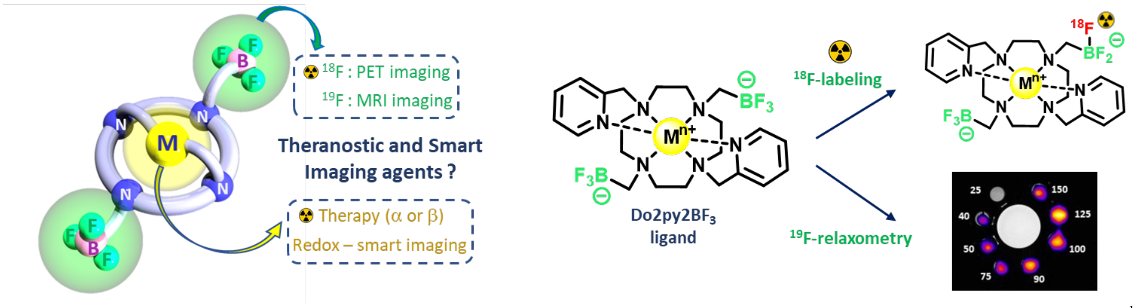

Figure 1 Concept of the theranostic and multimodal approach with trifluoroborated macrocycles, and example of Do2py2BF$_3$ allowing ^{18}F-radiolabeling and ^{19}F magnetic resonance detection.

Only a few of such fluorinated polyazamacrocyclic scaffolds have been described in the literature so far. For ^{18}F-labeling applications, the BF_3 (or SiF_5) unit has been introduced via large branched organic chains that are synthetically highly demanding,[2] or the cavity is occupied by a M-^{18}F synthon (Al or Sc)[3,4] preventing or limiting the use of the chelator for a variety of metal cations. CF_3 units have also been used for ^{19}F MRI smart agents, but do not offer the possibility of ^{18}F-radiolabeling.[5]

Therefore, we prepared new cyclen-based trifluoroborated chelators, that offer a compact molecular architecture, great stability in aqueous medium, and the ability to be easily ^{18}F-labeled via simple isotopic exchange, as well as produce ^{19}F magnetic resonance that can be observed with suitable detection limits. The synthesis and coordination chemistry of the ligands, as well as the physico-chemical characterization of the complexes and proof-of-concept for the dual ^{18}F/^{19}F applications will be presented herein.

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INFLUENCE OF A COORDINATING SULPHUR ATOM ON LUMINESCENT SINGLE-MOLECULE MAGNETS

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Keywords: Single-molecule magnets; luminescence; lanthanide; β-thioketone; crystal structures

Text: The field of molecular magnetism has witnessed remarkable progress in the last decades, fuelled by the discovery of single-molecule magnets (SMMs).[1] These unique molecular entities exhibit intriguing magnetic behaviour, originating from the presence of central metal ions surrounded by coordinating ligands.[2,3] The magnetic properties of these molecular structures have proved to be highly original, since they emanate from the molecule alone, rather than from a collective synergy (cooperativity) between molecules. Research into SMMs in the decades that followed saw the introduction of Ln^{3+} lanthanide ions into these complexes.[4] Most of these 4*f* ions have a high spin and strong intrinsic magnetic anisotropy, which are essential prerequisites for obtaining SMMs with excellent performances.[5] Some lanthanide ions also have very specific optical properties. As *f-f* transitions are forbidden by Laporte's rule, their absorption and emission bands are thin, and their lifetimes are long. Thus, when the lanthanide ion is coordinated to one or more specially designated ligands, it can be 'sensitised' by transferring energy from the ligand's excited state to the metal's excited state, which then re-emits this energy, possibly radiatively. In the pursuit of novel SMMs, the role of coordinating atoms within the ligands has emerged as a topic of significant interest. Among the diverse elements employed as ligands, sulphur stands out as a particularly intriguing coordinating atom due to its soft-donor character and its potential to impact both the magnetic and luminescent properties of metal complexes.[6] The aim of this work is to develop new SMMs complexes based on Ln^{3+} ions and β-thioketonate ligands, and the study of the correlation between their structures and properties.[7] A new family of Ln^{3+} (Tb^{3+}, Dy^{3+}, Er^{3+}, Yb^{3+}) mononuclear complexes based on β-thioketonate ligands has been isolated as single crystals. The magnetic and photophysical properties of a complex have been studied and rationalized by *ab initio* calculations to illustrate the correlation between the metal-ion environment and their SMM behaviours (Figure 1).

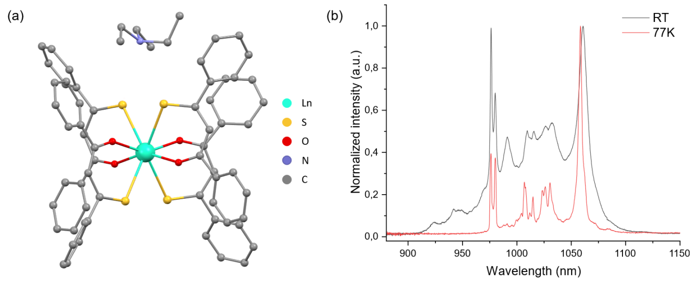

Figure 1 Cristal structure of $(Et_3N)[Ln(L)_4]$ (L = 1,3-diphenyl-3-thioxopropan-1-one). H-atoms removed for clarity (a). Room and low temperature solid-state emission spectra of $(Et_3NH)[Yb(L)_4]$ under irradiation at λ_{exc} = 413 nm (b).

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METALLOGELS OF SUPRAMOLECULAR NANOTUBES FOR SURFACE DEPOSITION OF SINGLE-CHAIN MAGNETS

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Keywords: Lanthanides, Nanotubes, Gel media, Surface deposition

Lanthanide coordination chemistry[1] is a very efficient tool to design magnetic and luminescent molecules. It also allows to turn them into materials and then devices.[2] Indeed, this is one of the best tools for building molecular edifices from lanthanide ions because it allows careful control of the ion environment and of the dimensionality of the final compound. This is particularly important for optimizing the magnetic properties of lanthanide-based molecules.

We will review several years of work of our team and collaborators on lanthanide-based single-chain magnets (SCM), that are molecules able to behave as magnets at the molecular scale. Then, we will illustrate how a SCM behavior can be observed on lanthanide–radical chains with original topologies such as chiral molecular nanotubes[3] and their derivatives.[4]

Then, we will illustrate how metallogels can be formed from these objects and their morphologic and magnetic properties preserved in the gel phase.[5] Last, on-surface gelation provides thick films as well as submonolayer deposits of supramolecular nanotubes on surface as evidenced by atomic force microscopy (AFM) observations. This study opens novel perspectives for the use of 1D molecular objects at the nanoscale for example as magnetic materials for the development of novel architectures for data storage and spintronics.

Figure 1. Molecular chains can be organized as supramolecular nanotubes that can be further tuned into metallogels for surface deposition purposes

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A COBALT MOLECULAR CATALYST FOR HYDROGEN EVOLUTION REACTION WITH RECORD ACTIVITY IN PHOSPHATE BUFFERED WATER SOLUTION

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Keywords: Green Hydrogen, Hydrogen Evolution Reaction, Electrocatalysis, Cobalt Complexes, DFT Calculations

The development of efficient electrocatalysts for the hydrogen evolution reaction (HER) from water is attracting a lot of interest, in the general framework of finding strategic processes toward renewable fuels. Among different possible electrocatalysts, those based on cobalt have shown very promising performance likely due to their intrinsic oxygen tolerance and efficient proton reduction ability.[1]

Herein, we report the results of an in-depth investigation on the utilization of a large family of water-soluble Cp*Co(III) molecular complexes, bearing bidentate ligand, as HER electrocatalysts in aqueous solutions.[2] We show that [Cp*Co(2-ampy)I]I (2-ampy = 2-aminomethyl-pyridine, **1**) is an extremely active catalyst for HER, exhibiting a record TOF of 109000 s^{-1} in phosphate buffered water solution (pH 7). The key to this remarkable activity stems from the establishment of a network of weak interactions in the second coordination sphere (Figure 1). As a matter of fact, both experimental and theoretical studies strongly suggest that the $-NH_2$ functionality of 2-ampy ligand acts as an anchoring and orienting group for $H_2PO_4^-$ through the establishment of an in-termolecular hydrogen bonding with it that, in turn, intermolecularly donates a proton to Co–H liberating H_2.

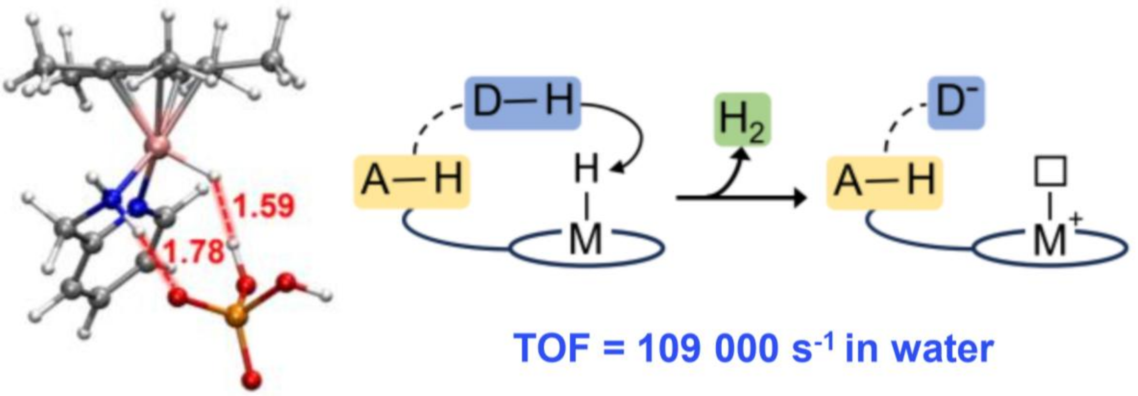

Figure 1 DFT-optimized structure of **1-H** interacting with $H_2PO_4^-$ that leads to hydrogen evolution.

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Design of supported catalysts for hydrogen production

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Keywords:

Hydrogen, electrocatalysis, nickel complex, redox-active ligand.

Text:

Numerous challenges for the upcoming decades arise from the worldwide reliance on fossil fuels as energy carriers and raw materials for industrial products. The reserve of these sources are finite, which make the interest of the research community to find an alternative source. Hydrogen is regarded as an "ideal" fuel due to its abundance and the environmental side since it only emits water vapors during combustion. The new challenge is to generate hydrogen from renewable and sustainable resources. In a previous work, we reported on the use of nickel bis-thiosemicarbazone complexes (NiTSC-R) as electrocatalysts in hydrogen evolution reaction (HER). A first series of catalysts was designed from chemical tuning of the ligand. Different substituents were placed in para position of the phenyl ring of the TSC ligand. The resulting electrocatalytic performances of the complexes indicated that the chemical nature of the substituent indeed influences the electrochemical and catalytic behavior of the system.[1] To get further insight into the key parameters controlling catalytic performances, we are now investigating the relative importance rested on the position of the substituent rather than on its chemical nature. In this work, we were inspired by the parent nickel catalyst being para-substituted with a methoxy group. We have prepared a new series of complexes having this group placed on different positions on the phenyl ring and considering multiple combinations of these positions. The resulting complexes were then evaluated for their capability to mediate electrocatalytic hydrogen evolution with the aim to establish structure-property relationships.

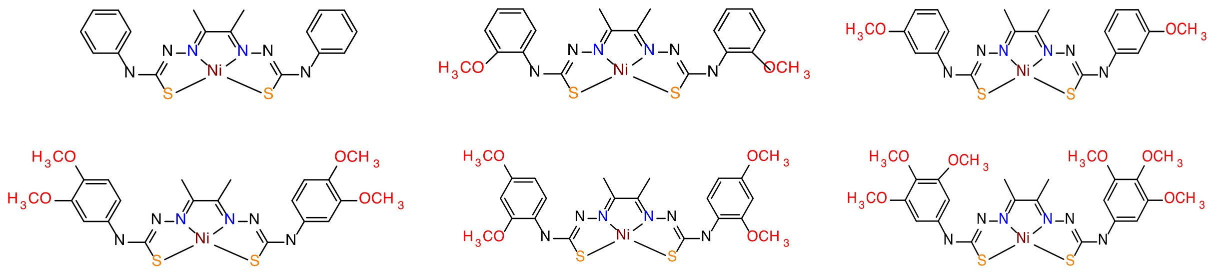

Figure 1: Series of complexes with different position of methoxy group.

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Femtosecond Spectroscopy of New Iron Bidentate Complexes with Extended Lifetimes

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Besides photo-voltaics, hydrogen (H_2) production via water splitting, and more specifically photocatalytic water splitting, is another avenue for sustainable and renewable energy production. Photo-sensitizers used in photocatalytic water splitting are in most cases organo-metallic photo-sensitizers (PS) based on noble metals, such as Ruthenium (Ru) or Platinum (Pt), but since a decade PS with Earth-abundant metals have emerged, including iron (Fe) [1,2]. Yet, if iron presents the tremendous asset of being nontoxic and much more abundant than ruthenium, complexes made with the former are much less efficient than the ruthenium-based ones, mainly because of the smaller 3d orbitals and reduced ligand field splitting. Hence, the low-energy Metal Centred (MC) states severely reduce the lifetimes in Metal-to-Ligand Charge Transfer (MLCT) states, thereby impairing the PS function. To address this issue, iron-based complexes based on N-heterocyclic carbene (NHC) ligands[3] and derivatives thereof are intensively investigated, recently leading to noticeable improvements of the performances of dye-sensitized solar cells[4]. Here we study the excited state lifetimes of bidentate Fe(II)-NHC complexes with a new rational design featuring quinoline-based ligands (Fig. 1A).

Femtosecond Transient Absorption Spectroscopy (TAS) reveals that two excited states are populated in parallel, with strikingly different lifetimes: a fast one, on the order of 1 ps, and a second longer-lived component, evidenced by the decay time of the excited state absorption band in the 380-430 nm range, the lifetime of which can exceed 100 ps in the best case (Fig. 1B). The longest lifetime of 120 ps is observed for the ligands with highest π-acceptance character, and lowest energy of the LUMO states (complex **366**, fig. 1A). Determining the nature of this state (^{3}MLCT or ^{3}MC) is of utmost importance, since ^{3}MLCT lifetimes reported for bi-dentate NHC-Fe(II) complexes are usually ≤ 20 ps[5]. To this end, the absorption spectra of the electro-chemically reduced and oxidized forms were measured. Simulating the differential spectrum of an MLCT state on the basis of the spectra determined by spectro-electrochemistry shows only partial agreement with the spectra observed by TAS (Fig. 1C).

We therefore examined the luminescence properties of these very weakly emissive complexes, both by steady-state and time-resolved luminescence experiments (streak camera, 10 ps resolution). The data show strong and long-lived contributions of most likely intra-ligand transitions, and our present effort lies in identifying short-lived components related to putative ^{3}MLCT states.

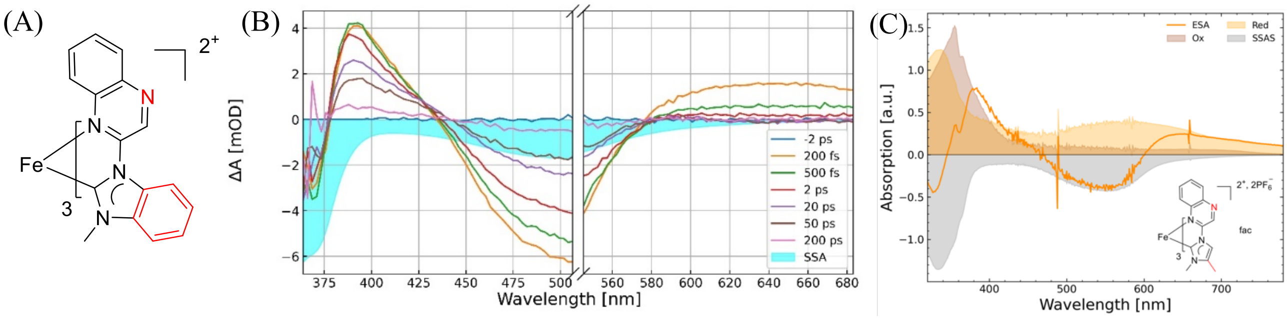

Figure 1 (A) Chemical structure of complex **366**. (B) Transient absorption spectra of complex **366**. The long-lived exc. state absorption (375-430 nm) and ground state bleach (450-570 nm) reveal an excited state with ≈120ps lifetime. (C) Absorption spectra of the reduced (yellow) and oxidized (brown) forms of complex **346**. The differential MLCT-type ESA spectrum (orange line) is simulated by subtraction of the ground state absorption of the neutral complex (grey).

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Factors Influencing the Excited-State Reactivity of Fe(III) and Other Transition-Metal Based Coordination Compounds

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Keywords: Iron Photosensitizers; Cage-Escape; Photochemistry; Coordination

Solar energy represents a promising renewable energy source. In natural and artificial photosynthesis, light absorption and catalysis are separate processes linked together by exergonic electron transfer. There is a plethora of organic transformations that can be sensitized to visible light, but the corresponding reaction mechanisms are not always straightforward. Here, we will present recent advances in the field of mechanistic photoredox catalysis using coordination compounds based on rare earth and earth abundant transition-metal based coordination compounds.[1] The emphasis is placed on the fundamental factors that govern reactivity, rather than a large substrate scope, which were studied by means of steady-state and time-resolved spectroscopic techniques[1d, 1e, 2] The focus is placed on cage-escape yields, *i.e.* the efficiency with which the radicals formed after excited-state electron transfer separate and escape the solvent cage.[1d, 1e, 2] We have shown that cage-escape yields could be modulated and, in some cases, were shown to increase when the driving force for photo-induced electron transfer increased.[2] Our results also highlight that these types of studies are highly needed as metal-to-ligand charge transfer excited state (MLCT) and ligand-to-metal charge transfer excited state (LMCT) behaved with different trends.

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Carbon dots surface chemistry and peptides design drive fluorescent properties: new tools for metal detection

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Keywords: carbon dots ; copper ; GHK peptide ;fluorescence

Text: The possibility to design rational carbon dots surface functionalization for specific analytical and bioanalytical applications is hindered by the lack of a full knowledge of the surface chemical features driving fluorescent properties. In a recent work, we have demonstrated the possibility to distinguish isobaric peptides, undistinguishable by common MSMS experiments, by using the fluorescent properties of specifically designed carbon dots.[1] The same approach has also been applied to monitor insulin aggregation.[2] Here, we report novel results on new carbon dots functionalized with peptides containing the GHK sequence to be used for copper detection. The reported results indicate the possibility to design amino and carboxyl enriched surface carbon dots to answer specific chemical requirements, paving the way for the use of these nanoparticles as a versatile and useful new chemical and biochemical tool.

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2. *G.A. Zingale, A. Distefano, I. Pandino, N. Tuccitto, V. Oliveri, M. Gaeta, A. D'Urso, A. Arcoria, G. Grasso.*
   Analytical and Bioanalytical Chemistry ***2023**, 415,1829.*

Ru(II) polypyridyl complexes and light: a promising combination in the design of powerful biomedical tools

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Keywords: Ruthenium complexes; photodynamic therapy, antimicrobial photodynamic therapy

Photodynamic therapy (PDT) still attracts increasing interest in the design of new anticancer as well as antibacterial agents. Among the main advantages, there is the precious chance to control the activation of a drug in a spatio-temporal manner, thus allowing to considerably limit, or even overcome, the most crucial drawbacks incurring with commonly employed drugs.[1]

In this context, the research of novel photosensitizers (PSs) based on inorganic compounds has driven much attention on Ru(II)-polypyridyl complexes (RPCs), an intriguing and versatile class of compounds with optimal features as PSs. Indeed, their chemical structures can be finely modified to conveniently tune important aspects, such as solubility in aqueous media, light-harvesting properties and singlet oxygen sensitizing capabilities, just to name a few.

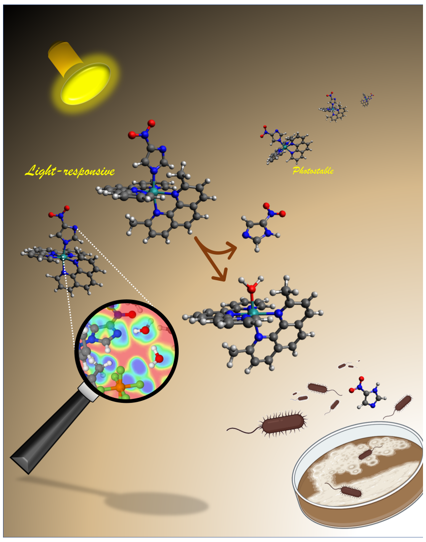

Figure 1: RPCs as photoresponsive tools for biological application.

In this contribution, it will be shown that the presence of highly charged polyamino-macrocycles into Ru(II)-scaffolds confers to the resulting complexes excellent solubility in aqueous media (a fundamental prerequisite for their biomedical application), beyond to strengthen their capacity to interact with key biological targets without affecting the good sensitizing properties of Ru(II) centers. Moreover, the employment of π-expansive chelates, such as the popular benzo[*i*]dipyrido[3,2-*a*:2',3'-*c*]phenazine ligand (dppn),[2] or the decoration of Ru(II)-cores with organic chromophores to give bichromophoric dyads, is a potent strategy that can be adopted to boost as much as possible the sensitizing properties of the resulting PSs.

In light of these considerations, several RPCs have been synthesized and characterized by our group and are presented, together with the evaluation of their biological activity on different cancer models including melanoma and ovarian cancer cells, as well as bacterial cells.

On the other hand, a crucial drawback of PDT, namely its classical reliance on molecular oxygen, still remains to be solved. Once again, RPCs give us suitable answers to solve this issue. Indeed, their ancillary ligands can be differently modified to result in photolabile complexes that release a bioactive ligand upon irradiation. On this basis, we realized a series of strained RPCs capable of photoejecting different analogues of metronidazole, a mainstay drug in the treatment of anaerobic bacterial infections, and, for the first time, the potential of the "*photorelease antimicrobial therapy*" under the therapeutically relevant hypoxic conditions was demonstrated.[3]

Even though much has still to be known and understood about ruthenium polypyridyl complexes, this blooming class of compounds continues to deserve our attention in the search for novel and effective therapeutic approaches.

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Cu^{II}-Dp44mT reactivity and selectivity towards biologically relevant thiols

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Keywords: ROS, oxidative stress, Cu^{II}-Dp44mT, thiols.

Reactive oxygen species (ROS) are fundamental for many cellular functions such as redox homeostasis, regulation of transcription factors, and signaling transduction[1,2]. However, an imbalance between the production and the scavenging of ROS induces oxidative stress, which might contribute to many pathologies[2]. Intracellularly, thiol-containing molecules and proteins can be involved in the formation of ROS, as they are reducing agents, hence a source of electrons for ROS production[3]. Furthermore, metal ions such as Fe and Cu are very good catalysts in the reaction that leads to the formation of hydroxyl radical, one of the most powerful oxidants among ROS[4]. In this frame, we were interested in thiol oxidation catalyzed by the copper complex of di-2-pyridylketone-4,4-dimethyl-thiosemicarbazone (Dp44mT). Dp44mT belongs to the class of α-N-heterocyclic thiosemicarbazones, and it has been proven to be cytotoxic in the nM range in cell cultures[5]. Cu alone can catalyze the oxidation of thiols to disulfides in aerobic conditions with the production of ROS, a process that is enhanced by the coordination of this metal ion by Dp44mT (Fig.1)[6].

It is important to understand the reactivity and selectivity of Cu^{II}-Dp44mT with different biologically relevant thiols. Therefore, glutathione, cysteine, N-acetylcysteine, D-penicillamine, and two model thiol-disulfide oxidoreductases glutaredoxin and thioredoxin were investigated in the presence of physiologically relevant GSH concentration to explore the reactivity of Cu^{II}-Dp44mT compared to free Cu^{II}. By means of UV-Vis spectroscopy, EPR spin scavenging, and measurement of dioxygen consumption, it has been assessed that Cu^{II}-Dp44mT oxidized thiols faster and produced hydroxyl radicals faster than free Cu^{II}. Comparing GSH and Cys in physiological relevant concentration, Cu^{II}-Dp44mT is more reactive with Cys, but it is selective for GSH. Therefore, GSH protects Cys and Cys-residues against potential deleterious oxidation by Cu^{II}-Dp44mT. This investigation contributes to better understand the interaction between Cu^{II}-Dp44mT and mixtures of thiols in the intracellular environment.

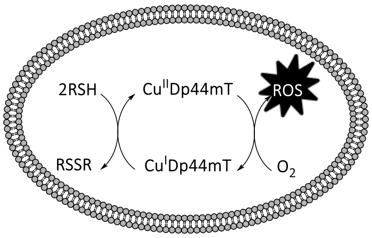

Figure 1. Thiol reduction and ROS production catalyzed by Cu^{II}-Dp44mT in intracellular environment.

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Uranium(VI) chelation by desferrioxamine B: from solution binding studies to a new analytical device for environmental monitoring

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Keywords: DGT samplers, siderophore, solution equilibria, solid/liquid extraction, speciation

Uranium mining, nuclear fuel production and reprocessing, massive use of phosphate fertilizers, and coal combustion are the main sources of uranium discharges in the environment. The monitoring of contaminated sites requires new breakthroughs in analytical chemistry in order to evaluate the impact of anthropogenic releases, the contribution of natural sources, transfers between the various biosphere compartments, and the risks of contamination of food chains.

Diffusive Gradients in Thin-films (DGT) devices are particularly attractive and versatile on-field sampling tools.[1] They are used to passively pre-concentrate *in natura* the potentially bioavailable labile fraction of trace contaminants, before their quantification in the laboratory. However, the commercially available DGT samplers recommended for uranium and most of those described in the literature, incorporate a non-selective ion exchange resin (*e.g.* Chelex-100®) or adsorbing material (*e.g.* TiO_2).[2,3] Depending on the deployment conditions, their performances for determining the labile U(VI) concentration in aquatic environment can be unsatisfactory, because these DGT samplers are not selective enough. Besides the saturation of the binding sites by the major competing ions present in fresh- or seawaters (*i.e.* Ca^{2+}, Mg^{2+}), high carbonate levels might also hamper the uptake of U(VI), which is mainly present in the form of triscarbonato complexes of $[M_xUO_2(CO_3)_3]^{(4-x)-}$ general formula (M = Ca or Mg, $x = 0–2$).

To overcome these limitations, new chelating resins were prepared by covalent grafting of the emblematic trishydroxamic siderophore desferrioxamine B (DFO) on hydrophilic polymer beads bearing carboxylate groups. This molecular strategy and choice of chelator relied on thorough solution coordination studies of the UO_2^{2+}/DFO^{3-} system, that combined potentiometric and spectroscopic (UV-vis, Raman, ^{17}O NMR, X-ray absorption) measurements. Three complexes of 1:1 stoichiometry have been identified and their stability constants determined,[4] allowing to predict the uranyl speciation in media simulating natural waters. The lecture will also cover the synthesis and characterization of the DFO-based solid/liquid extraction resin,[5] as well as the laboratory validation tests of the DGT samplers made thereof. Finally, the results of the first field-tests performed in the Essonne River will be presented.

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UNRAVELING AIE IN ZINC(II) COORDINATION COMPLEXES: ROLE OF LIGAND STRUCTURE AND MECHANISTIC INSIGHTS

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Keywords: Aggregation-Induced Emission (AIE), Zinc (II) coordination complexes

Text: Aggregation-Induced Emission (AIE) is a captivating phenomenon observed when certain molecules exhibit intensified fluorescence upon molecular aggregation or packing in condensed phases. [1] In this study, our focus lies in the investigation of AIE within the context of coordination complexes, specifically involving two ligands L_1 and L_2, as well as their zinc(II) complexes ZnL_1 and ZnL_2.

While the detailed compounds and specific mechanisms behind AIE are reserved for the conference presentation, our research centers on the distinct photophysical properties exhibited by these coordination complexes. Notably, we observed intriguing AIE behavior in complex ZnL_2, a remarkable occurrence considering that neither ligands L_1 nor L_2 themselves demonstrate AIE characteristics. Complex ZnL_1, similar to L_1 and L_2, does not exhibit AIE. It is worth noting that ligands L_1 and L_2 are structurally very similar, with subtle differences accounting for the observed variations in AIE behavior.

Our comprehensive studies, including UV–vis absorption and emission spectroscopies in solution and the solid state, offer valuable insights into the AIE properties of complex ZnL_2. Additionally, we explored the fluorescence behavior of ZnL_2 in solvents with varying ratios of water and ACN, revealing optimal conditions for AIE enhancement (Figure 1). Furthermore, we present X-Ray structural data for complex ZnL_2.

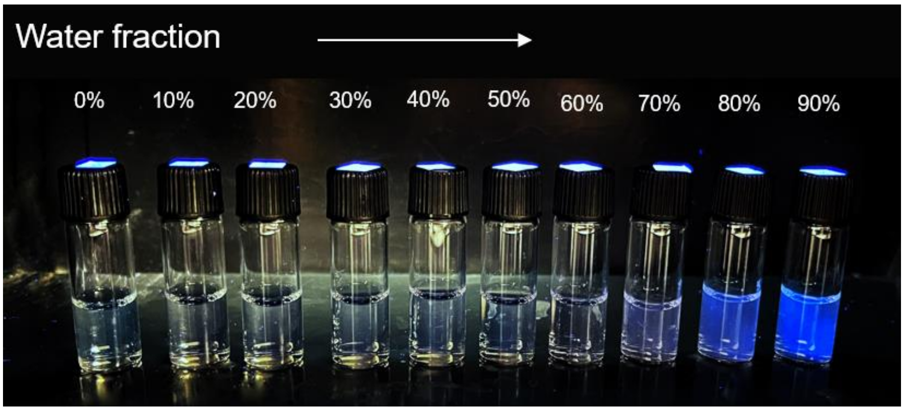

Figure 1 The fluorescence photographs under UV light of 10^{-5} M ZnL_2 in mixed solvent of water and ACN system with different water fractions

We look forward to sharing the complete results and all relevant details at the conference, contributing to the evolving knowledge of AIE in coordination complexes and its potential applications across various fields.

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Fluorescent Blue-emissive Zinc(II) Coordination Complexes with Bis(imidazo[1,5-*a*]pyridine)methane Ligands

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Keywords: Imidazo[1,5-*a*]pyridine ligands; Zinc(II) complexes; Fluorescence

Imidazo[1,5-*a*]pyridines have achieved significant attention due to their unique chemical and biological properties and potential applications.[1] From a synthetic perspective, they offer a broad range of functionalization possibilities, enabling the alteration of their photophysical properties by introducing several substituents. Additionally, these compounds exhibit interesting luminescence properties (i.e., large Stoke shifts, good photostability and high quantum yields) both in solution and in the solid state.[2]

When properly functionalized, they can act as ligands toward transition metals, the luminescent behavior of the resulting complexes being highly influenced by the substituents on the heterocyclic ring.

In our ongoing research on d^{10} metals compounds with *N*,*N*-[3] and *N*,*O*-coordinated[4,5] imidazo[1,5-*a*]pyridine ligands, we recently obtained species bis(1-methylimidazo[1,5-a]pyridin-3-yl)methane ($\mathbf{L^H}$) (Figure 1) which has demonstrated excellent luminescent properties. Two other derivatives have been easily prepared by introducing a methyl ($\mathbf{L^{Me}}$) or benzyl ($\mathbf{L^{Bz}}$) residue on the methylene bridge.

The corresponding zinc(II) complexes have been synthesized and fully characterized both in solution (^{1}H, ^{13}C NMR) and in the solid state (X-ray). In solution, they show an intense blue, fluorescent emission (λ_{max} = 416-418 nm) which has been rationalized by means of TD-DFT calculations.

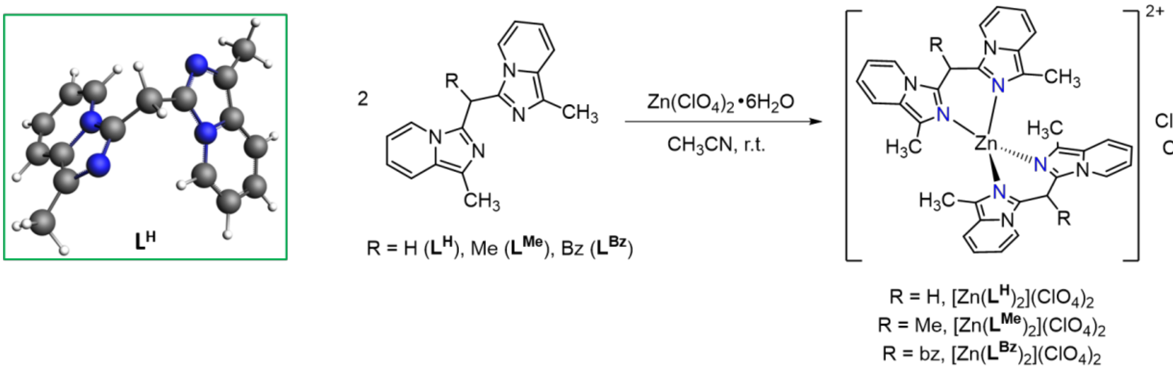

Figure 1. Bis(imidazo[1,5-*a*]pyridine)methane ligands and their zinc(II) complexes investigated in this study.

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Strong Zn(II) and Mg(II) Cationic Lewis Acids: Synthesis, Structure, and Reactivity in Selective Catalysis

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Keywords: Zinc, magnesium, carborate, Lewis acid, catalysis

Sustainable chemistry calls for the development of catalytic processes to access valuable compounds in efficient, affordable and less harmful ways. The use of earth-abundant and non-toxic metals for homogenous catalysis represents a challenging path that still requires significant improvements.

Electrophilic Lewis acid metal cations, especially abundant and biocompatible Zn^{2+} and Mg^{2+}, constitute a method of choice for the activation of substrates for catalytic applications. Supporting ligands (such as NHCs) coordinated to the metal center allow for greater stability and some level of reactivity, but may result in a reduced electrophilicity.[1] Further enhancement of the Lewis acidity is even possible by accessing "ligand-free" metal cations provided the use of chemically inert and weakly coordinating anions[2] such as carborate $[R\text{-}CB_{11}Cl_{11}]^-$. In particular, access to unprecedented "pseudo-naked" Zn^{2+} and Mg^{2+} ions is now possible with such anions.[3]

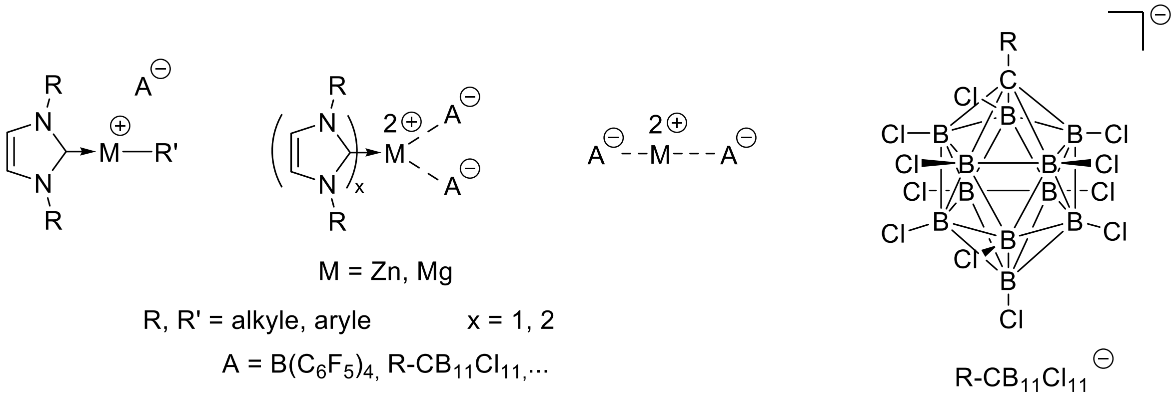

Figure 1 Zn(II) and Mg(II) cations as strong Lewis acids

These Lewis acid metal cations readily activate various polar or unsaturated substrates. Fast catalytic hydrosilylation (as well hydrogenation transfer catalysis) of alkenes/alkynes readily proceed at RT. Reactivity was also observed for the catalytic reduction of carbonyl compounds with silanes. CO_2, a more challenging substrate, can also be reduced by $HSiEt_3$ in the presence of dicationic Lewis acids.

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Pyridine dissociation energy measurement in organogold complexes and its application in reactivity and catalysis studies

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Keywords: organogold, dissociation energy, π-backdonation, catalysis

Through their steric and electronic effects, ligands play a crucial role in inorganic chemistry, with direct implications in organometallic catalysis, biomedicine or material science. Thus, methodologies have been developed to compare ligands with each other in order to rank their donating abilities to rationalize experimental results. Within this context, Tollmann developed a methodology using metal-CO complexes to rank donating abilities of phosphines and NHC ligands by measuring the vibration frequency of the CO ligands by IR spectroscopy.[1] Later, Huynh used a similar methodology to rank ligands by measuring the ^{13}C chemical shift of the carbenic carbon in metal-NHC complexes.[2] Our group has developed a methodology based on mass spectrometry techniques ranking the donating ability of phosphine and NHC ligands by measuring the bond dissociation energy of a CO ligand in [L-Au-CO]+ complexes.[3] However, all these approaches suffer from the same limitations: the need to use model complexes potentially different from the ones used in the real context and the lack of absolute measurement of the bond dissociation energy (BDE).

We present here the first absolute measurement of the BDE of pyridine ligands in a panel of 33 new organogold(III) complexes of the types [(C^C)Au(L)(pyr)]+ (L = PPh3 or NHC) and [(C^N^C)Au(pyr)]+ containing variously substituted pyridine ligands. The methodology relies on the observation of the dissociation of the pyridines upon collision with a gas by mass spectrometry. Experimental BDE values were validated by comparison with theoretical values obtained by calculations. This new descriptor appeared more reliable to discuss Au-pyridine bond strength than classical ones including Au-N bond length obtained by XRD and $\Delta\delta^1$H NMR. We applied this new descriptor for the investigation of π-backdonation in the studied Au(III) complexes and for the rationalization of their catalytic properties in an intramolecular hydroarylation reaction of alkyne.[4]

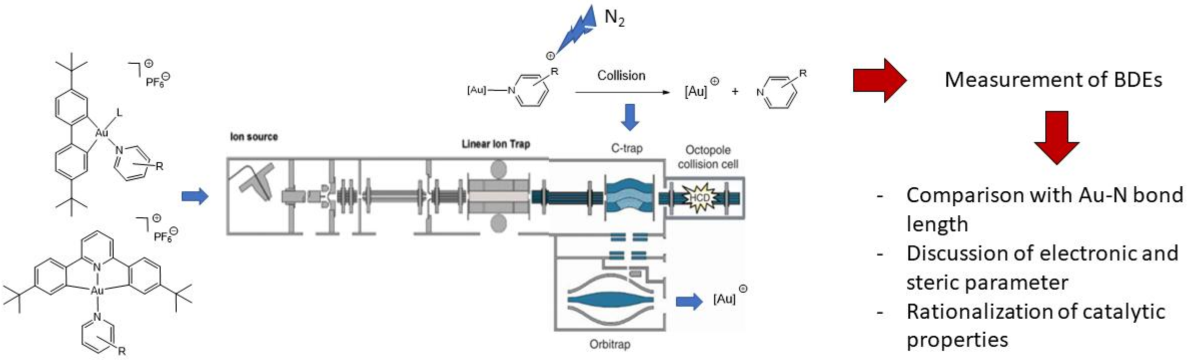

Figure 1. Scheme of the experimental setup and summary of the results

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$M(NMe_2)_4$ (M = Ti, V) and tert-Butylamine reaction: simple reagents, … but great complexity and diversity in the products formed

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Keywords: Titanium; Vanadium; Imido complexes

In the last few decades, imido complexes of transition metals (TM) have attracted growing interest due to their implication in many stoichiometric or catalytic processes, as well as for their potential use as precursors to inorganic materials (metal nitrides). Imido complexes are now accessible through a variety of synthetic protocols, depending on the metal studied and the imido function needed. Despite the fact that many imido complexes of TM have been prepared (and in particular for early and mid-TM), there is still a need to discover new imido functions with particular properties or reactivity, and new imido precursors for enhanced catalytic activity or new applications. Some years ago, we initiated a research program to investigate the general synthesis of early TM terminal or bridging imido complexes from commercially available $M(NMe_2)_4$ (M = Ti, V) and primary amines RNH_2.[1] We reported that, in the presence of trimethylchlorosilane, the important synthons $M(=NR)Cl_2(NHMe_2)_2$ are available in a very convenient one-pot reaction, and with the possibility to generate a great diversity of terminal imido complexes. Other "base-free" imido precursors of the type "$\{M(NR)Cl_2\}_n$" could also be obtained by changing the experimental protocol.[2] More recently, while preparing the tert-butyl-imido analogue of such V-phosphine adducts, $V(=N^t Bu)Cl_2(PR_3)_2$ that were used as catalyst for olefin polymerization,[3] we noticed that the isolation of a well-defined corresponding intermediate was not as straightforward as for the aryl-imido Ti- or V-congeners. This observation incited us to study in more detail the reactions leading potentially to the formation of such elusive ^{t}Bu-imido species. Herein we provide our observations on the reaction of $V(NMe_2)_4$ with $^tBuNH_2$ followed by treatment with Me_3SiCl, as well as chemical insight into the same reaction conducted with $Ti(NMe_2)_4$ leading to mixture of diverse terminal or bridging imido multinuclear species.

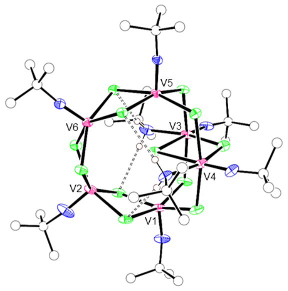

Figure 1: One example of a V-complex that was obtained.

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INVERTED LIGAND FIELD AND EFFECTS ON Au(III) AND Pt(IV) REACTIVITY

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Keywords: electronic structure; inverted ligand field; oxidative addition; gold(III); platinum(IV)

Gold and platinum complexes are nowadays ubiquitous in chemistry in view of their application in many fields such as catalysis, nanomedicine, sensors *etc*.[1] In any case, many aspects of the reactivity of gold and platinum, especially in the highest oxidation states (III for gold and IV for platinum), remain still unclear and require a more detailed attention.[2]

Herein, we present a revised analysis of the electronic structure of square planar gold complexes or clusters in the framework of the Inverted Ligand Field (ILF). [3,4] The analysis of the electronic structure (especially on the Lowest Unoccupied Molecular Orbital, LUMO, in Figure 1) reveales that the metal maintains the d^{10} configuration.[5-7] The effects of the ILF on the reactivity have been also elucidated.

The electronic structure of many octahedral platinum complexes have been also drastically revised especially in combination with electronegative elements such as halogens and chalcogens.[8] The investigation revealed that in most cases the five d platinum orbitals are invariably full, thus the empty antibonding orbitals, usually localized on the metal, are mainly centered on the ligands. This outcomesuggests a questionable assignment of oxidation state IV. The analysis supports the occurrence of the ILF in all cases with the only exceptions of the Pt−F and Pt−O bonding. Finally, a revised picture of '*oxidative'* addition of a Se−Cl linkage to a square platinum complex has been proposed.

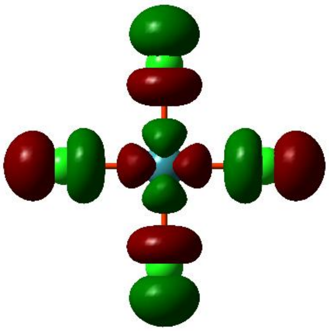

Figure 1. Lowest Unoccupied Molecular Orbital (LUMO) of $AuCl_4^-$.

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A computational insight on the aromatic amino acids conjugation with $[Cp^*Rh(H_2O)_3]^{2+}$ by using the MTD/FMO3 approach.

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Keywords: Metal drugs; $[Cp^*Rh]^{2+}$, FMO3, Pair interaction energies, metadynamics

Rh(III) complexes showed promising pharmacological activities with potential applications in several therapeutic areas [1]. Among these complexes, the $[Cp^*Rh(H_2O)_3]^{2+}$ cationic complex was found to be able to react specifically with Tyr amino acid side chain of G-protein-coupled receptor (GPCR) peptides by means of highly chemoselective bioconjugation reaction, at room temperature and at pH 5-6 [2]. In order to deepen the mechanism of this chemoselective conjugation, we studied the ligand exchange reaction between $[Cp^*Rh(H_2O)_3]^{2+}$ and three small molecules, namely p-cresol (pC), 3-methylimidazole (3MI) and toluene (T), selected as mimetic of aromatic side chains of Tyr, Trp and Phe, respectively, by using metadynamics (MTD) [3] and the *ab initio* fragment molecular orbital (FMO) method [4]. Within the FMO framework, the complexes were split in fragments (Figure 1A) and the total energy was then computed as a function of the pair interaction energies (PIEs). The MTD/FMO approach allowed us to characterize and monitor how the conjugation reactions evolve (Figure 1B), by giving a new insight on this high chemoselective process and suggesting novel potential applications of Rh(III) metal drugs containing the $[Cp^*Rh]^{2+}$ scaffold. Our results indicated that the high selectivity for Tyr side chain might be related to phenol OH group, able to affect both thermodynamics and kinetics of ligand exchange reactions, due to its ability to act as both H bond acceptor and donor. This information can be used to design new metal drugs containing the $[Cp^*Rh]^{2+}$ scaffold targeting specifically Tyr residues involved in biological/pathological processes, such as Tyr-kinase dependent phosphorylation and protein-protein interactions.

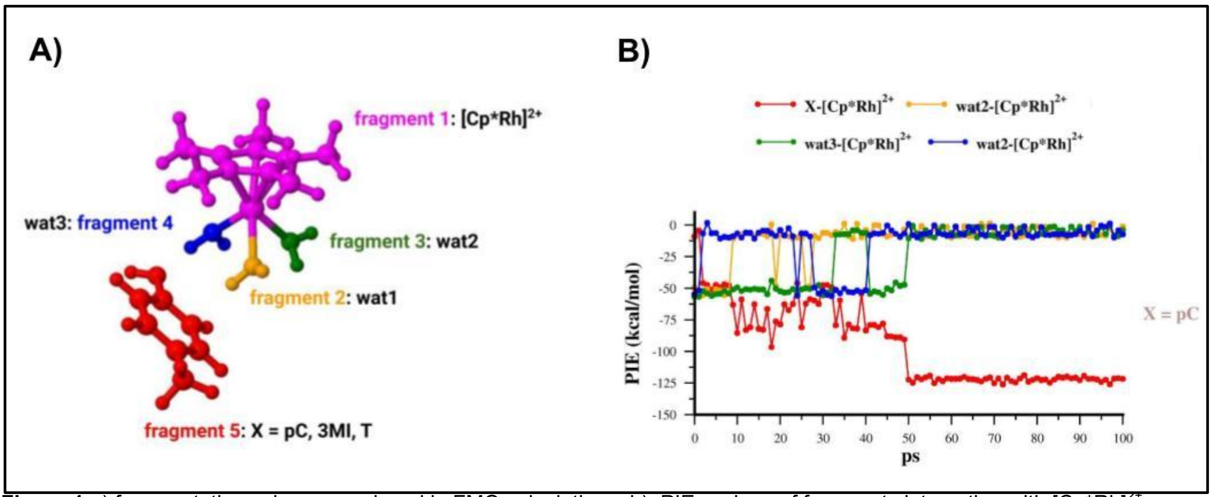

Figure 1 a) fragmentation scheme employed in FMO calculations; b) PIEs values of fragments interacting with $[Cp^*Rh]^{2+}$ computed for the sampled structures of MTD run.

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Metal organic frameworks based on metal-bis(dithiolene) ligands

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Keywords: metal-bis(dithiolene); conductivity; MOF; functional materials; porosity.

Text: The preparation of electroactive ligands bearing an extended π-core to build self-assembled structures such as Metal-Organic Frameworks (MOFs, also known as porous coordination polymers: crystalline porous materials made of metal ions/clusters and organic linkers,[1] is a very active field for the last decade. Unfortunately, most of these networks are not conductive because of their huge HOMO-LUMO gap and/or weak orbital overlap between the ligand and the inorganic part.[2] Well-known electroactive building blocks such as tetrathiafulvalene-tetrathiabenzoate (TTFTB) have been largely explored.[3] This ligand was associated with Zn(II) to produce a MOF that displays 5 Å diameter cylindrical pores, an overall 39% pore volume, and a conductivity of $1.34*10^{-7}$ S/cm. An analogous MOF was prepared using the Ni(II)-bisdithiolene-tetrabenzoate (Ni(II)-BDTTB) as a linker; this MOF shown interesting properties as a glucose sensor but its conductivity has not been yet studied. Metal-bis(dithiolene) complexes show good conducting properties, e.g. metal-bis(maleonitriledithiolate) ($M(mnt)_2$) respectively showing a conductivity of 40 S/cm and 9 S/cm for the Ni(II) and Au(III) dithiophene-TTF salt.[4] Ni(1,3-dithiole-2-thione-4,5-dithiolate)2 shows a superconducting behavior at 5 K as its tetramethylammonium salt.[5] Using such linkers within MOF structures should therefore provide porous materials with good conducting properties. These salts are known to yield neutral open-shell conductors, in aprticular with Au(III), which is of the outmost interest for the synthesis of conductive porous materials as no inner counter-ion is required such as for TTF.

This project is focused on the use of Ni(II) and Au(III)-bis(dithiolene) complexes as metalla-ligands bearing carboxylates or pyridines coordination unit to prepare closed-shell or open-shell neutral networks exhibiting good electrical conductivity.(**Figure 1**)

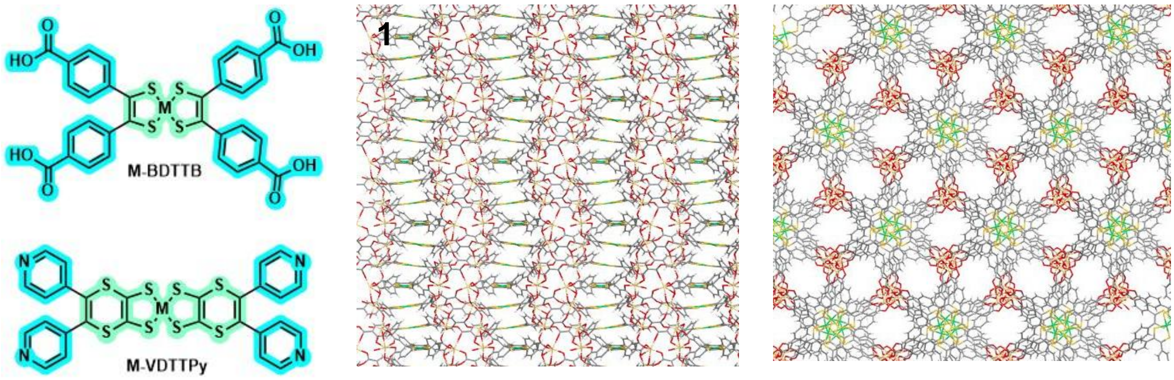

Figure 1 Ligands structures (left) and X-Ray structure for Ni(II)-BDTTB-Cd(II) MOF (right) : (1) a axis view (2) c axis view

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INTERFACIAL COORDINATION CHEMISTRY OF SINGLE TRANSITION METAL IONS ON SURFACES

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Keywords: Interfacial coordination chemistry; open-shell metals; magnetic spectroscopy

Text: Atomically dispersed species are part of the emerging class of heterogeneous catalysts known as single-atom catalysts (SACs). Their catalytic properties can be crucially modulated and even enhanced by the chemical interaction with a solid support. This effect, known as electronic metal–support interaction, encompasses charge transfer, orbital overlap, coordination structure, etc., in other words, all the crucial features of the chemical bond. Atomic dispersion ensures maximum atom utilization and uniform active sites, while the nature of the chemical interaction between the metal and the oxide surface modulates the catalytic activity of the metal active site by tuning the energy of the frontier orbitals. [1]

Many spectroscopic techniques are able to inform on the geometric and electronic structure of isolated single metal ion sites, but either they yield information averaged over the bulk or they lack description of the intimate features of chemical bonding, which include covalency, ionicity, electron and spin delocalization. All of these can be recovered at once by measuring the magnetic interactions between open-shell metals and the surrounding nuclei with Electron Paramagnetic Resonance (EPR) spectroscopy.

In this talk we will present our efforts in combining magnetic spectroscopy data to elucidate the coordination chemistry of interfacial complexes spontaneously formed when a transition metal ion interacts with an inorganic solid support. [1,2,3]

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Thermodynamic study of shaping in solution of lanthanide-based coordination polymers

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Keywords: Lanthanides, coordination polymers, thermodynamics, configurational entropy

Text:

Over the past few decades, there has been significant research on lanthanide-based coordination polymers due to their interesting optical properties, making them highly relevant for various applications, such as anti-counterfeiting taggants.[1] These polymers consist of metallic ions connected by organic ligands such as 1,4-benzene-dicarboxylic acid (also known as terephthalic acid). They can form mono-, bi-, or three-dimensional networks. Lanthanides are commonly considered as the largest family of chemically similar elements, enabling the creation of microcrystalline powders incorporating multiple lanthanide ions.

When these ions are randomly dispersed among the metallic sites, the resulting coordination polymer forms a perfect "molecular alloy".[2] Alternatively, with organized distribution, core-shell particles can be engineered. Previous studies have shown that achieving epitaxial growth is challenging due to the various unpredictable phenomena occurring in solution during syntheses (Figure 1).[3] In this study, we present a thermodynamic analysis of lanthanide-based coordination polymers syntheses using terephthalic acid as a ligand. Our aim is to understand the synthesis intricacies, particularly concerning the formation of future core-shell particles and explore strategies to master their production.[4]

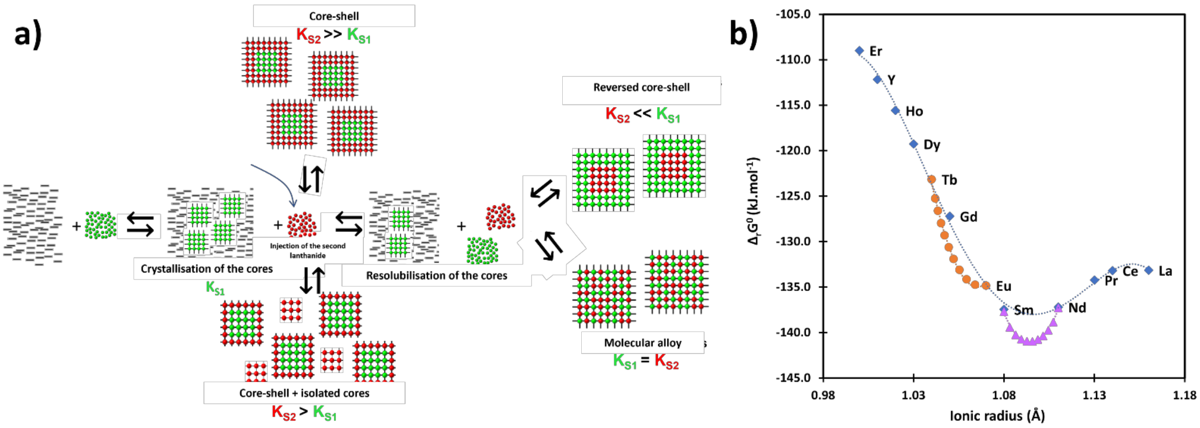

Figure 1 : a) Possible equilibria in solution during syntheses of core-shell particles; b) Reactional free enthalpies of homo- and hetero-nuclear coordination polymers with terephthalic acid as ligand.

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NIR-CPL active Yb(III) complexes bearing both central and axial chirality

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Keywords: Ytterbium; NIR-CPL; Binol; Lanthanide complexes

A growing interest is rising about NIR emitting Ln(III) complexes because of their potential use in the biological and medical field.[1,2] The use of CPL (Circularly Polarized Luminescence) in the NIR spectral range, could make these species also good candidates as materials for optical fibers [3] or laser systems. [4]

New NIR-CPL active Yb(III) complexes have been synthesized by combining two ligands involving different types of chirality: the central and the axial one. The tetracoordinated ligand N, N'-bis(2-pyridylmethylidene)-1,2-(R,R or S,S) cyclohexanediamine (L), thanks to its two stereocenters, shows central chirality, while the enantiomeric species 1,1'-binaphthyl-2,2'-diol (BINOL), exhibit axial chirality. By reacting these two different ligands with Yb(III), in 1(Yb):1(L):2(BINOL) stoichiometric ratio, we could obtain two couples of enantiomers, diastereoisomers to each other. CPL analysis showed how the axial chirality dominates, in this case, determining the sign of the spectra (Figure 1a and 1b). Furthermore, from the spectroscopic characterization of the complexes, we found thanks to the collection of decay times of the $^2F_{5/2}$ Yb excited state, that the species bearing BINOL R shows a longer lifetime compared to the one bearing BINOL S. This result can find a possible explanation, which is suggested by DFT calculations. Indeed, YbL(*S*-BINOL)$_2$ seems to have a molecule of solvent closer to the metal ion than in the case of YbL(*R*-BINOL)$_2$ (Figure 1c and 1d). As a consequence, the Yb(III) luminescence of the former complex should be more quenched by multiphonon relaxation mechanism (MPR).

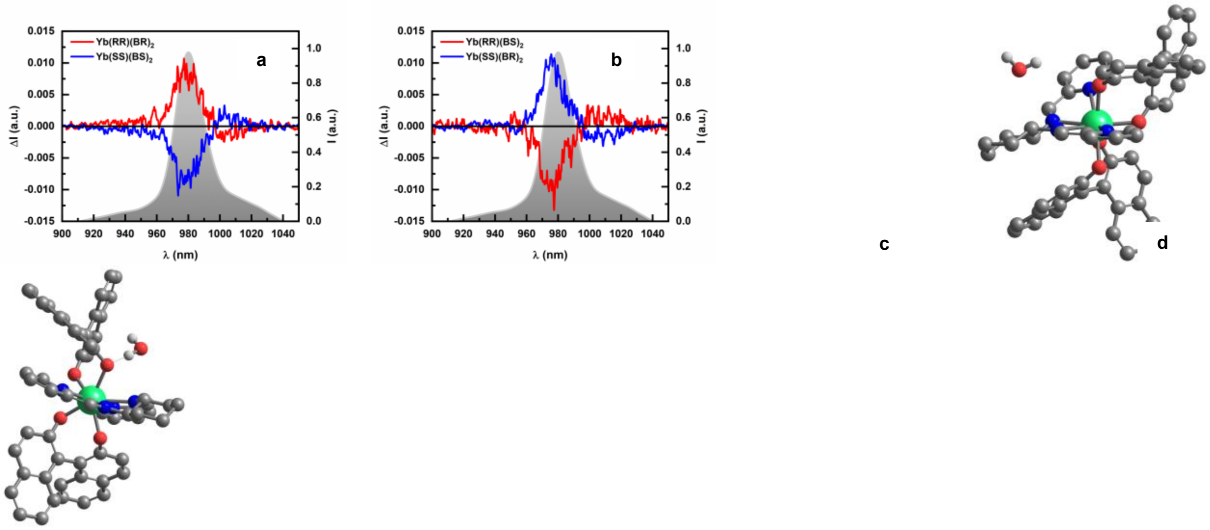

Figure 1 Left: NIR-CPL spectra of 1 mM CD$_3$OD solutions of the two enantiomeric couples of the investigated Yb(III) species: a) [Yb(*R*,*R*-L)(*R*-BINOL)$_2$]Na (red)/[Yb(*S*,*S*-L)(*S*-BINOL)$_2$]Na (blue); b) [Yb(*R*,*R*-L)(*S*-BINOL)$_2$]Na (red)/[Yb(*S*,*S*-L)(*R*-BINOL)$_2$]Na (blue). The normalized total emission for each couple is traced in the background. λ_{ex} = 365 nm. Right: Minimum energy

structures of the isomers (both bearing *R,R*-L) with an additional water molecule (used to model methanol): c) complex with two BINOL R; d) complex with two BINOL S.

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TUNING CHAOTROPICITY: CHAOTROPIC PROPERTIES OF $\{P_2W_{15}Mo_3\}$ FOR RARE EARTH ELEMENT RECOGNITION

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Keywords: polyoxometalates, super-reduction, rare earth elements, chaotropic behavior

Polyoxometalates (POMs) are of interest for the study of their electrochemical properties due to their capability to store a vast number of electrons. The super-reduction processes and the corresponding structures are, however, less explored.[1]
In this communication, we will first present the super-reduction process of $[P_2W_{15}Mo_3O_{62}]^{6-}$ Dawson structure (notated $\{P_2W_{15}Mo_3\}$-0) and its six-electron reduced version $\{P_2W_{15}Mo_3\}$-VI'. Both species exhibit stability under ambient conditions, making them ideal candidates to investigate chemical property changes associated with the reduction process. The $\{P_2W_{15}Mo_3\}$-VI' species features three Mo-Mo bonds in the $\{Mo_3\}$ triad and terminal water molecules on the Mo sites, verified by single-crystal X-ray diffraction (SC-XRD) and extended X-ray absorption fine structure (EXAFS) measurements. This structural insight may significantly impact the originally super-chaotropic properties of the POM, influencing its solution behavior. [2] To test this hypothesis, we investigated the ion-pair interactions of our POMs with rare earth elements (REE) using multinuclear nuclear magnetic resonance techniques (^{31}P, ^{95}Mo, and ^{183}W NMR) for solution studies and SC-XRD for deciphering the interactions in the solid-state. In this communication, we will also present this set of data revealing that super-reduced POM $\{P_2W_{15}Mo_3\}$-VI' exhibits significantly stronger interactions compared to $\{P_2W_{15}Mo_3\}$-0 while both compounds exhibit the same anionic charge. Furthermore, we will evidence that the measurements of unusual NMR nuclei (^{95}Mo and ^{183}W) represent an attractive method to probe the ion-pairing of POMs.

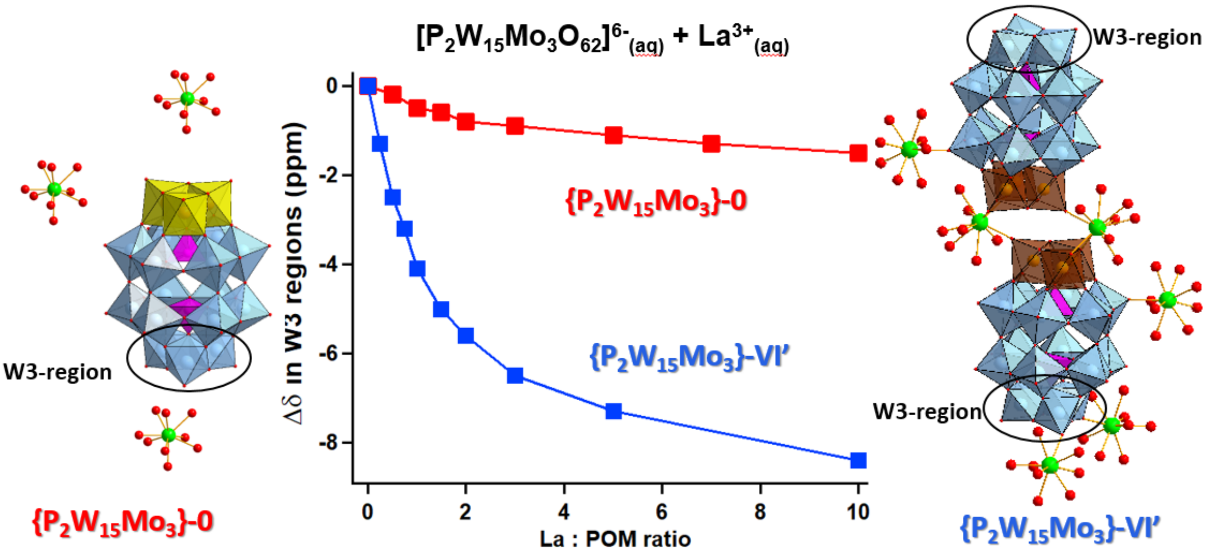

Figure 1 Comparison of the relative chemical shifts observed in ^{183}W-NMR during titration experiments with La^{3+} ions. The oxidized and reduced form of $\{P_2W_{15}Mo_3\}$ is compared based on their W3 regions. Color code: light-blue polyhedra, W^{VI}; yellow polyhedra, Mo^{VI}; brown polyhedra, Mo^{IV}; pink polyhedral, P; red spheres, O; green spheres, La.

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Zinc catalysts for the synthesis and chemical depolymerization of aliphatic polyesters; a contribute to the circular economy of bioplastics

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Keywords: chemical recycling; bioplastic, zinc catalysts

The oil derived plastics offer the advantages of high durability and low costs. Nevertheless, these properties represent a grave drawback at end-of-life, as every year 50 million tons of plastic waste are retained into landfills or spread into the environment.[1,2] The severe consequences of plastic pollution require the introduction of new strategies and materials to convert the current linear economy of plastics to a circular model.

In this context, aliphatic polyesters, such as polylactide (PLA), offer great opportunities because they combine good mechanical properties with biodegradability.

Although these features design a green profile for PLA, its current production and waste management show some weaknesses in terms of sustainability. The catalyst for the industrial production of PLA is classified as a toxic compound, while its recycling is not still planned. [3]

The chemical recycling of PLA, with production of platform molecules, is a desirable strategy to implement a circular model economy in which a material can be recycled virtually ad infinitum.

Herein we report the synthesis of new and easy-to-obtain zinc complexes, which revealed to be exceptionally efficient to promote both the synthesis and the chemical degradation of PLA.

These catalysts showed excellent performances Ring Opening Polymerization (ROP) of lactide even when the process was carried out under industrial conditions.

The same complexes also showed high efficiency in the chemical degradation of PLA via alcoholysis.

Both processes were conducted in full sustainability, guaranteed by the non-toxic nature of zinc and by environmentally friendly reaction conditions, such as the absence of solvent and a low catalyst loading.

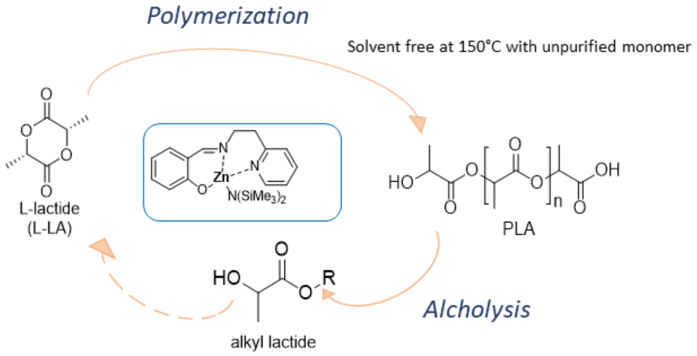

Figure 1 Circular model for synthesis and chemical recycling of polylactide

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POSTER

CONTRIBUTIONS

Cobaltacycles for C-H bond activation under oxidative conditions

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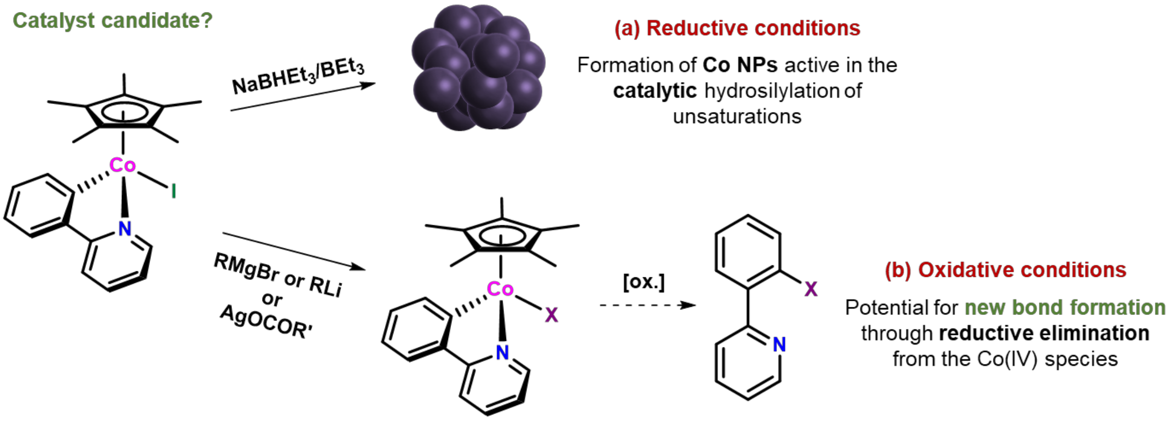
Keywords: Cobalt; C-H bond activation; catalysis; oxidation; reductive elimination

Cobalt metallacycles are very powerful candidates for C-H bond functionalisation chemistry, especially due to the interesting parallels that can be drawn from the chemistry of Ir and Rh, all while providing valuable insights into the chemistry of other 3d row metals. Still, understanding the unique set of properties and reactivity of these cobalt-base complexes, as well as their reaction mechanisms, poses an important challenge. It is thus crucial to carry out in-depth studies of the behaviour of these Co-complexes under different conditions. One example of this is their surprising transformation into nanoparticles in the presence of reductive hydride sources under catalysis conditions, capable of hydrosilylating aromatic carbonyls and nitriles, which is not observed for the Ir equivalent.[1] In parallel, under oxidative conditions, once in their Co(IV) form, CoCp*(2-phpy)X complexes show capricious behaviours depending on the nature of the X-ligand (halide, carboxylate, alkyl, aryl, etc.). Thus, a small library of new cobaltacycles was synthesised by varying the X-ligand, using known and new reaction pathways, notably involving RMgBr and RLi or silver salts. Three main pathways are observed experimentally after oxidation: (i) the reductive elimination of functionalized 2-phenylpyridine (2-*phpy*-X), (ii) the cyclocondensation of the non-innocent Cp* with 2-*phpy* or (iii) the decomposition by 2-*phpy*H hydrodemetalation.[2] Therefore, the question that arises is how can the reactivity be predicted in order to design a system capable of achieving the formation of new C-C bonds: the innovative approach of using the independent gradient model/intrinsic bond strength index (IGM/IBSI) method as a predictive tool was introduced, locally evaluating non-covalent interactions between reactive centres of the complex as a function of the X ligand, successfully and reliably predicting the experimental reaction outcomes.[2]



(a) Reductive conditions

Formation of **Co NPs** active in the **catalytic** hydrosilylation of unsaturations

(b) Oxidative conditions

Potential for **new bond formation** through **reductive elimination** from the Co(IV) species

Figure 1 Observed reactivities of [CoCp*(2-*phpy*)I] under (a) reductive conditions and (b) oxidative conditions

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New Weakly Coordinating Anions of type $[In(OTeF_5)_4(THF)_2]^-$ and $[In(OTeF_5)_6]^{3-}$

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Keywords: Weakly Coordinating Anion; Teflic acid; Indium salt; Coordination Chemestry.

Recently, the reactivity of vinyl cations has been exploited to design new reactions. Our subsequent research has shown the interest in using Weakly Coordinating Anion (WCAs) such as [Al(ORF)4]- (RF = C(CF3)3) to promote bimolecular vinylation of aromatics via vinyl cation intermediate. (Fig. 1)[1] However, the generation of vinyl cations that are sufficiently electrophilic through heterolytic Csp^2-X (X = Cl, Br, F, OSO_2R …) cleavage remains a very challenging task. We assume that using other WCAs which exhibit even weaker coordinating properties than those used previously, we can improve the reactivity of vinyl cations and overcome the current limitations. Recently, Riedel's team reported the synthesis and characterization of species of type $[Y][M(OTeF_5)_4]$,[2] (M = Al and Ga; Y = Li, K, Na, Ag, H, Ph_3C, Ph_4P, C_9H_{13}, Me_2C ...).

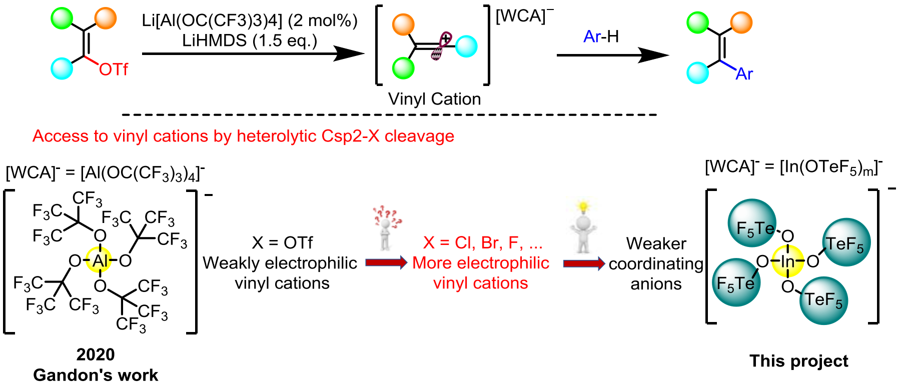
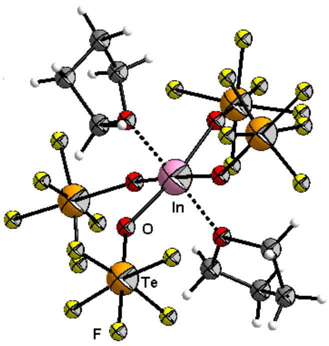
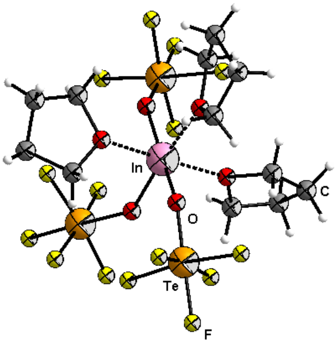
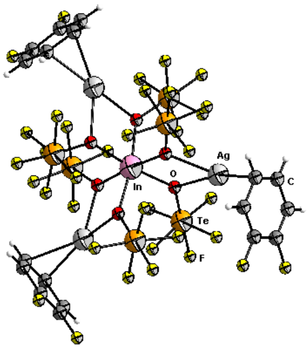


Figure 1 : Bimolecular vinylation reaction via vinyl cation







To extend the repertoire of WCAs, we were interested in indium and more particularly on the synthesis of unprecedented $[Y][In(OTeF_5)_4(THF)_2]$ (Y = Ag, Ph_3C, $(Ph_3PAu)_2Cl$, Ph_4P) as well as $Ag_3[In(OteF_5)_6]$. Here we will present the synthesis and the spectroscopic characterization as well as the X-ray structures of salts of WCAs $[In(OTeF_5)_4(THF)_2]^-$ and $[In(OTeF_5)_6]^{3-}$.

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

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Keywords: NIR emitters; Cu(I) complexes; bimetallic complexes; light-emitting devices

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.[1] 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.[2] 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.[3,4] 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^P)(N^N–N^N)Cu(P^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 790 nm and X-ray analysis reveals two interligand π–π-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 leads to the successfully fabrication of the fist example 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%.[5]

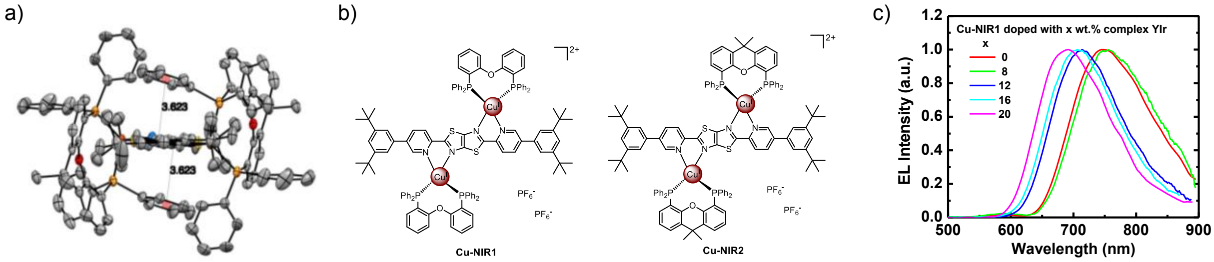

Figure 1 a) ORTEP diagram of compound Cu-NIR2 b) Cu-NIR1 and Cu-NIR2 structures c) EL spectra of the LECs based on complexes Cu-NIR1 under different host:guest doping ratio.

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A new water-soluble supramolecular complex for O_2 reduction

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Keywords: Cytochrome c oxidase, hemoprotein model, supramolecular complex, dioxygen reduction

Cytochrome c oxidase (CcO) catalyses the reduction of dioxygen (O_2) to water via a four-electron pathway by using a heme/copper hetero-binuclear active site. This finely tuned reactivity is only possible because of the high degree of sophistication of the peptide structure that surrounds the “active” metallo-porphyrin unit. In these molecular scaffolds, the polypeptide envelope controls the solubility, the access of exogenous ligands, and the reactivity of the central heme. Due to the extreme sophistication of these natural systems, the design of functional and structural hemoprotein models has always been a synthetic challenge.

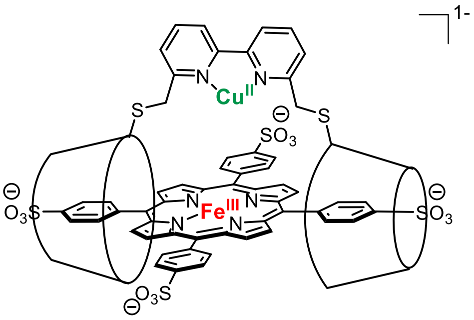

Figure 1. Molecular structure of **Fe^{III}TPPS/Cu^{II}Bipy-CD_2** supramolecular complex

In collaboration with the group of Prof. Kitagishi, specialized in the synthesis and studies of water-soluble hemoproteins models [1], a new functional model of CcO **Fe^{III}TPPS/Cu^{II}Bipy-CD_2** was prepared for O_2 reduction (Figure 1). This model combines an iron tetraphenylporphyrin sulfonate **Fe^{III}TPPS**, and a cyclodextrin dimer with a copper-binding bipyridine linker **Cu^{II}Bipy-CD_2**. The latter provides water solubility and mimics a globular environment. This work aims to study O_2 binding and reactivity of this new model in aqueous medium.

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TAILORED SYNTHESIS OF MIXED-LIGAND MOLECULAR GOLD NANOCLUSTERS

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Keywords: Gold; Nanoclusters; N-heterocyclic carbenes; Luminescence; Bioactivity

We report on a new method to synthesize molecular gold nanoclusters (AuNCs) stabilized by a mixed ligand sphere composed of PPh_3 and di-N-heterocyclic carbene (di-NHC) ligands. The method is based on the reaction of a preformed, PPh_3-stabilized AuNC with dinuclear di-NHC gold(I) complexes and enables the production and isolation of clusters with different nuclearity and ligand stoichiometry, depending on the di-NHC properties and reaction conditions.[1] In particular, the interaction of di-NHC gold(I) complexes, with general formula $[(\text{di-NHC})Au_2Cl_2]$ with well-known $[Au_{11}(PPh_3)_8Cl_2]Cl$ clusters provides three new classes of AuNCs through a controllable reaction sequence. The synthesis involves an initial ligand metathesis reaction to produce $[Au_{11}(\text{di-NHC})(PPh_3)_6Cl_2]^+$ (type **1** clusters), followed by a thermally induced rearrangement/metal complex addition with the formation of Au_{13} clusters $[Au_{13}(\text{di-NHC})_2(PPh_3)_4Cl_4]^+$ (type **2** clusters). Finally, an additional metathesis process yields $[Au_{13}(\text{di-NHC})_3(PPh_3)_3Cl_3]^{2+}$ (type **3** clusters). The electronic and steric properties of the employed di-NHC ligand affect the product distribution, leading to the isolation and full characterization of different clusters as the main product. A type **3** cluster (Figure 1) has been also structurally characterized. Type **3** clusters were found to be strongly emissive in solution, reaching quantum yields among the highest ever reported for this kind of molecules.

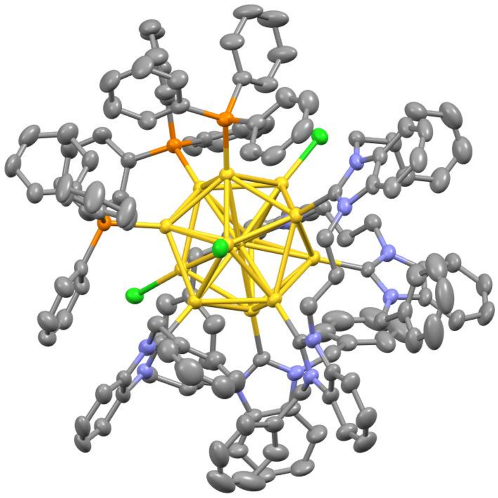

Figure 1 Crystal structure of a type **3** cluster $[Au_{13}(\text{di-NHC})_3(PPh_3)_3Cl_3]^{2+}$

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Constrained HBED derivatives: a potential class of chelating agents for clinical imaging applications

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Keywords: HBED; gallium; manganese; PET.

Positron Emission Tomography (PET) is a widely used diagnostic technique that relies on specific biomolecules labeled with positron (β^+)-emitting isotopes. ^{68}Ga is a leading choice for PET due to its advantageous features ($t_{1/2}$ = 1.13 h, $I_{\beta+}$ = 89%, $E_{\beta+\ avg}$ = 830 keV). Moreover, the possibility to exploit the same metal ion to perform more than one imaging technique is intriguing and Mn^{2+} seems a promising candidate. It represents a bimodal imaging agent for PET (^{52g}Mn, $t_{1/2}$ = 5.6 days, $I_{\beta+}$ = 29%, $E_{\beta+}$ = 575 keV) and MRI (Mn^{2+}, S = $^5/_2$ h.s., slow electronic relaxation, and rapid H_2O exchange rate). To guarantee that the emitted radiation is solely directed in the proximity of the tumor site, the metal must be tightly coordinated to the tumor-targeting molecule through a chelating agent. This chelator must form a highly thermodynamically stable and kinetically inert complex with the metal.

Macrocyclic chelators (eg. DOTA) generally exhibit slow kinetics of metal complexation that requires harsh radiolabeling conditions (high temperature) incompatible with most biomolecules used as targeting vectors. Acyclic chelators offer an intriguing alternative. Their complexes generally exhibit slightly lower thermodynamic stability compared to macrocyclic counterpart, but complexation kinetics are usually significantly faster and require mild conditions.

Among them, HBED[1] stands out as one of the most effective acyclic chelator for ^{68}Ga, displaying a high thermodynamic stability ($\log K_{ML}$ = 38.5 - 39.6). The potential N_2O_4 octahedral coordinating environment can fulfil the necessary characteristics for a successful Ga^{3+} complexation.

In the present study, a new constrained HBED-based chelator has been synthesized: N,N′-Di(2-HydroxyBenzyl)-(1,2-Cyclohexanediamine)-N,N′-Diacetic acid (**HBCD**, see *Figure 1*, left) and thoroughly characterized. The idea was to constrain the HBED structure to enhance the stability of the formed metal complexes. As first study, Ga^{3+} complexation in D_2O and MeOD-*d₄* was easily performed at room temperature and followed via NMR, revealing the probable formation of different geometric isomers (as for HBED[2]). In D_2O the equilibrium was shifted to a major species by simply adjusting the pH at ~7-8 (see *Figure 1*, right). Ga^{3+} complexation was confirmed also via LC-MS and UV-Vis titration of HBCD with $Ga(NO_3)_3$ was carried out.

As next steps, the coordination of other small hard metal ions (Fe^{3+}, Cu^{2+} and especially Mn^{2+}) will be studied. The structure of HBCD will be then modified with different ligand pendants to tune the coordination feature of the ligands and the rigidity of the system. The insertion of one functional group for the conjugation to a targeting vector will be explored.

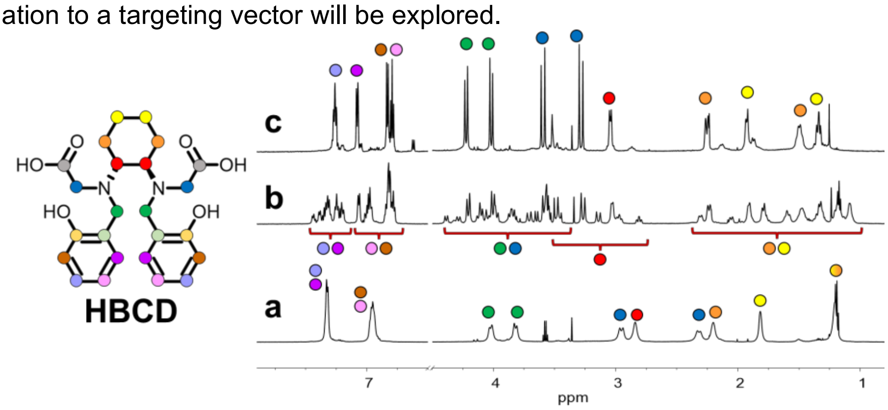

Figure 1 Structures of HBED (left) and ^{1}H NMR spectra (right) in D_2O (600 MHz) of HBCD at pH 4.58 (a), HBCD-Ga complex at pH 1.45 (b), HBCD-Ga complex at pH between 7 and 8 (c).

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Iron-based complexes: modulating their chemical structure for understanding their cellular fate with photoacoustic imaging

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Keywords: Iron complexes, N-heterocyclic carbenes, optical imaging, cancer

Text: Polypridine-iron(II) complexes displayed anticancer properties at nanomolar concentration and high biosafety, highlighting their therapeutic potential.[1] Nevertheless, their stability in a biological environment is debated because such complexes are non-emissive and their cellular accumulation and pharmacokinetics cannot be explored by standard fluorescence approach. The light absorption and non-radiative relaxation of iron(II) complexes however make them trackable using the emergent photoacoustic imaging (PA),[2] an interesting alternative that relies on the 'light-in sound-out principle', *i.e.* photoactivation of an agent capable of converting the absorbed light into heat for thermal expansion of its surroundings and acoustic waves production.[3] Therefore, we synthesized a family of polypridine-iron(II) complexes and their analogs bearing far more σ-donating N-heterocyclic carbene (NHC) ligands, aiming at enhancing the stability of the corresponding complexes and exploring their effects on the therapeutic properties of iron(II) complexes. We discuss the effects of polypridine or NHC ligands on the synthesis, activity in PA imaging, stability and anticancer effects of the corresponding iron(II) complexes.[4]

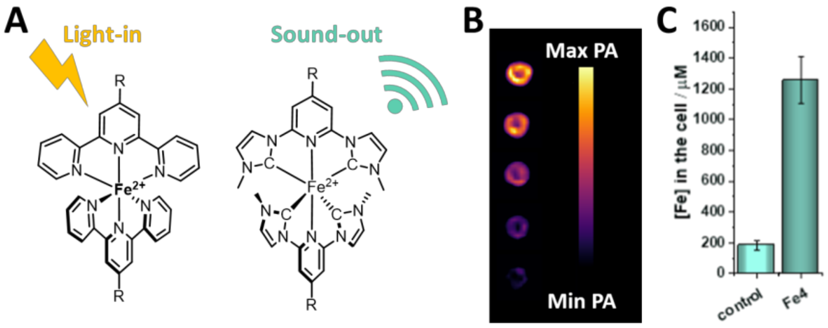

Figure 1 A) General design of iron(II) complexes, their B) photoacoustic imaging and C) cellular uptake by cancer cells.

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Intercomparison study of DGT devices with dihydroxamate-based binding gels for uranium(VI) sampling in freshwater

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Keywords: DGT samplers, resin grafting, dihydroxamic ligands, uranyl binding

Mining activities, production and use of nuclear fuel, processing of spent fuel and storage of nuclear wastes may lead to the release of uranium into the environment, its transfer between the different compartments of the biosphere, and the ultimate contamination of trophic chains.[1] Nowadays, the monitoring of contaminated sites requires new breakthroughs in analytical chemistry in order to assess in detail the impact and bioavailability of actinides discharged into aquatic environments. In that respect, Diffusion Gradient in Thin films (DGT) devices are particularly attractive tools for the passive sampling of various contaminants in aquatic environments or sediments.

Unfortunately, the most frequently used and commercially available binding gels for uranium, namely the Chelex-100® ion-exchange resin or the TiO_2-based Metsorb® material, behave poorly in carbonate-rich, hard fresh- or seawaters.[2,3] To overcome these limitations, we relied on a biomimetic approach for designing efficient pincer-like UO_2^{2+} chelators, considering dihydroxamic siderophores like schizokinen or rhodotorulic acid, known for their high binding affinity for metal ions (Fe^{3+}) in environmental media.[4] These siderophores and our abiotic ligands bear two terminal hydroxamate bidentate groups able to coordinate the uranyl cation in its equatorial plane (Figure 1).[5] Equilibrium constants for complex formation with UO_2^{2+}, and interfering species Ca^{2+}, and Mg^{2+} were determined by potentiometry. High affinity for the former and selectivity with respect to the two latter interfering species prompt us to graft covalently one of these binders on a hydrophilic organic resin (Sephadex®), which was then incorporated in an agarose binding gel.

Performances of the DGT samplers thus designed to accumulate uranium(VI) in natural fresh water will be presented and compared to the experimental results obtained for two other resins, Chelex-100® and Metsorb®. These validation tests were performed in the laboratory, using synthetic seawater spiked with uranium.

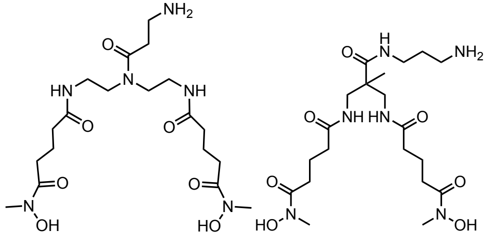

Figure 1. Dihydroxamic ligands used for grafting on a hydrophilic resin

Acknowledgements: This work has been supported by IRSN, the ANR (French National Research Agency) grant n° ANR-17-CE08-0053 (PLUTON project), and the French program NEEDS Environnement (CNRS). The Conseil Regional de Bourgogne Franche-Comté (T.F.), the Conseil Regional de Bourgogne (O.F.), and the EU program FEDER are also acknowledged for granting PhD fellowships.

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Cobalt, Iron and Nickel Complexes Bearing Iminophosphorane Ligands as Catalyst for the Hydrosilylation of Carbonyles

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Keywords: non-noble transition metal complexes, iminophosphorane ligands, hydrosilylation

Text: Nowadays, rare-earth metals are widely used in industry for homogeneous catalytic processes, especially Pt and Pd, despite their high cost and low abundance on earth. The actual tendency, regarding environmental challenges, is to replace these metals with non-noble transition metals. Iron, cobalt and nickel are the three metals belonging to the same column of the periodic table as industrially used metals such as ruthenium, rhodium and palladium. They offer advantages like lower costs and environmental sustainability. Combining these metals with electron rich ligands such as NHC (*N*-heterocyclic carbene) has already led to interesting performances in catalysis: cobalt derivatives have been used, for example, for alkene hydroboration[1] and transfer hydrogenation of C=O and C=N bonds,[2] nickel complexes for the of Ar-OR' derivatives[3] and iron ones for the hydrogenation of alkenes[4] or the hydrosilylation of carbonyl derivatives.[5]

In our group we focus on the development and study of iminophosphorane ligands which are electron richer than NHCs. Indeed, the P=N function in these ligands is a strong σ and π donor that can be viewed as the nitrogen analogue of phosphonium ylide. Therefore we were interested in studying Fe, Co, Ni complexed supported by mixed pyridine-iminophosphorane complexes. We will present the different ligands and complexes synthesized and their characterizations. The reactivity of the various complexes will be discussed, and preliminary results concerning the hydrosilylation of acetophenone will be shown, under mild conditions and using small catalytic amounts of complexes.

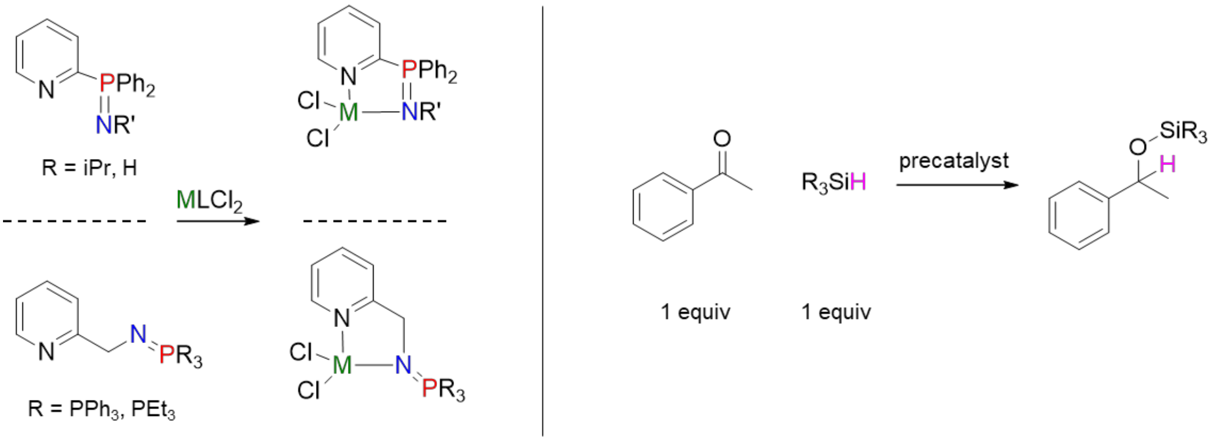

Figure 1 left: Coordination reactions, right: hydrosilylation of acetophenone

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Multidimensional Coordination Polymers based on the alloxazine core: Properties and Applications

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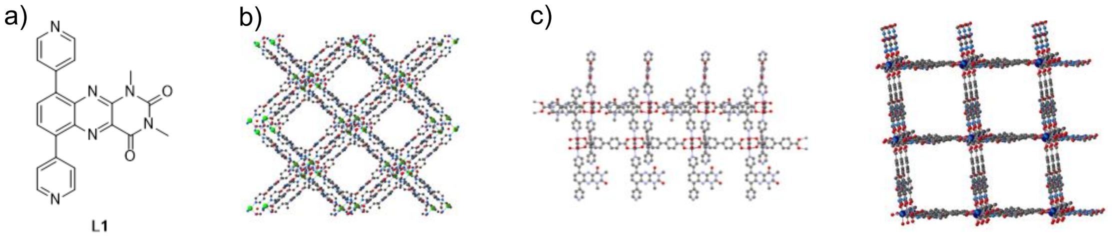
Keywords: Materials, Metal-Organic Frameworks, Redox activity, Alloxazine, Pillared Compounds.

Metal-Organic Frameworks (MOFs) are today well known for their porosity and their properties for adsorbing gas, delivering drugs, or storing energy[1]. A redox effect due to the presence of their metallic center or organic part allow interesting additional properties (conduction, ion intercalation). One of the challenges today in this field is to propose new redox active core centered on their organic part which will contribute to their electron or ionic conductivities in the case of use in energy storage devices.

For these reasons, our laboratory focused on the use of Alloxazines, bio-inspired compounds. Allowing the presence of three stable redox states[2], the alloxazine motif promoted as ligand can be a promising candidate for synthesizing new redox active MOFs.



L1$Co_2(NO_3)_2$ **L1**$BPDC_2Co_2$ **L1**$BPDC_2Co_2$

Figure 1 : a) Redox active organic ligand containing an alloxazine core, b) Coordination polymers based on alloxazine core obtaining by the two component strategy c) MOFs based on alloxazine core obtaining by the three-components strategy (BPDC : 4,4'-BiPhenylDiCarboxylic acid).

We have successfully synthesized a large library of organic ligand favorizing the MOFs formation (**Figure 1a**), based on the alloxazine core. By combining them with a metal salt, mono and bidimensional (**Figure 1b**) coordination polymers containing the alloxazine core have been formed. Then by using a three components strategy[3] (by combining two different organic ligands and one metal salt) we have obtained bi and tridimensional robust Metal Organic Frameworks (**Figure 1c**).

The physico-chemical and electrochemical properties of these new MOFs have been studied in the solid state. They present a certain porosity allowing them to adsorb and release gas. Some of them have been also used as electrode materials in ionic batteries and their electrochemical behavior has been studied.

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A photocatalytic approach for the synthesis of L-shape bicyclic NHC ligands

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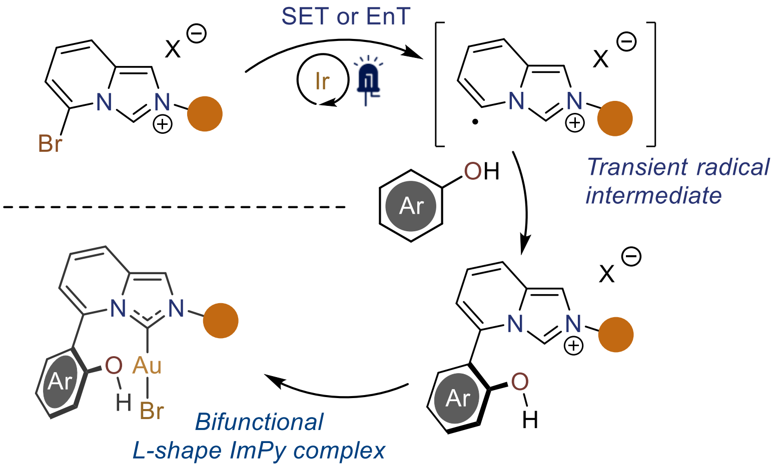
Keywords: Carbenes, photocatalysis, heterocycles, C-C coupling

L-shape *N*-Heterocyclic Carbene (NHC) based on the imidazo[1,5-*a*]pyridine (ImPy) scaffold have recently gained considerable interest as the true carbene ligand analogues of the popular dialkylbiarylphosphines, better known as Buchwald phosphines.[1] Nevertheless, the substitution pattern of ImPy ligands is still rather limited due to synthetic access issues.

In this communication, we present an efficient and versatile visible light photocatalytic strategy to access L-shape bifunctional ImPy ligands laterally-functionalized by a phenol group. Mechanistic investigations supported by density functional theory (DFT) reveal that the excited state of the iridium photocatalyst undergoes either a reductive quenching (SET process) or an energy-transfer quenching (EnT process) depending on the nature of the counterion of the 5-bromoimidazo[1,5-*a*]pyridinium substrate salt. Moreover, the bifunctional character of these new family of L-shape ImPy ligands is demonstrated by the preparation of a gold(I) complex exhibiting a free OH function capable of intermolecular hydrogen bonding.[2]



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ORGANOPLATINUM-BRIDGED CYCLOTRIBENZYLENE DIMERS

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Keywords: alkyne ligands; chirality; copper; cyclophanes; platinum

Text: Cyclotribenzylenes (CTBs)[1,2] are bowl-shaped compounds, generally of C_3 symmetry. They are useful building blocks for making cryptophanes[3] and hemicryptophanes.[4] Originally constructed from covalent bonds, cryptophanes can also be obtained by transition metal-directed self-assembly.[5] CTBs in which the substituent of one phenyl ring differs from those of the two other phenyl rings are asymmetric. Representatives, which combine carbonitrile (-CN) and alkyne (-C_2H) substituents, were synthesized as racemic mixtures and resolved by HPLC on chiral stationary phases. Two of these compounds were used to prepare platinum-bridged CTB dimers, in which Pt(II) is bound to the CTBs via Pt-alkynyl bonds in *cis*-configuration. The organometallic complexes were examined by mass spectrometry and NMR spectroscopy, which indicated that they were obtained as mixtures of diastereoisomers (a *meso* or *syn* form and a pair of chiral *anti* forms) when racemic CTBs were used. Enantiomerically pure complexes were prepared from resolved CTBs, which allowed us to distinguish the NMR signals of the chiral and *meso* forms in the diastereoisomeric mixtures. In certain conditions, the platinum complexes played the role of a pincer π-alkynyl ligand for Cu(I) coming from the copper iodide used as an auxiliary in their preparation.[6] The Cu^+ cations could be easily removed by treatment with sodium cyanide, affording the mononuclear bis-cyclotribenzylene complexes.

In earlier work, we had investigated the self-assembly of metallo-cryptophanes from C_3-symmetric carbonitrile-functionalized CTBs and $[M(dppp)]^{2+}$ complex subunits (M = Pd, Pt; dppp = 1,3-bis(diphenylphosphino)propane).[7] We envisioned that the current platinum-bridged CTB dimers could be used as direct precursors for the preparation of metallo-cryptophanes containing an organometallic bridge. The results of our investigations in this direction will be presented and discussed.[8]

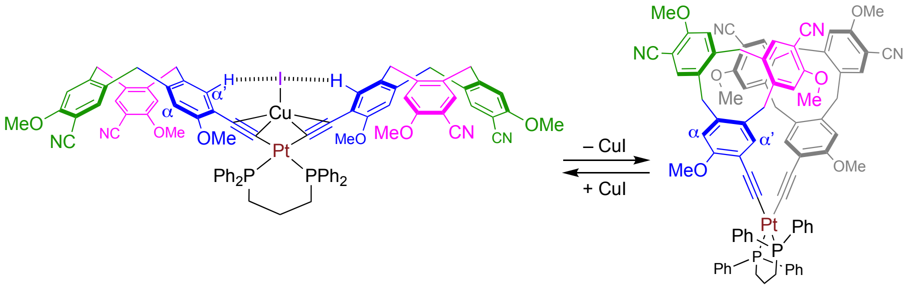

Figure 1 Illustration of the chemical processes involving the platinum-bridged CTB dimers and the resulting conformational changes

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Synthesis and study of redox-active bioinspired molecular units for electron transfer and energy storage

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Keywords: electroactive molecules**,** redox-flow; post-fonctionnalisation; C-H activation; radical species.

Redox flow batteries store energy in scalable reservoirs containing redox-active molecules and are the subject of sustained development in the energy storage sector. In order to store a sufficient quantity of electrons, these molecules must be soluble (ideally in water), thermodynamically and electrochemically stable, and have a low molecular weight.[1]

Flavins (alloxazines/isoalloxazines) are a class of bio-sourced molecules capable of reversibly storing electrons.[2] They can be solubilized in aqueous media and have a low reduction potential.[3] However, they have certain limitations, notably poor cycle stability and a tendency to dimerize.[4] The functionalization of flavins, necessary to modulate their properties through the addition of solubilizing and electron-donor/attractor groups, is also their major problem, as the only sites that can be modified are the nitrogens of the uracil subunit and the aromatic ring. The latter is difficult to functionalize selectively, and the groups needed to modulate flavin properties generally have to be introduced early in the synthesis and more specifically before the condensation step, leading to the formation of different regioisomers thus causing difficulties in separation.[3]

We will present our work on the selective functionalization of redox-active bioinspired alloxazine and isoalloxazine derivatives to modulate their redox properties and solubility towards their implementation in redox-flow batteries. A general functionalization method was developed based on methylated alloxazine-catechol (**1**, Figure 1) via a C_9-position selective bromination or bis-bromination (C_6/C_9) sequence followed by Suzuki-Miyaura pallado-catalyzed cross-coupling to introduce different moieties. Several methods were tested to generate water-soluble flavins, yielding a small library of water-soluble molecules under neutral pH, slightly basic and acidic conditions.

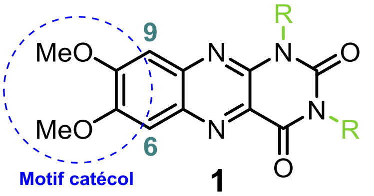

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Figure 1: Catechol-alloxazine derivatives.

A method for flavin functionalization via radical transfer using a copper complex had been developed in the laboratory. In contrast to the mono-bromination set up, which enabled functionalization at C_9 only, selectivity at C_6 via a radical mechanism was elucidated using DFT calculations (Dr. C. Gourlaouen). A high electron density is observed on the C_6 carbon compared to the C_9. Copper is therefore of considerable importance in modulating this selectivity. This mono-functionalization is interesting from a molecular weight point of view (cf. techno-economic constraints of redox-flow batteries).

To meet the structural requirements outlined above, we have set up a method for the selective post-functionalization of flavin at C_9 or C_6/C_9 from flavin ligand, and a selective method at C_6 from the copper complex. A small library of water-soluble molecules has now been synthesized, and redox-flow battery analyses are underway.

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Asymmetric Salphen metal complexes as Viral G-quadruplex stabilizer: Synthesis, Characterization, and interaction profile

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Keywords: Metal complexes, SarsCov-2, Synthesis, G-Quadruplex, antiviral drugs

The evolution of the COVID-19 pandemic,[1] caused by the SARS-CoV-2 virus, has evidenced the necessity to understand, at a molecular level, the mechanisms behind viral replication and reproduction and to find pharmaceuticals or vaccinal measures in case of an epidemic or pandemic event. In the last 10 years, there has been considerable progress in DNA targeting drugs, in particular those designed for selectively binding non-conventional DNA motifs. DNA and RNA G-rich sequences, for example, can form four-stranded structures organized in stacked guanine tetrads. These structures are enriched in highly conserved sequences and located in significant position within the human and viral genomes. For such a reason, they are considered appealing targets for anticancer and antiviral drugs. [2,3]

We will show how, through combined computational/experimental methods, our research group has successfully predicted two SARS-CoV2 putative G4 (PQS) structures, namely RG-1 and RG-2,[4,5] Furthermore, we will describe another human PQSs G4-RNA, located in the Open Reading Frame (ORF) of TMPRSS2, protein involved in the internalization of the virus in host cells.[6]

Metal complexes of Schiff base ligands can selectively bind G4 structures due to their chemical and structural properties.[7] We will present our synthesized novel metal complexes with asymmetrical Salphen ligands, incorporating both neutral and charged substituents (Fig. 1). Their selectivity towards viral and human G4s, in water solution, is tested by spectroscopic and computational approaches. Preliminary results have demonstrated the promising ability of these asymmetric complexes to selectively bind RNA G4s structures. Ongoing studies are directed toward the investigation of the biological activity of our asymmetric Schiff base metal complexes.

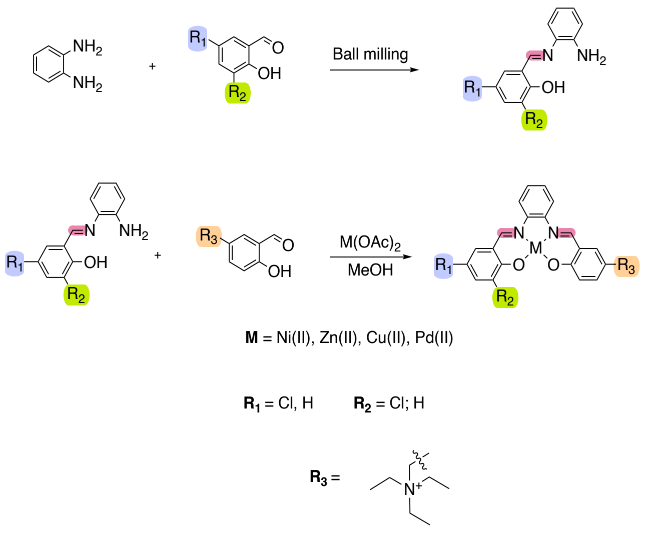

Figure 1. Synthetic routes for the preparation of ligands and metal complexes

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Design of photoactive macrocycles: new phototherapy tools for the control of infectious diseases

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Keywords: NHC macrocycles, photophysical properties, biological evaluation, antimicrobials, X-ray structures

Text:

Our research work deals with the preparation, through different pathways, of new symmetrical and asymmetrical macro-*bis*-heterocyclic *bis*-imidazolium potential carbene (NHC) ligands (L1-L6) and pincers (L1'-L3')[1]. We focus on the study of their complexation properties, with the objective to develop new photoactive transition metal complexes with enhanced photophysical properties for phototherapy applications. Some of the compounds have shown interesting intrinsic photophysical and biological properties, with a production of singlet oxygen ($^1O_2$) after light excitation (λ=290 nm), in yields of up to 84% in D_2O for some of the macrocycles obtained, opening the way to a photodynamic therapy approach.
We describe also the synthesis in a quick two-steps pathway of a novel symmetric tetra-imidazolium-*bis*-heterocycle (C1-C7) family with the objective to synthesize biologically active supramolecular assembly. Amongst them C7[2] was specifically analyzed for its photophysical properties, for a potential application in theragnostic (fluorescence). C7 was thus screened for its biological activity, in particular against important human pathogens of viral, fungal and bacterial origin, and we described a possible inhibitory mechanism on the bacterial cell wall synthesis, using electron microscopy and molecular docking tools.

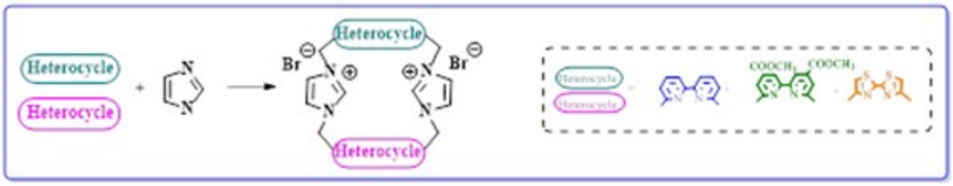

Figure 1

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Chiral supramolecular assembly based on Cu^{II}/Cu^{I} redox change

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Keywords: coordination chemistry, cyclic voltammetry, copper complexes, chirality, metallopolymers

The association of polytopic ligands and metal sources create a new class of materials that has emerged in the last decades: the metallopolymers. [1] Depending on the nature of the metal and the ligand, metallo-supramolecular polymeric assemblies have a large range of properties. If chirality is brought by the ligands, the reversibility of the dative bond can lead to a supramolecular chiral recognition between the metal complexes. A self-discrimination or a self-recognition can be electrochemically-induced, generating homochiral or heterochiral complexes. [2]

Our recent advances in this field will be presented. We will describe how the Cu^{I}/Cu^{II} redox transition shows a chiral self-recognition or a self-discrimination through X-ray diffraction and electrochemical studies. This phenomenon is also observed with the metallo-supramolecular copolymers, based on the ditopic version of these chiral ligands.

Chiral Responsive Materials

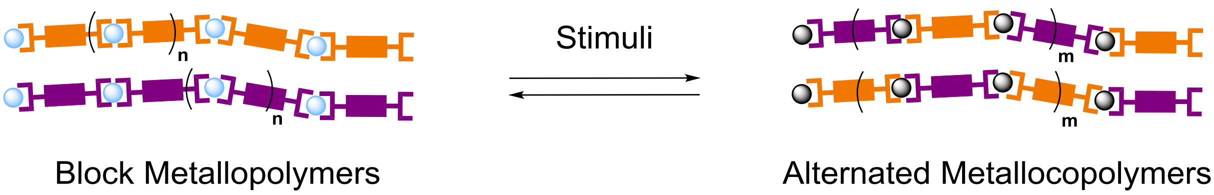

Figure 1 Principle of the electrochemically-induced control of the metallo-polymer arrangement: generation of block or alternating metallopolymers through the selective formation of homoleptic (*left*) or heteroleptic complexes (*right*).

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Coordination of $Al(C_6F_5)_3$ *vs* $B(C_6F_5)_3$ on Group 6 End-On Dinitrogen Complexes: Chemical and Structural Divergences

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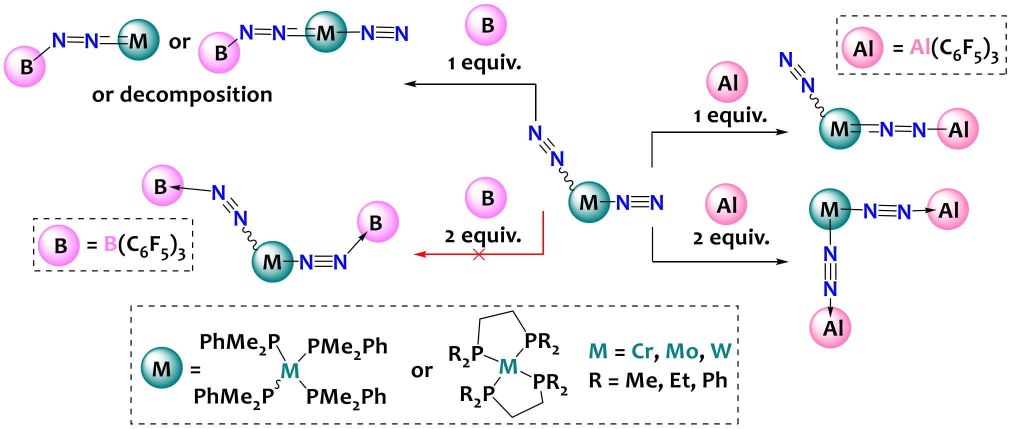
Keywords: Lewis Acid, Aluminium, Dinitrogen Activation, Group 6 Metals.

Text: Since the first transition metal dinitrogen complex reported in 1965, the discovery of an efficient and mild process for dinitrogen reduction became a holy grail for chemists. One way of achieving this is to develop new molecular design strategies that take inspiration of the Mo-nitrogenase enzymes, which efficiently catalyse the reduction of N_2 to NH_3 at ambient temperature and pressure.[1] The central idea of this project is to reproduce in synthetic complexes key features of their active site (FeMo-cofactor). One approach to glimpse this chemistry is to combine N_2 complexes with Lewis acids (LAs) to mimic the H-bond donors present in the second coordination sphere of FeMo-co. These LAs interact with metal-bound N_2 resulting in the enhancement of metal backbonding (*i.e.* pulling electron density from the metal) and thus its polarisation and activation - *push-pull* mechanism. In this context, our laboratory reported the coordination of *tris*(pentafluorophenyl)borane (BCF) on Group 6 end-on dinitrogen complexes allowing its functionalisation with mild electrophiles (R_3Si-H, $B(C_6F_5)_2$-H) that parallels the Frustrated Lewis Pair (FLP) chemistry.[2,3] Inspired by these preliminary works, we wanted to investigate how a stronger LA than BCF can induce differences in the resulting chemistry. Consistently, the aluminium analogue of BCF, *tris*(pentafluorophenyl)alane – $Al(C_6F_5)_3$ (AlCF)[4] – is a suitable candidate as this LA is known to be a Lewis Superacid.[5,6] We present here a comparative study concerning the coordination of AlCF *versus* BCF on group 6 (M=Cr, Mo, W) *bis*-dinitrogen phosphine species - $[M(N_2)_2P_n]$ (P=PMe2Ph, dmpe, depe, and dppe; n=4 or 2). This study has enabled us to access a new family of bridging dinitrogen aluminium adducts of general formula $\{AlCF(\mu\text{-}N_2)\}_mM$ (m=1 or 2) comprising single and double aluminium dinitrogen adducts that have been fully characterised in solution and in the solid state (Scheme 1, right). These results contrast with those of BCF, where only four mono adducts featuring structural divergences (compared to the Al analogues) are isolated and where decomposition reactions are observed when using some of the starting *bis*-dinitrogen materials (Scheme 1, left). Furthermore, using two equivalents of AlCF on $[M(N_2)_2P_n]$ leads to the isomerisation from a *trans* to a *cis* configuration forming *cis*-$[\{AlCF(\mu\text{-}N_2)\}_2MP_n]$ products where the two $AlCF(\mu\text{-}N_2)$ fragments are orthogonal (Scheme 1, bottom left). The proximity of these two activated dinitrogen motifs may pave the way for new reactivity with small molecules (H_2, CO_2, alkene, alkyne etc.) and redox agents.



Scheme 1 General picture of the reaction of $Al(C_6F_5)_3$ *versus* $B(C_6F_5)_3$ with $[M(N_2)_2P_n]$ complexes.

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Artificial heme-enzymes for the development of sustainable functional materials

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Keywords: Artificial metalloenzymes; Mimochromes (MCs); Catalytic bionanoconjugates

In recent decades, the field of enzyme design and engineering has become increasingly captivating for the scientific community, primarily due to its remarkable capability to introduce a wide range of functions into both natural and engineered protein structures.[1] This versatility is achieved using an array of innovative tools and strategies, allowing researchers to modify and optimize enzymes for various applications. Within this dynamic landscape, Mimochromes (MCs) have emerged as a prominent class of artificial metalloenzymes. MCs are the product of a meticulous process involving miniaturization and extensive redesign, drawing inspiration from the active sites of heme proteins.[2] They are characterized by reduced size (~3 kDa), which allows them to effectively bridge the worlds of metalloproteins and small-molecule complexes. This blending combines the exceptional catalytic abilities of natural enzymes with the adaptability of synthetic catalysts, opening up a realm of possibilities for diverse applications. Among MCs analogues, MC6*a stands out, as it proficiently modulates the reactivity of various metal ions in oxidation[3-5] and energy-related[6] catalytic processes. Our ongoing studies delve into the immobilization of MCs on a variety of surfaces for the construction of functional nanomaterials. Notably, FeMC6*a exhibits a strong affinity for binding to differently shaped gold-based nanomaterials while maintaining its structural integrity and catalytic activity.[7]

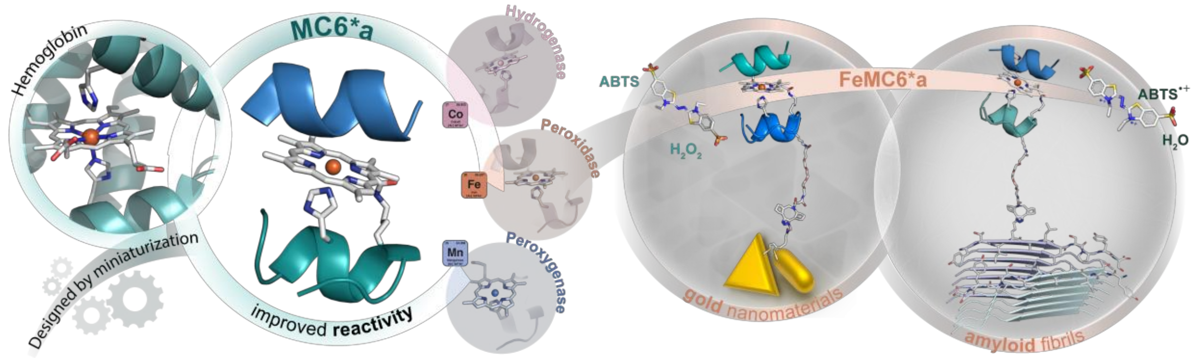

Figure 1 Representation of the Mimochromes miniaturization process and its applications.

Furthermore, our research efforts have extended to the development of sustainable nanomaterials by integrating MCs into entirely peptide-based nanostructures. In this innovative approach, we modify amyloid-forming peptide sequences to functionalized catalytic fibrils. In particular, FeMC6*a has been covalently conjugated to fibrils using the click chemistry approach. Structural and catalytic investigations have validated the immense potential of this approach in producing catalytic amyloid materials, promising exciting advancements in the realm of nanobiotechnology.

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Highly phosphorescent N^C^N-Pt(II) complexes: synthesis, functionalization and application

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Keywords: Cyclometalated platinum(II) complexes; Phosphorescence; Bio-imaging; OLED

Platinum(II) complexes having a terdentate 1,3-di(2-pyridyl)benzene (N^C^N) ligand present fascinating luminescent properties, useful for electroluminescent devices, sensors, bioimaging and photodynamic therapy.

The structure of the complex can be functionalized in different ways, *e.g.* by inserting moieties on the central cyclometalated benzene or on the pyridine rings, and by varying the ancillary ligand on the metal center. As a consequence, also the photophysical properties of the compounds can be tuned on the basis of the structural modification [1].

Up to now many substituents, both aliphatic and aromatic, have been tested on the central benzene ring, while only few examples of functionalization on the pyridines have been reported [2-3]; the insertion of new moieties (such as 4-NPh_2-phenyl, 2-thienyl, mesityl, *etc.*) leads to increased luminescence Quantum Yields (up to 100%) and more in general to improved photophysical properties.

Furthermore, the replacement of the chloride ligand on the platinum can be a useful method to furtherly functionalize the molecule through the reaction with suitable species; examples can be the exploitation of a click reaction between an azide on the Pt and an alkyne (to give a triazole [4]) or of an isothiocyanate with thiolates. Such modifications open the way for different applications in the biological field.

This contribution aims to show the latest results in the synthesis and investigation of functionalized N^C^N-Pt(II) complexes having remarkable luminescent properties.

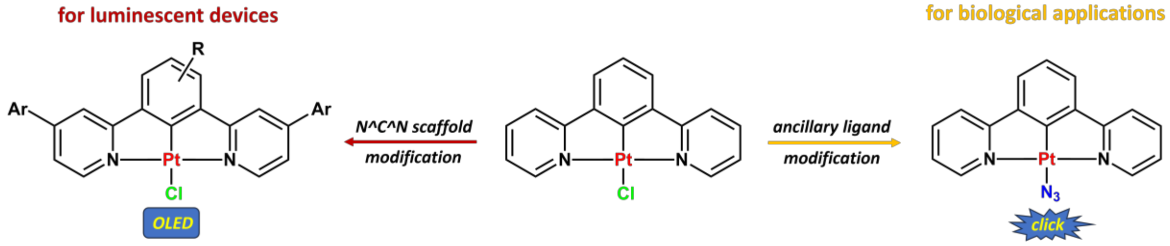

Figure 1. General scaffold and possible applications of the discussed N^C^N-Pt(II) complexes.

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SUPRAMOLECULAR METALLOPOLYMERIC GELS PHOTO-RESPONSIVE UNDER VISIBLE LIGHT

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Keywords: metallopolymers; photoresponsive materials; metallogels; supramolecular polymers

Text: Photoresponsive soft materials (e.g. organogels, hydrogels) that are able to provide photomechanical response under an external light stimulation are an interesting class of functional materials.[1] Indeed, photonic stimulus is of particular interest because for it can be applied wireless with precise spatiotemporal resolution. In this respect, we herein report a class of supramolecular metallopolymers whose structure can be easily functionalized and, thus, stimuli-responsiveness can be straightforwardly introduced.[2] Following previous investigations made by the group on metallopolymers and their metallogels that required UV light to photo-isomerize,[3-4] herein we present a novel series of photo-active supramolecular metallopolymeric gels that show responsiveness under visible light excitation, namely under green light at λ_{exc} = 530 nm. The molecular design includes homo- and hetero-metallopolymers that contain photoresponsive ditopic ligands with divergently-oriented coordination sites, such as terpyridines (Figure 1). In these new metallopolymers the shift of the absorption spectrum of the photo-isomerizing unit is achieved by introduction of electron-withdrawing atoms (i.e. fluorines) onto the azobenzene photoswitchable groups. Supramolecular polymerization is achieved upon coordination with Zn^{II} and Co^{II} ions under suitable metal-to-ligand ratio. On the other hand, linear and branched alkyl as well as tetra(oxyethylene) chains ensure solubility of the final metallopolymers in either organic or aqueous media. Theirs optical properties in solution have been characterized by UV, NMR, and steady-state and time-resolved fluorescence techniques. The so-prepared metallopolymers can act as gelating agents at very low to moderate concentration, ranging from 0.6 wt.% to 7.0 wt.% when *N*,*N*-dimethylformamide or either ethanol with water are used as solvent mixtures. Overall, gelation time depends on the coordinated metal, temperature, quantity, the mass percentage and the type of ligand employed. Finally, irradiation tests with a specific visible wavelength indicate that photo-induced gel-to-sol transition is observed and associated with color-change due to the isomerization of the fluorinated azobenzene ligands.[5] This gel-to-sol transition is irreversible under light or heating condition. Finally, the ratio of the isomerized and non-isomerized metallopolymers can be determined by ICP-MS.

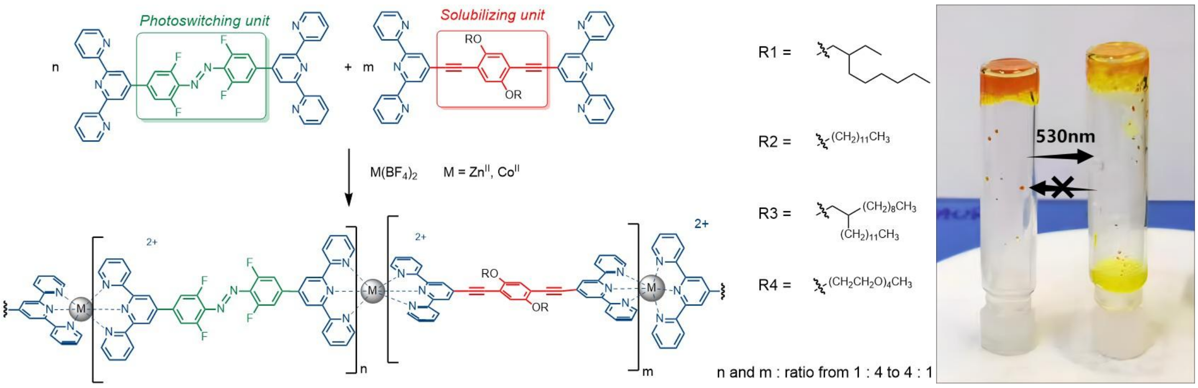

Figure 1. Chemical structure of the different photoresponsive Zn^{II} and Co^{II} metallopolymers investigated; sample of Zn^{II} **MP-R4** at 7.0 wt.% in DMF : H_2O = 1:3 before (*left vial*) and after (*right vial*) 5 hours of irradiation upon λ_{exc} = 530 nm LED light. (MP-R4 = metallopolymer with R4 as substrate of solubilizing unit).

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Synthesis and delivery of N-heterocyclic carbene platinum complexes for the treatment of glioblastoma

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Keywords: Glioblastoma; N-heterocyclic carbene; platinum; cancer stem cells; nanoencapsulation

Considering the current standard of care, glioblastoma is a deadly brain tumor with a devastating prognosis mainly due to cancer stem cells (CSCs) [1-3]. Due to side effects and the emergence of resistance over time against other cancer types, platinum-based medications like cisplatin and oxaliplatin are of limited efficacy [4-5]. Platinum complexes containing N-heterocyclic carbenes (NHCs) have recently been identified as potential therapeutic options for glioblastoma because it has been shown *in vitro* and *in vivo* that they successfully eradicate glioblastoma stem cells by targeting mitochondria [6-7].

Here, novel NHC-Pt complexes were designed and synthetized to simultaneously eradicate glioblastoma differentiated (U87-MG TMZ-sensitive) and stem cells (NCH21K). All the NHC-Pt compounds exhibited *in vitro* cytotoxicity against both cell lines [8]. Additionally, nanoencapsulation of the best candidates was done in order to address the issue of poor solubility in water. Two methods were evaluated, namely liposomes and lipid nanocapsules, which have never previously been used for NHC-Pt complexes encapsulation. Vectorization was successful, and it resulted in a similar cytotoxic activity of the compounds compared to their non-encapsulated counterparts. This step was crucial to consider those new drugs for *in vivo* studies. The perspectives are to incorporate the NHC-Pt complexes into hydrogels to achieve a localized and controlled delivery of the compounds.

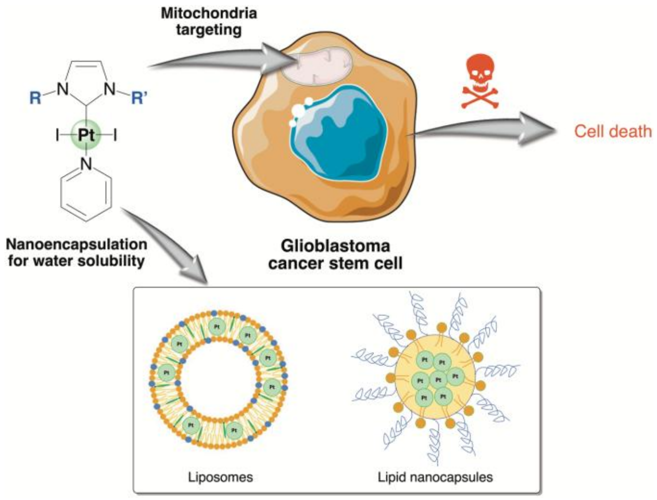

Figure 1

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Switching between ligand-centered to metal-centered redox activity in acridine/ane-pincer cobalt complexes

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Keywords: pincer complexes, electrochemistry, small molecule activation

Pincer-supported transition metal complexes are emerging as promising catalysts for small molecule activation, playing a pivotal role in advancing applications within the energy domain.[1-2]

To control and enhance the reactivity of the coordinated transition metal ion for the reductive activation of small molecules (e.g., protons for H_2 production, CO_2, N_2, etc.), tuning the pincer properties is crucial.

In this study, we have successfully synthesized and characterized a Co^{II} complex supported by a previously-reported acridine-based PNP-donor pincer[3] (Co**L**^{ON}, Fig. 1a). However, its redox activity is centered on the aromatic skeleton of the ligand. Through ligand design, we have thus isolated a parent Co^{II} complex supported by a novel acridane-based PNP-pincer (Co**L**^{OFF}, Fig. 1b), exhibiting metal-centered redox activity, as evidenced by electrochemical data (Fig. 1c). Ongoing efforts are directed towards comparing the reactivity of Co**L**^{ON} and Co**L**^{OFF} with small molecules.

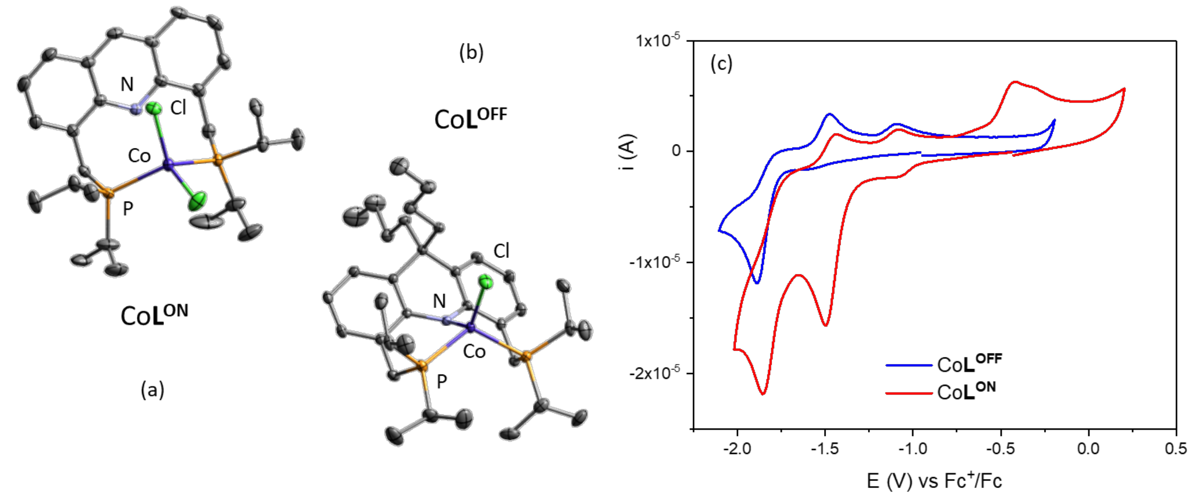

Figure 1. Single crystal X-ray structures (a, b) and cyclic voltammetry (MeCN 0.1 M TBAPF$_6$, GC, 100 mV·s^{-1}) of Co**L**^{ON} and Co**L**^{OFF}.

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A STABLE AND TRUE-BLUE EMISSIVE HEXACOORDINATE SI(IV) N-HETEROCYCLIC CARBENE COMPLEX AND ITS USE IN OLEDs

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Keywords: fluorescence; silicon complexes; NHC ligands, OLEDs, density functional theory

Despite the widespread use of silicon and its compounds in research and industry, coordination compounds of this earth-abundant element are rarely investigated with regards to optoelectronic properties, with most research focused on elemental Si, Si-phthalocyanines, silanes and siloxanes.[1]
Following some previous studies from some of us on versatile *pincer*-type O^C^O N-heterocyclic carbenes (NHCs)[2] we decided to attempt coordination on Si(IV). Our idea was that their LX_2 structure, characterised by a central benzimidazolylidene moiety and stabilised by two chelating phenolic groups would be suited for oxophilic metals with high oxidation state and, indeed, we are hereby reporting the synthesis, chemical, structural and photophysical and electroluminescence characterization of the first example of an homoleptic, neutral, hexacoordinate luminescent Si(IV)-NHC complex, namely **$Si(OCO)_2$**, that is highly stable in solution and in the solid state.[3] Optical properties were further elucidated by means of time-dependent density functional theory (TD-DFT) calculations.
Remarkably, solid samples of **$Si(OCO)_2$** show intense narrow blue emission peaking at λ_{em} = 418 nm with a photoluminescence quantum yield (PLQY) of 32% (Figure 1). This fluorescence, ascribed to an intraligand charge transfer (^{1}ILCT) transition enhanced by the rigid environment of the dense crystal packing, is retained in spin-coated thin film samples at 10 wt.% doping level in polymer matrices. Finally, we employed **$Si(OCO)_2$** in the fabrication of proof-of-concept organic light-emitting diodes (OLEDs) which show peak external quantum efficiency (EQE) of 1.3% (0.8 cd A^{-1}), maximum luminance of 2566 cd m^{-2} and saturated true-blue emission.
In conclusion, this study will provide a taste of the untapped potential behind the chemistry of Si(IV)-NHC complexes for the design of stable emitters with application in electroluminescent devices.

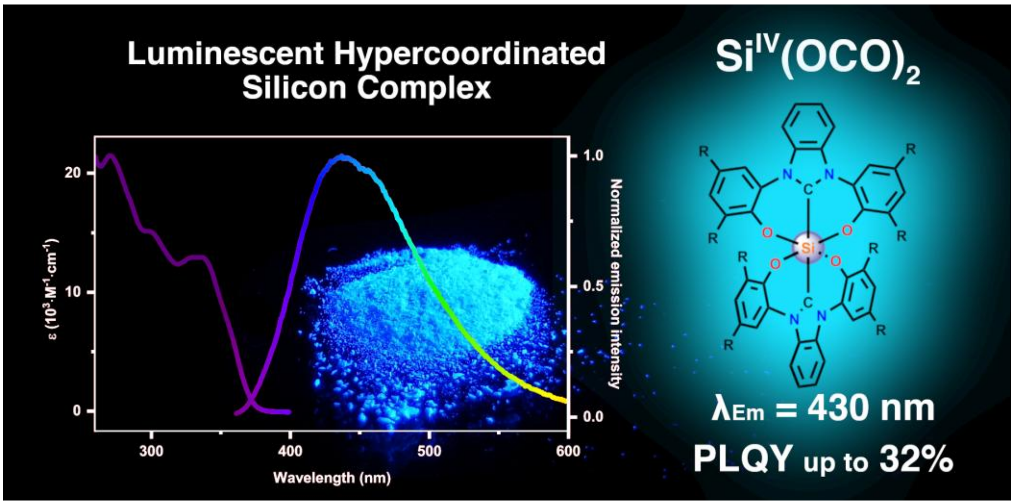

Figure 1 – Complex **$Si(OCO)_2$** shows intense blue emission peaking in the 420-430 nm range.

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Optical properties of biphenyl Au(III) complexes with Phosphine Ancillary Ligands

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Keywords: Excited states, Gold(III), Organophosphorus compounds, TD-DFT

Despite the harsh conditions required for their synthesis, Au(III) complexes have attracted increasing interest for their potential applications in several domains and especially as emitters in OLEDS.[1] The design of Au(III) complexes with satisfactory emission properties is a challenge. The high oxidation state of the gold cation strongly stabilizes the gold orbitals pushing the Metal-to-Ligand Charge Transfer (MLCT) states to higher energy than in for example their isoelectronic Pt(II) complexes. The emission properties of such complexes are dominated by Ligand-to-Metal Charge Transfer (LMCT) and Metal-Centred (MC) states. Associated to the flexible square-planar geometries of the gold cation, those states can lead to strong geometry distortions quenching the luminescence properties. We present here the emission properties of a series of biphenyl Au(III) complexes (Figure 1) with various Phosphine Ancillary Ligands[2]. These complexes display bright luminescence in solid state with quantum yield up to 0.39. On the contrary, in solution (CH_3CN) emission is quenched. A full theoretical investigation by mean of (TD-)DFT has allowed a full rationalization of the emission properties.

Figure 1: Structure of one of the studied complexes (left) and electron density difference (right) between the ground and the first triplet state at Franck-Condon geometry. In red are electronically depleted area and in green electronically enriched area.

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FUNCTIONALIZED BORAZINES BY NITROXIDE RADICALS: NEW LIGANDS FOR THE DESIGN OF MOLECULE-BASED MAGNETS

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Keywords: Borazine; Nitroxide Radicals, Molecular Magnetism

Text: Borazine ($B_3N_3H_6$) are heterocyclic boron-nitrogen compounds, well known as the “Inorganic benzene” due to the B=N bonds which are isoelectronically and isostructurally equivalent to the C=C bond. [1-3] Despite such similarities, the electronic properties of borazine are different from those of benzene, due to the significant difference in the electronegativity between boron and nitrogen atoms [4], which results in a low aromaticity of the borazine ring compared to benzene. In the frame of our research on molecule-based magnets, [21-23] a new borazine derivative functionalized by nitroxide free radicals, has been synthesized as a milestone in open-shell inorganic benzene. The crystal structure was determined from X-ray diffraction on single crystal and it acertains the grafting of three nitroxide radicals. In the solid state the temperature dependence of the magnetic susceptibility evidences weak intramolecular antiferromagnetic interactions between the three radicals with strong intermolecular antiferromagnetic interactions between two nitroxide moieties of two neighboring molecules. EPR spectroscopy at 80 K evidences the coexistence of species with S=1/2 and S=3/2 ground-state in frozen glassy solution. Comparison with theoretical data support the hypothesis that these are ascribed to different molecular conformations having different orientations of the nitroxide radicals with respect to the borazine core. In the fluid solution at room temperature the high nitroxide mobility results in an motionally-averaged interactions result S=1/2 spin state for the molecule. In summary, we are convinced that, this archetypal molecule represents a potential ligand for the design of molecule-based magnets.

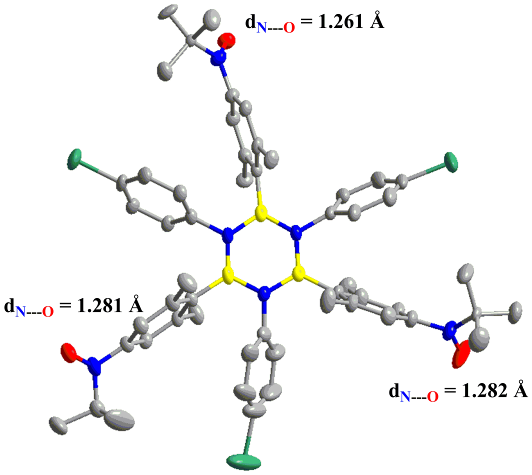

Figure 1: Crystallographic structure of the asymmetric unit of **5** represented with thermal ellipsoid plot at a 50%

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REDUCTION OF KETONES BY THIO-NHC MANGANESE(I) CATALYSTS

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Keywords: Hydrogenation, Ketones, Bidentate Mn(I) catalysts.

The hydrogenation of ketones is an important chemical transformation that has broad application in organic synthesis,[1] industrial processes,[2] and pharmaceutical production.[3] The reduction of carbonyl compounds is excellently performed by many complexes containing noble metals such as ruthenium, rhodium or iridium.[4] The scarcity of precious metals, their high price and toxicity however diminish their attractiveness for catalytic applications. First-row transition metals such as Fe and Mn, that are inexpensive and environmentally friendly are now of particular interest for catalytic reduction.[5] In 2019, some of us reported one of the most efficient Mn-based catalyst for ketone hydrogenation based on a bidentate Phosphine-NHC Mn(I) system that exhibited a non-classical metal-ligand cooperative H_2 activation mode.[6] Interest has arisen in the synthesis and study of analogous bidentate Thio-NHC Mn(I) complexes to establish whether such species could exhibit a similar behavior and compare their catalytic activity with both their Thio-NHC-Ni [7] and Phosphine-NHC Mn(I) analogues.[6] In this communication, we will present the synthesis of several Thio-NHC Mn(I) complexes and their catalytic abilities for the hydrogenation of ketones (Figure 1).

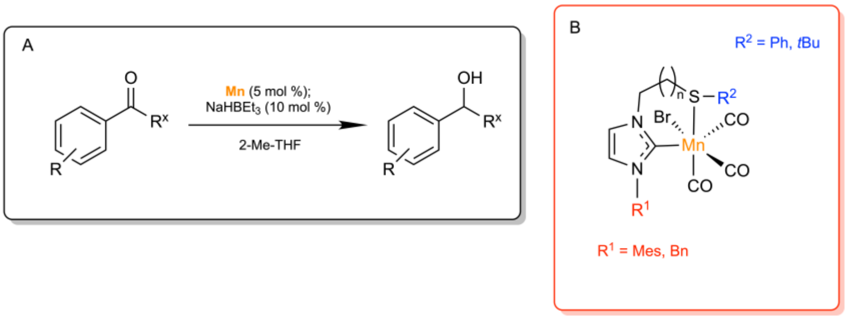

Figure 1. A) Reduction of ketones using B) various Thio-NHC Mn(I) catalysts.

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Nickel complexes for hydrogen oxidation and production without overvoltage

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Keywords: Ni complex; Catalysis; Dihydrogen production; Dihydrogen oxidation

The design of efficient transition metal (platinum-free) catalysts for H^+/H_2 conversion is a prerequisite for the large-scale deployment of fuel cells and electrolysers[1]. Many inorganic catalysts are available for the electrochemical production of hydrogen[2], but they work in a unidirectional way and with a high "overvoltage", *i.e.* under conditions that are much more reducing than what is allowed by thermodynamics. This overvoltage implies that a device that produces hydrogen by electrolysis of water dissipates as heat a fraction of the electrical energy that makes it work. This is an obstacle for the construction of devices to temporarily and efficiently store (without energy loss) the intermittently produced energy by wind or solar power. A small number of bioinspired mononuclear nickel complexes developed over the last five years can catalyse both the oxidation and the production of hydrogen at high rates and under very energy efficient conditions. These complexes belong to the large family of molecular catalysts known as "DuBois"[3]. They are Ni complexes in a phosphorous environment, bearing bioinspired amine groups that promote proton transfer and heterolytic dihydrogen splitting. The ligands are functionalised with substituents (R and R' in Figure 1A) that significantly modify their catalytic properties. Two examples of complexes, based on the generic structure, are represented in Figure 1 (panels B and C).

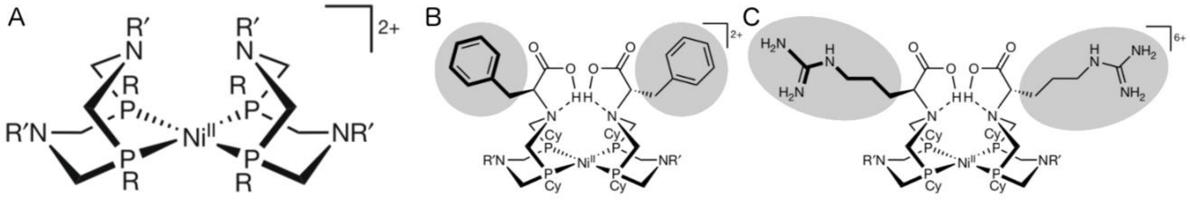

Figure 1 A: Generic structure of a “DuBois” complex; B and C: Examples of “DuBois” complexes

The goal of my work is to understand how structural details determine the kinetics of the catalytic cycle steps and the catalyst properties in this family of mononuclear Ni complexes. My studies rely on recently proposed kinetic models in the BIP group, that allow the use of electrochemical methods to decipher catalytic mechanisms of bidirectional redox catalysts in an effort to understand what makes them work in an (ir)reversible way, with or without overpotential[4,5]. Novel complexes were synthesized with an aromatic ring on the phosphine and amino acids on the amine. Preliminary electrochemical analyses were performed.

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EVOLUTION OF COPPER(II) COORDINATION SPHERE FORMED OF *N*-ALKYLATED CYCLAMS WITH 1,2,3-TRIAZOLE PENDANTS - EFFECT OF HETEROCYCLIC UNIT

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Keywords: *N*-alkylated cyclam; 1,2,3-triazole; copper(II) coordination; bifunctional chelator; PET imaging

The 1,4-disubstituted 1,2,3-triazoles have become a powerful tool for chemical ligation of two molecules and have found multiple applications. Besides being used as a stable linker, the metal complexation capacity of this heterocycle has also been explored by many research groups. Indeed, both N2 (inverse triazole) and N3 nitrogen atoms (regular triazole), as well as C5 carbon atom are capable of coordinating metal ions.[1,2]
We have developed original chelation systems with the ability to complex copper(II) as a bifunctional chelating agent for nuclear medical applications.[3] These chelators are built on the basis of *N*-functionalized cyclams engineered with two 1,2,3-triazole heterocycles allowing both metal coordination and connection to two targeting biomolecules. Homodimeric conjugates obtained by this way are an attractive option to enhance *in vitro/vivo* targeting efficiency.[4]

These *N*-alkylated cyclam ligands shown rapid complexes formation, their copper(II) ion coordinating properties were evaluated by solid state structural analysis and various spectroscopic studies in solution. Promising properties in 64-copper complexation have demonstrated that these systems can be valuable bifunctional chelating agents for Positron Emission Tomography (PET) applications.

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HKUST-1 and CPO-27 (Co)- based porous microspheres: Innovative composites materials for environmental applications

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Keywords: metal organic framework, chitosan, microspheres, cryogels, composite

Metal Organic Frameworks (MOFs) is a class of porous materials that emerged in the 2000s. These materials have invaded several fields of chemistry thanks to their high porosity and structural flexibility. However, their use in industrial fields remains limited due to their difficult processing and their low chemical and thermal stability. The combination of MOFs with polysaccharides such as chitosan is one of the strategies adapted to overcome these limitations and to obtain composites for different shaping like monoliths, films, or microspheres [1].
According to several studies reporting the use of chitosan for the growth of MOFs in the form of microspheres, it is commonly reported that a supercritical CO_2 drying step is strongly required in order to avoid the porous structure collapse [1,2]. Despite its numerous advantages, this drying method also has some disadvantages: high cost and long processing time. In our studies, and in order to overcome the stability and shaping limitations of MOFs and avoid supercritical drying drawbacks MOF-74 (Co) and HKUST-1 were chosen as one of the most famous MOFs studied to combine with graphene oxide and to grow in a chitosan matrix in mild conditions, followed by a freeze-drying step to prepare high crystalline porous microspheres (beads).

Figure 1: As-prepared HKUST-1 based microspheres (left) and MOF-74 (Co) based microspheres (right).

The as-prepared cryogels were used for CO_2 adsorption where they showed very good performances (2.59 mmol/g at 298 K and 5.38 mmol/g at 273 K in for HKUST-1 based composites). In order to probe their large environmental applications, adsorption tests of other gases are currently in progress.

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STUDY OF THE ESTERIFICATION OF LEVULINIC ACID WITH 1,6-HEXANEDIOL PROMOTED BY ZN(II) CATALYSTS

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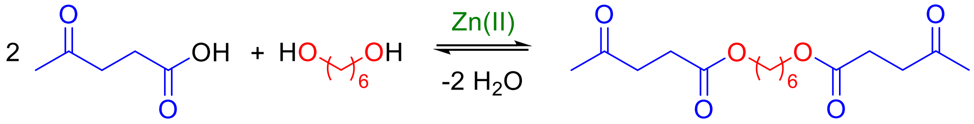
Keywords: Levulinic acid, 1,6-Hexanediol, Esterification, Zinc catalyst, Imino-pyridine ligand.

In response to the increasing demand for environmentally friendly chemicals, researchers have recently shifted their focus toward the conversion and utilization of biomass. A notable product derived from lignocellulosic biomass is Levulinic Acid (LA), which can be obtained through various methods utilizing raw materials such as glucose, fructose, sucrose, and other sugars.[1] LA plays a central role in the chemical industry, primarily serving as a precursor for pharmaceuticals, solvents, anti-freeze agents, and more.[2] Its esters (Levulinic Esters - LE) are very intriguing, thanks to their versatility in applications, like plasticizers, lubricants, and additives. In particular, esters of polyols play a significant and multifaceted role in various industrial formulations.[3]

The production of LE entails the esterification reaction between LA and alcohols, constituting an equilibrium process accompanied by the formation of water. The inclusion of a catalyst is typically necessary to enhance productivity. Over the years, different catalytic systems have been explored, with a discernible trend favouring the utilization of Lewis acids.[4] Among these, zinc(II) salts and complexes have emerged as particularly noteworthy, showcasing, on one hand, remarkable activity in this type of reaction, and, on the other hand, affordability and biocompatibility.[5]

Therefore, this study examined the esterification reaction between LA and a polyol, 1,6-hexanediol, utilizing, as catalysts, simple inorganic salts of zinc(II) and its complexes with imino-pyridine ligands (Scheme 1).



***Scheme 1**: Esterification reaction of Levulinic Acid with 1,6-hexanediol using Zn(II) catalysts.*

This study incorporated the screening and synthesis of catalysts, aiming to heterogenize them, with an NMR methodology to assess the selectivity for mono-esters and di-esters, as well as to monitor the changes in the composition of the mixture during the course of the reaction.

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M.M. and F.R. are grateful to Italian Ministero dell'Università e della Ricerca for the financial support provided through the LabSolv project "Lactic acid based new green Solvents: design synthesis and use in catalysis", Progetti di Ricerca di Rilevante Interesse Nazionale -Bando 2022, Prot. 20229P7PPM.

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Stimuli-sensitive luminescent multimetallic Cu(I) assemblies bearing very unusual bridging aqua ligands.

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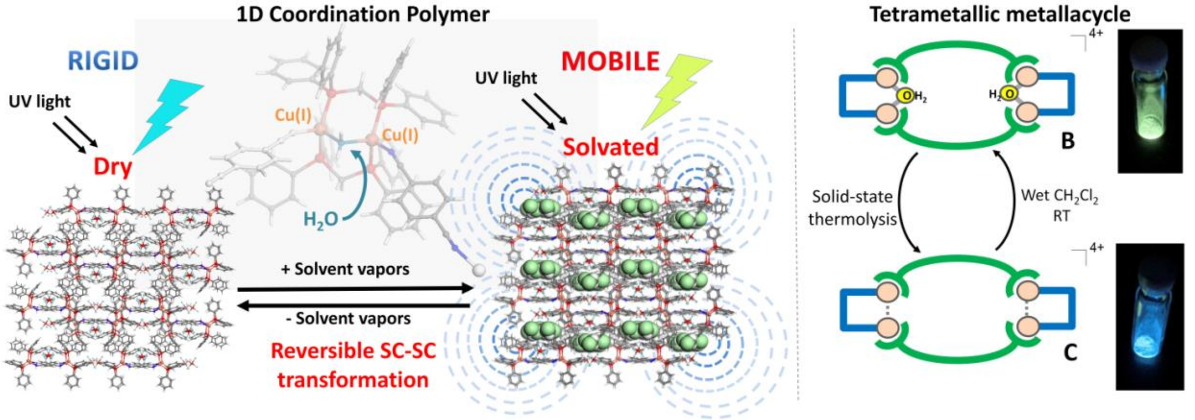
Keywords: Cu(I), Solid-state luminescence, Stimuli-sensitive materials, Polymetallic assemblies, Thermal transition

An increasing interest is devoted to Cu(I) metal complexes as attractive new photoluminescent materials for lighting and stimuli-sensitive sensors applications, taking advantage of both the various photophysical properties and the large flexibility of the coordination sphere exhibited by derivatives based on this ion.[1] Using a specific pre-assembled luminescent Cu(I) bimetallic precursor bearing significant conformation flexibility, a series of discrete and polymeric Cu(I) luminescent assemblies[2] has been previously obtained. In this contribution, an extension of this study will the presented with the description of luminescent Cu(I) multimetallic assemblies bearing Cu(I) bimetallic subunits in which a very unusual bridging aqua ligands are observed.[3] Detailed photophysical properties of these derivatives will be discussed together with their original solid-state vapochromic[3] or thermal transition behaviors.



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Design of novel catalysts bearing s-heptazine-based ligand for electrocatalytic CO_2 reduction reaction.

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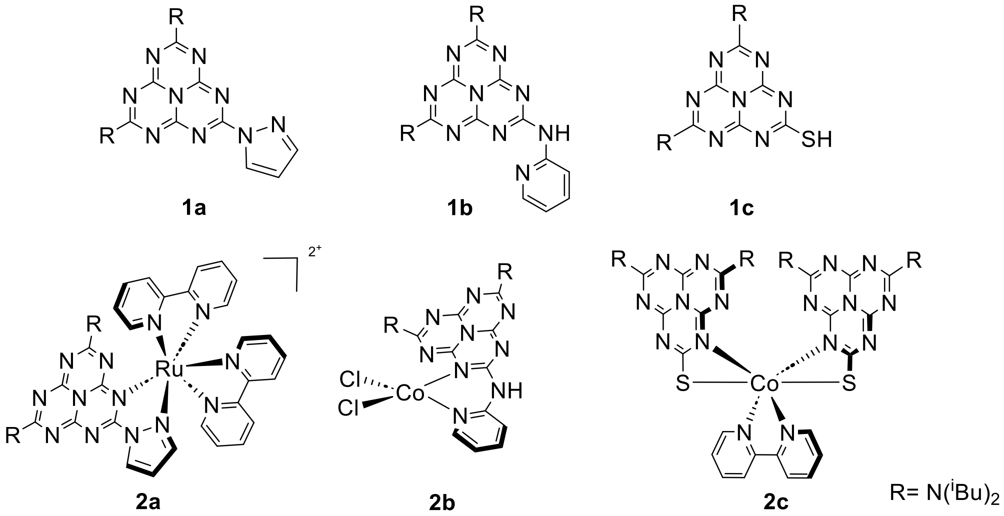
Keywords: s-heptazine, complex design, DFT calculation, CO_2 reduction

Heptazine derivatives are a family of polycyclic compounds that are obtained from graphitic carbon nitride materials (g-CN). The heptazine building blocks have a high nitrogen to carbon ratio while possessing an extensive conjugated π-system, making them strongly electron-deficient molecules. They present also three tunable positions that can be selectively substituted[1] and a high chemical stability. Heptazine unit have not received much attention until recently, functionalization of this molecule is still challenging[2] and some difficulties remains. Despite the advantages that such a family of molecules could offer as supporting ligands for molecular catalysis, the use of a metal center directly coordinated by heptazine has not been yet reported in the literature.

Here, we report the synthesis of new heptazine-based ligands and their ruthenium and cobalt complexes. Three new heptazine-based ligands were synthesized, isolated and characterized by elemental analysis, ^1H, ^{13}C NMR, cyclic voltammetry, ESI-MS and UV-VIS spectroscopy (Fig. 1, 1a, 1b and 1c). From 1a, 1b and 1c, three different complexes were synthetized. 2a and 2b were the first complexes using heptazine unit, and single crystals were obtained allowing to determine the X-ray structure of the complex. Both complexes were characterized using spectroscopic techniques (NMR, UV-Vis, EPR) and cyclic voltammetry (CV) analysis. The nature of the bond between the metal center and the new heptazine ligand was investigated using theoretical calculation. Complex 2c was inspired by the molecular catalyst $[Co(bpy)(PyS)_2]$, known to convert CO_2 into formate.[3] This complexes will be used as homogeneous molecular catalysts for electrochemical reduction of CO_2.



1a 1b 1c

2a 2b 2c

R= N(^{i}Bu)$_2$

Figure 1 Heptazine-based ligands and associated complexes synthetized for this study.

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GROUP 11 CTCs BASED MATERIALS: SOLUTION AND SOLID STATE STUDIES AND POTENTIAL APPLICATIONS

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Keywords: CTCs, CTCs-based materials, Donor-Acceptor supramolecular assemblies, optoelectronic materials

The synthesis of materials having optoelectronic properties is a growing area of research due to their applications in sensing, OLED technology, and semiconductors for OFET or OPVs. In this context, the 11th group metals Cyclic Trinuclear Metallacycles (CTCs), have been demonstrated to be valid candidates.[1] CTCs are a particular class of organometallic cyclic compounds made of anionic ditopic heteroaromatic or carbeniate bridging ligands and M(I) coinage metals. Theoretical studies demonstrated that the CTCs act as π-acidic species or π-basic species, depending on the nature of the bridging ligands, substituents, and the type of coinage metal (order of increasing π-basicity: Triaz < Pz < Carb < Py < Im and Ag < Cu < Au).[2] For these intrinsic properties, CTCs can form isolable and stable adducts in the solid state with cations, simple or extended aromatic molecules, or CTCs with complementary π-acidic/π-basic properties; the formation of these adducts results in the modulation of their photophysical and/or the activation of semiconducting properties.[1] Recently our research group has synthesized and fully characterized, both in solution and in the solid state, a series of mixed Au(I)/Ag(I) and Au(I)/Cu(I) stacked products, obtained by the combination of π-basic gold(I)-imidazolate CTC with π-acidic silver(I) or copper(I) pyrazole CTCs.[3] Most of the stacked products displayed solid-state enhanced photoluminescence if compared to the starting CTCs and a good bench and thermal stability, which places these compounds as promising emitting materials for OLED technology applications. Moreover, we showed how the intercalation of coronene, a highly symmetric polycyclic aromatic molecule, with π–acidic silver(I) or copper(I) pyrazolates CTCs, gave rise to stable products with diminished direct and indirect band gaps compared to the pristine compounds, calculated respectively in 2.27 and 2.78 eV in one case, which are values featuring these materials in the semiconductor band gap range useful for application in OFETs or OPVs.[4] Besides the solid state, the formation of charge-transfer Au(I)/Ag(I) or Cu(I) stacks was found even in solution as confirmed by PGSE studies, with binding constants calculated from UV-Vis/NMR titrations up to 4.67×10^5 L/mol.[4] Conversely, the Ag(I) or Cu(I)/coronene adducts were scarcely soluble in most organic solvents, and once dissolved, they almost completely afforded to the pristine compounds as demonstrated by ^{1}H-NMR experiments. In this communication, we critically discuss the syntheses and characterizations as well as the possible applications of these two classes of CTC-based materials.

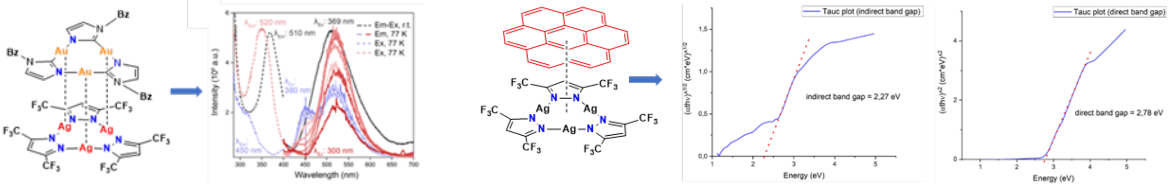

Figure 1. Scheme of a representative example of mixed Au(I)/Ag(I) stacked product and solid-state photoluminescence study (left). Scheme of the hybrid adduct, {[3,5-$(CF_3)_2$pz]Ag}$_3$@Coronene, and solid-state Tauc plots, with indirect and direct band gap calculations (right).

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Novel Fe(III)-based MRI diagnostic probes as a sustainable alternative to the current use of Gd(III) complexes

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Keywords: Fe(III) complexes, MRI contrast agents, NMR relaxometry.

Text: The low but increasing environmental contamination by anthropogenic gadolinium(III), resulting from the widespread use of Gd(III)-based MRI contrast agents,[1] has spurred the quest for viable alternatives. High-spin Fe(III) complexes could represent an attractive solution since they combine interesting magnetic properties with an enhanced safety profile, given that ferric ions are highly regulated and play a relevant role in numerous physiological processes.[2]

We recently investigated $[Fe(EDTA)]^-$ and $[Fe(CDTA)]^-$ as model systems to evaluate the efficacy (relaxivity) of monohydrated Fe-chelates as T_1 agents for MRI.[3] At typical imaging magnetic fields, the relaxivity is limited by the electronic relaxation time of the metal ion and the fast tumbling of the complexes. A well-established strategy used in the case of Gd(III)- and Mn(II) complexes is to replace one or more carboxylic groups with the corresponding amides to modulated the overall charge. This chemical substitution has also a notable impact on the stability and kinetic inertness of the systems. We prepared two novel derivatives of $[Fe(CDTA)]^-$ by replacing one and two carboxylic groups with the corresponding diethylcarboxamide moieties and investigated the changes on the ^1H and ^{17}O NMR relaxometric properties, thermodynamic stability, kinetic inertness and redox activity.

The results of this study could represents a contribution towards a better understanding of the effects of the chemical nature of the donor groups on the coordination and magnetic properties of Fe(III) complexes of relevance as potential MRI probes.

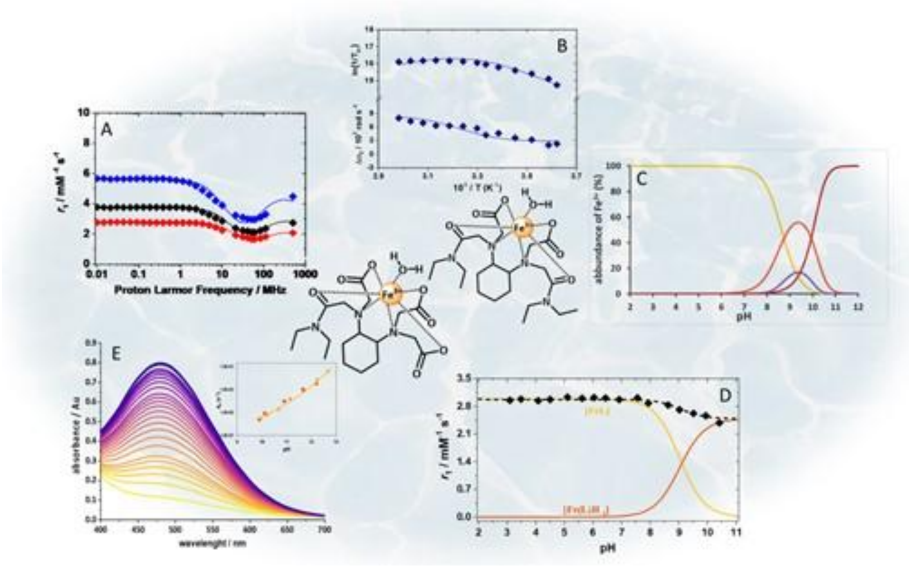

Figure 1 Graphical summary of all the technique used for the characterization of the Fe(III) complexes. (A) ^1H NMRD profiles at three different temperatures. (B) Reduced ^{17}O NMR transverse relaxation rates (top) and chemical shifts (bottom), at 11.74 T. (C) Species distribution diagram of the bisamide derivative. (D) Relaxivity values as a function of pH (◆) and fitted contribution of the different species. (E) Absorption spectra of the bisamide derivative.

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NADH REGENERATION WITH $HP(O)(OH)_2$ CATALYSED BY IRIDIUM PYRIDINE-2-SULFONAMIDATE COMPLEXES

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Keywords: NADH regeneration; homogeneous catalysis, iridium complexes, reaction mechanism

NADH (Nicotinamide Adenine Dinucleotide in the reduced form) is a coenzyme that plays a central role in several energy-conversion processes of living organisms and in a large variety of biocatalytic redox reactions, where it acts as an electron and hydrogen carrier.

Owing to its high cost, the utilization of NADH in large-scale applications is necessarily related to the possibility of its catalytic regeneration from the oxidized form, NAD^+, by the reaction with affordable reducing agents such as formic acid [HC(O)OH] or phosphonic acid [$HP(O)(OH)_2$].

We recently showed that [Cp*Ir(R-pysa)NO_3] (pysa = κ^2-pyridine-2-sulfonamidate; R = H, 4-CF_3, and 6-NH_2) complexes, are excellent catalysts for the chemical regeneration of NADH in combination with phosphonic acid $HP(O)(OH)_2$ as hydride source, with activity approaching that of enzymes.[1]

Herein, we report the results of in-depth experimental and computational mechanistic investigations that allowed to draw a compelling reaction pathway for the hydrogenation NAD^+ catalysed by [Cp*Ir(R-pysa)NO_3] complexes in the presence of $HP(O)(OH)_2$.[2]

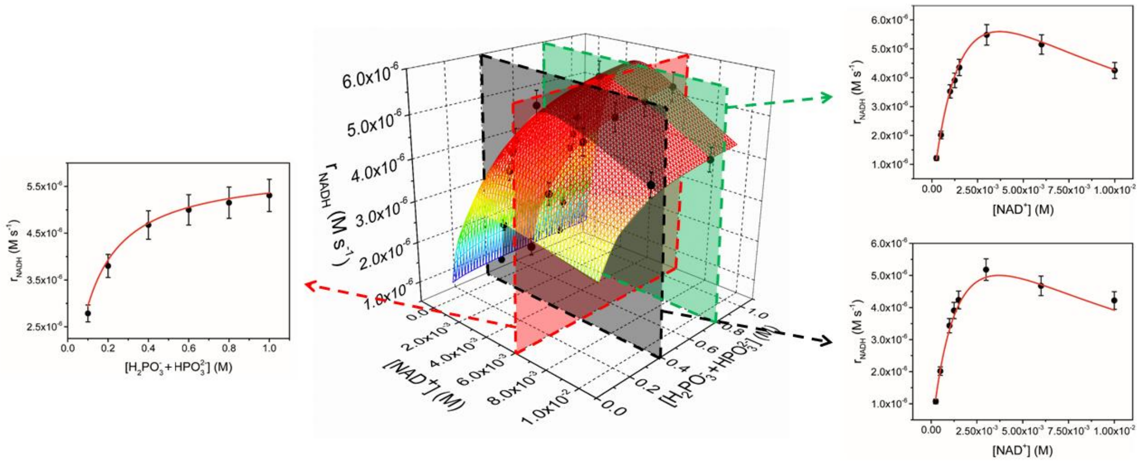

Figure 1 Global fitting of 3D and 2D trends of initial rate of reaction (r_{NADH}, M s^{-1}) *versus* concentration of reactants (NAD^+ on the right and phosphonic acid on the left) for the NADH regeneration with phosphonic acid mediated by an [Cp*Ir(H-pysa)NO_3] complex (Experimental conditions: T = 313 K, [cat] = 5 mM, pH = 6.58).

Multiple catalytic experiments revealed non-linear trends of the initial rate of NADH formation (r_{NADH}) with the concentration of the substrates, which were modelled with an *ad hoc* kinetic law (Figure 1). Integration of the kinetic results with NMR spectroscopic and theoretical studies suggested the presence of two slow steps, namely generation of a coordinative vacancy on the metal and P–H bond activation, that may be turnover limiting depending on the relative concentration of phosphonic acid used. Remarkably, the coordinative vacancy is generated *via* pyridine decoordination from Ir, affording a *pseudo*-tricoordinated species that activates phosphite anions more favourably. The establishment of a hydrogen bonding network between the phosphonic acid and both coordinated H_2O and amide moieties is functional for P–H bond activation, which would not occur otherwise.

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DEVELOPMENT OF COUMARIN-no3py DERIVATIVES FOR THERANOSTIC APPLICATIONS IN NUCLEAR MEDICINE

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Keywords: Nuclear Medicine; Coumarin; MCT1; no3py; theranostic

Text:
Coumarins are natural phyto-compounds known since the 19th Century, their scaffold has attracted the attention of synthetic and medicinal chemists for decades and showed a large variety of biological activities, such as anti-inflammatory, antibacterial, antioxidant, and anticoagulant [1]. One of the recently developed MCT1 inhibitor (7ACC2) that reached clinical trials is a coumarin derivative, so this family of compounds deserves a great deal of attention [2].

MCT1 is a membrane protein responsible for the transport of lactate and other monocarbon units normally expressed in healthy tissues. However, in some cancer lines its expression results dysregulated and allows the establishment of the “Warburg effect”. This mechanism explains the aggressive character of specific tumoral types and allows MCT1 to be a potential target for theranostic applications in oncological field [3]. To date, only few molecules acting as inhibitors for MCT1 are known [2], and their interactions within MCT1 pocket have been elucidated by Xray crystal data [4].
At first, some *in silico* experiments were performed in order to evaluate the interaction between a library of drawn derivatives of 7ACC2 with a fluorine atom and MCT1. The most interesting compound was synthetized and characterized. Biological assays are ongoing and the radio-fluorination with 18-F will be performed soon.

However, the main drawback of 18-F being its very short emission half-life and its use limited to diagnostic applications, hence we have explored the the bifunctional chelator (BFC) approach to envision Copper (II) isotopes radiolabelling. This would indeed allow to perform both diagnosis and therapy exploiting different copper radionuclides (64-Cu and 67-Cu), reaching the so called “theranostic-pair approach”. A chelating system suitable for Copper (II) must be grafted on the targeting vector while reducing the impact on the interaction with the target protein as much as possible. A specific design of the chelator must then be used including to preserve the overall charge of the radiopharmaceutical. For such a goal, an “in-house” bifunctional polyazamacrocycle, namely *no3py* and its new analogue bearing sulfonic pendants (*no1py2pys*) to allow a neutral chelate will be conjugated to the targeting vector using a PEG chain as a spacing linker.

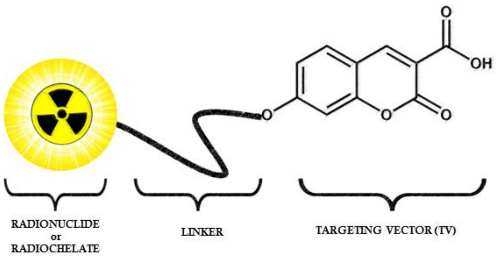

Figure 1 Bifunctional chelator approach

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Sulfur-functionalized N-heterocyclic carbene complexes of Ru(II): coordination mode & catalytic activity

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Keywords: ruthenium, N-heterocyclic carbene, catalysis

N-heterocyclic carbenes (NHCs) are recognized as good ligands for their remarkable thermal stability, tunable steric and electronic properties and high sigma-donor propensity. Combined with transition metals, they have numerous applications in catalysis.[1] Although most NHCs are monodentate ligands, the chemistry of hybrid NHCs bearing an additional Lewis base site (often anchored to an N, P or O atom) has attracted considerable interest over the past decade and continues to do so today.[2] S-functionalized NHCs are still a less exploited class of ligands,[3] but they have nevertheless 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 and sulfur functionalized NHC ligands. The intrinsic prochirality or chirality of the ruthenium and sulfur centers (upon coordination) is expected to lead to a complex diastereomeric mixture. In this work, a series of cationic (κ^2-C,S)[Ru(II)(η^6-cymene)(NHC-S][PF_6] complexes have been prepared and fully characterized. Interestingly, in each case only one diastereomer (in the form of an enantiomeric pair) was observed. DFT calculations, VT-NMR and X-ray diffractometry were performed to discuss the factors (hemilability, sulfur inversion, steric, etc.) that might control this selectivity.

Finally, these ruthenium complexes were evaluated for their catalytic activity in various acceptorless dehydrogenation transformations.[5]

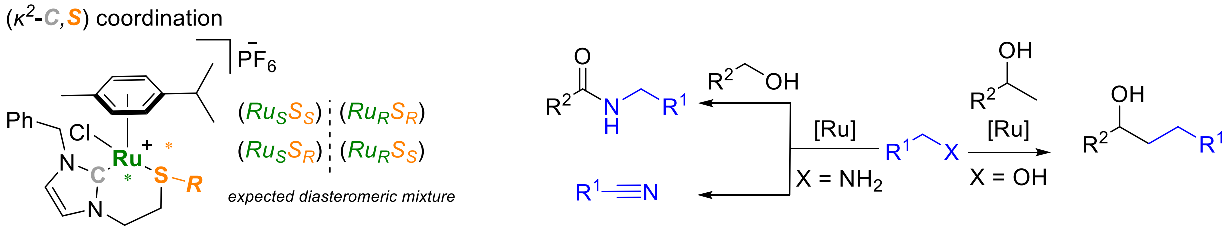

Figure 1 (Ru(II)(η^6-cymene) complexes) and their applications in catalysis

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CLUSTERING SIX ELECTRONS WITHIN "DAWSON-LIKE" POLYOXOMETALATE

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Keywords: Polyoxometalates; Electrochemistry; Multinuclear NMR; PCET process; Metal-metal bonds

Text: Polyoxometalates (POMs) represent one class of fascinating inorganic compounds built from transition metals in their highest oxidation states (V^{5+}, Mo^{6+}, and W^{6+}). One of the most striking properties of POMs is their ability to exchange massively electrons in aqueous solution, making them highly relevant "electron reservoirs" for developing innovative electrochemical energy-storage systems such as redox flow batteries. For instance, the Cronin's team has recently demonstrated that the classical Dawson-type POMs $[P_2W_{18}O_{62}]^{6-}$ can accept up to 18 electrons without POM decomposition.[1,2] Curiously, the fundamental investigations about the structure and reactivity of such super-reduced POMs remain largely unexplored. [3] The purpose of my PhD project is to fill this lack of knowledge.

In this communication, we will show that the "Dawson-like" POM $[H_2AsW_{18}O_{60}]^{7-}$ can undergo a disproportionation process during its massive electron uptake, leading to species containing three metal-metal bonds as evidenced by X-ray diffraction, multi-nuclear magnetic resonance spectroscopy (^1H and ^{183}W NMR), extended X-ray absorption fine structure (EXAFS), UV-vis, and voltammetry techniques. [4] This result evidences that electron storing within metal-metal bonds is not a unique property of Keggin-type POM as postulated since the 70s. Besides, we will demonstrate that the presence of an electron-rich triad in the "Dawson-like" POM allows its post-functionalization with additional tungstate ions, generating a chiral molecule that is also the largest W^{IV}-containing POMs known to date.

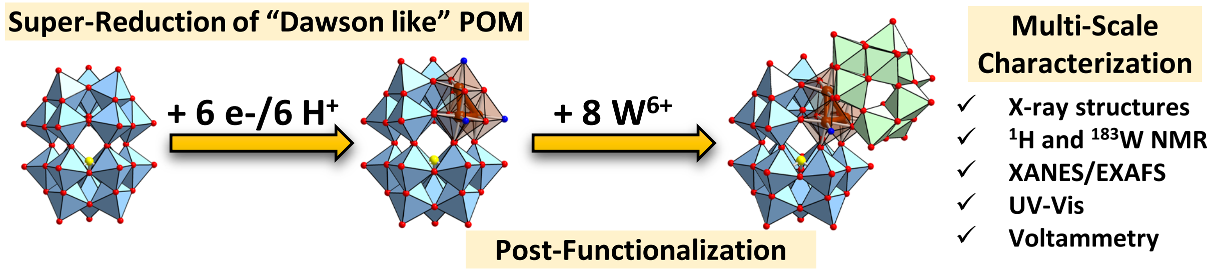

Figure 1 left) Schematic representation showing the formation of $[AsH_2W_{18}O_{60}]$-VI', compound induced by the six-electron reduction of $[AsH_2W_{18}O_{60}]^{7-}$ in acidic solution and **left)** all characterizations done on the six-electron reduced compound.

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Confining Cavity-shaped Ligands for the Selective Metal-Catalyzed Oligomerization of Ethylene

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Site web : https://institut-chimie.unistra.fr/equipes-de-recherche/ecmc-confinement-moleculaire-et-catalyse/

Keywords: Cyclodextrin, phosphine, metal encapsulation, ethylene oligomerization

P,N and diphosphine bidentate ligands have been built on methylated α- and β-cyclodextrin (α- and β-CD) platforms.[1],[2] Thanks to the particular orientation of their donor atoms lone pairs, these cavity-shaped ligands are able to form *cis*-chelate complexes with various d^8 metal cations within the CD cavity. In stark contrast with cavity-free analogs, metal inclusion in the CD cavity was shown to promote exclusive formation of 1:1 CD ligand/metal chelate complexes at the expense of bis(phosphine) ones. The catalytic properties of all cavity-shaped nickel(II) complexes were tested for ethylene oligomerization with alkylaluminum compounds (MMAO and MAO) as cocatalysts and compared to their cavity free analogs. Unlike the latters, the cavity-shaped catalytic systems were shown to promote the formation of α-olefins (up to 91 % of 1-butene) and proved to be very robust.

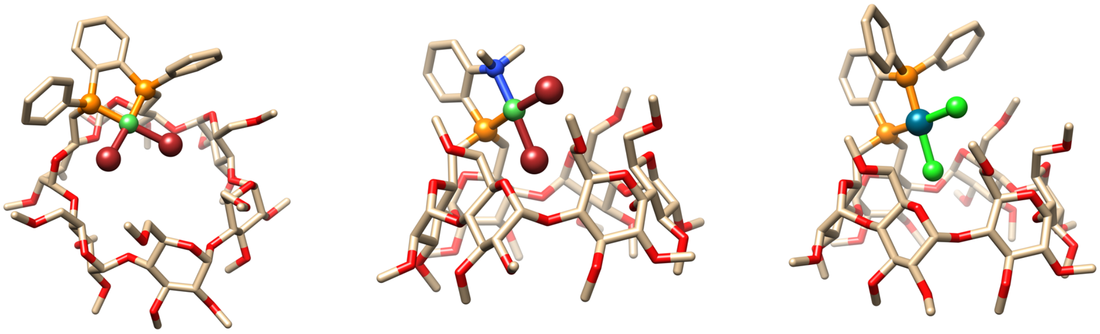

Figure 1 X-ray crystal structures of cavity-shaped, *cis*-chelate Ni(II) and Pd(II) complexes displaying metal encapsulation.

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New Au(I)NHC-peptide conjugates for a potential targeted anticancer therapy

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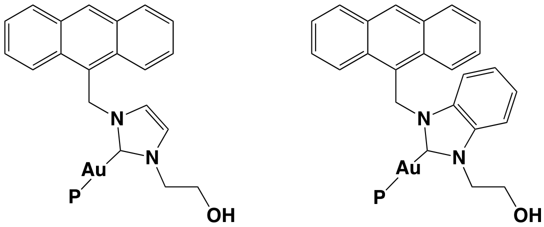
Keywords: anticancer treatments; gold(I) complexes; targeting peptides.

In recent decades, a growing interest in Au(I)-based complexes arose as promising candidates in the search for new anticancer therapeutic drugs. Although the mechanism of action for which gold-based compounds causes cellular apoptosis in cancer cells has not been completely clarified yet, it is commonly accepted that thioredoxin reductase (TrxR) inhibition plays a pivotal role. [1] At the physiological level, this mitochondrial enzyme maintains the cell's redox homeostasis; interestingly, it is often overexpressed in tumour cell. In searching for selective anticancer treatments, targeting strategies are worthwhile to explore. The latter involves the identification of specific molecular biomarkers that are overexpressed in cancer cells and the designing of drugs that can interact specifically with them to obtain a preferential drug's accumulation and selective activity on cancer cells. In this project, we present six new conjugates (Figure 1) where two Au(I)-based complexes were linked to three different targeting peptides. The first peptide, C-βAla-RGD, is largely used to target the integrin receptors, frequently overexpressed on several cancer cell lines.[2] The second selected peptide, CrFrFrF, can potentially target mitochondria, allowing the drug to accumulate in this organelle, where TrxR is mainly present.[3] The third strategy involves the conjugations to PRLcYSWHE; indeed, the luteinizing hormone-releasing hormone (LHRH) was employed as a targeting moiety to recognize LHRH receptors, overexpressed on the plasmic membrane of ovarian cancer cells.[4] Biological tests on ovarian cancer A2780S and A2780R cell lines, respectively sensitive and resistant to cisplatin, were carried out to evaluate the cytotoxicity of the six conjugates, comparing the results with those of the free complexes not bearing the peptides. The same tests were performed on HSkMC, a healthy cell line, to assess the selectivity index.



1 a-c **2 a-c**

1a P= C-β-RGD
1b P= CrFrFrF
1c P= PRLcYSWHE

2a P= C-β-RGD
2b P= CrFrFrF
2c P= PRLcYSWHE

Figure 1 structures of the six new Au(I)NHC-peptide conjugates

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A Chiral [2 + 3] Covalent Organic Cage Based on 2,2'-BINOL Units

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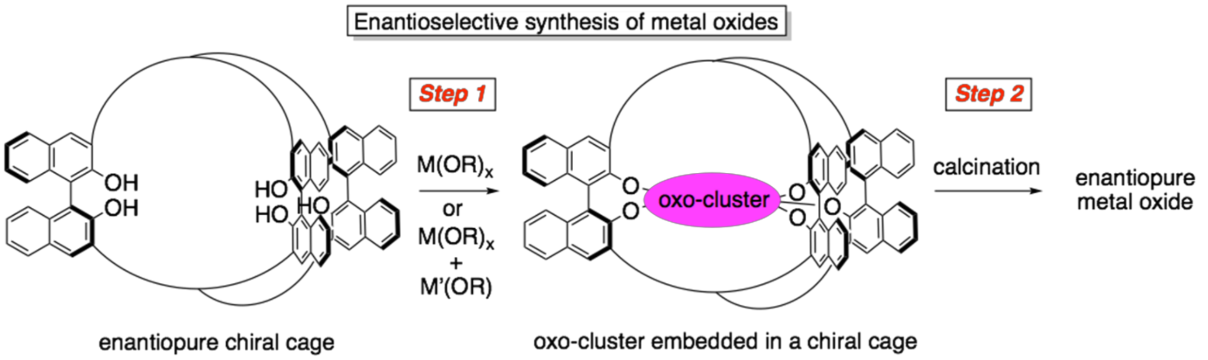
Keywords: covalent organic cage, self-assembly, chirality

Chiral covalent organic cage is an emerging class of architecture with various applications such as gas separation, chiral separation, and catalysis.[1] Combining dynamic covalent chemistry and chiral building blocks, self-assembly of chiral cages can be achieved.[2] We designed chiral cages for the development of a general strategy combining self-assembled cages and oxo-cluster chemistry to access enantiopure inorganic materials. Chiral information transfer from the covalent organic cage to the oxo-cluster embedded inside the cage cavity can be envisaged through the coordination of transition metals with coordination sites covering the cavity of the cage. Then, after a step of calcination, the purely inorganic material can be obtained. In this contribution, dynamic imine bonds and 1,1'-bi-2-naphtol derivatives as the chiral building block were used for the self-assembly of an enantiopure [2+3] cage with the OH groups pointing inside of the cage. The imine bonds were further reduced to afford a stable amine cage which can be used to explore different types of enantiorecognition processes.



Proposed strategy for the elaboration of enantiopure inorganic materials using chiral covalent cages.

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Ni^{II} PNP-pincer complex as CO$_2$RR electrocatalyst

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Keywords: CO$_2$RR; Electrocatalysis; Nickel complex; Pincer.

The conversion of carbon dioxide into chemical feedstocks and fuels is critical due to the increasing concentration of greenhouse gases in the atmosphere. One viable approach involves the electrocatalytic reduction of CO$_2$, also known as CO$_2$ reduction reaction (CO$_2$RR), utilizing molecular catalysts based on non-noble transition metals. In this regard, only a few examples of pincer-supported (N/C-donor) nickel complexes are reported as CO$_2$RR homogeneous electrocatalysts. [1-4]
This ligand platform represents an appealing alternative in molecular catalysis, thanks to the robustness of the tridentate geometry and the tunability in both electronic and steric properties.
We have thus explored the CO$_2$RR activity of a Ni^{II} complex bearing a Milstein–type pincer ligand (Figure 1, a) in DMF and acetonitrile. Weak acids namely water, phenol and trifluoroacetic acid were tested as proton sources. As shown by cyclic voltammetry (Figure 1, b) the complex reduces CO$_2$ in wet DMF. Controlled potential electrolysis (CPE) highlighted the selectivity towards the formation of two-electron-reduced C$_1$ species over the hydrogen evolution reaction (HER). Further analysis *via* gas cromatography, NMR and ion cromatography are currently ongoing. Mechanistic insights are provided by spectro-electrochemistry and EPR experiments.

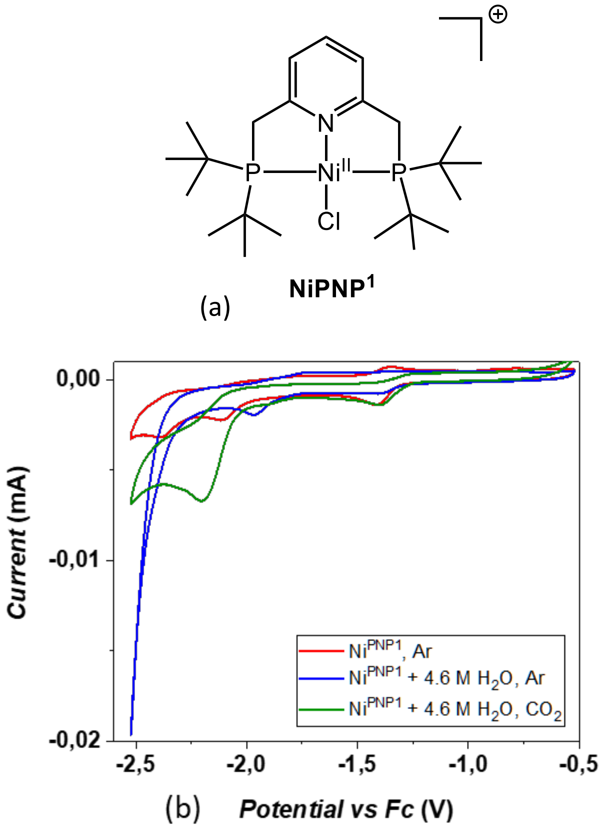

Figure 1 (a) Ni^{PNP1}, (b) CVs indicating CO$_2$RR activity for Ni^{PNP1}

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FUNCTIONAL LIGANDS BASED ON 2,1,3-BENZOTHIADIAZOLE FOR LUMINESCENT AND MAGNETIC COMPLEXES

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Keywords: 2,1,3-benzothiadiazole, Schiff bases, transition metal complexes, luminescence, magnetic properties

Text: 2,1,3-benzothiadiazole (BTD) is a well-known electron acceptor fluorophore.[1] The association of coordinating groups with BTD unit, extensively used in the structure of molecular precursors or polymers for organic electronics and also in redox switchable donor-acceptor systems, finds interest in the access to functional ligands and derived complexes.

Our strategy is to synthesize functional ligands containing the BTD moiety in order to access novel complexes provided with photophysical and magnetic properties.

The work presented here focusses on the synthesis and characterization, together with DFT calculations, of two families of chelating ligands, bearing BTD unit (Fig. 1) and their transition metal complexes with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) centers. The photophysical and magnetic properties of the new complexes will be presented.[2-5]

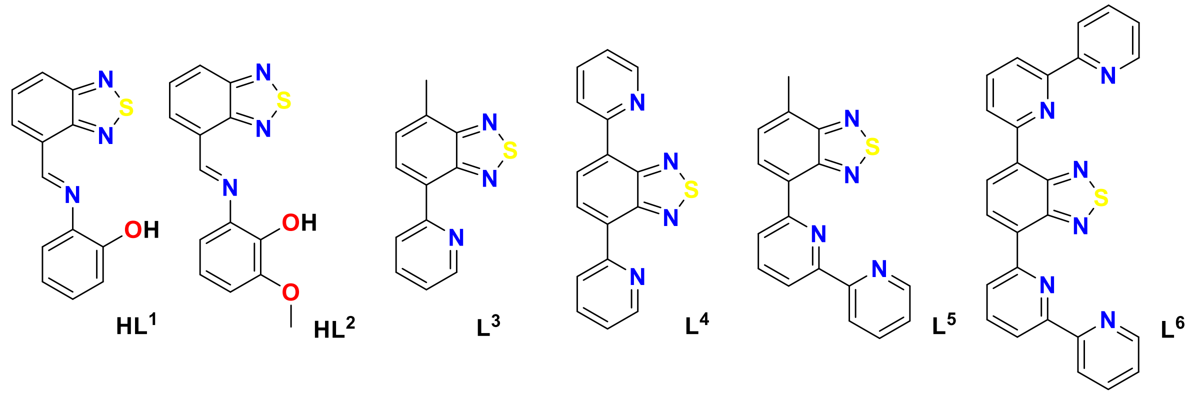

Figure 1 Ligands developed in this work.

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Cationic gold catalysis enhanced by ionic liquid media: a convenient system for direct hydroarylation of alkynes

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Keywords: gold catalysis; alkynes; hydroarylation; ionic liquids

Cationic gold catalysis has experimented a rapid development in the last two decades. The high π-acidic character of gold species opened a whole series of opportunities for hydrofunctionalizations of unsaturated molecules.[1] Among them, our research group is interested in the direct hyroarylation of alkynes with (hetero)arenes[2] as an alternative synthetic route for organic synthesis: direct access of coumarins was selected as a case study (**figure 1**, **A**). Ionic liquids are here employed as reaction media due to their ability to stabilize the cationic species in solution, together with a favorable environment for the proton transfer (**figure 1**, **B**).[3] As an overall effect, enhanced catalytic activity and increased stability of the system are recorded.[4]
We present here a detailed analysis of the medium structure effect on the system behavior. Parametrization of the system was achieved by taking standard descriptors that are found in the literature. In particular, the affinity toward gold and the H-accepting ability of anions[5] were considered together with the average polarity of the medium and its microstructural organization in polar/unipolar microdomains[6]. As well, the presence of Brønsted acid additive was considered as a further variable.
This analysis led to interesting results, allowing us to reach high catalytic activities at gold complex loads down to 0.01mol%. Further analyses demonstrated the opportunity to swap the chemo-selective behavior of a series of substrates (*para*-methoxy-aryl alkynoates) to the formation of spirocyclic structures,[7] enhancing the synthetic potential of our system. A better understanding of these aspects can help us to accomplish tougher challenges, such as the activation of other electron-rich unsaturated molecules (*e.g.* isocyanates and nitriles).

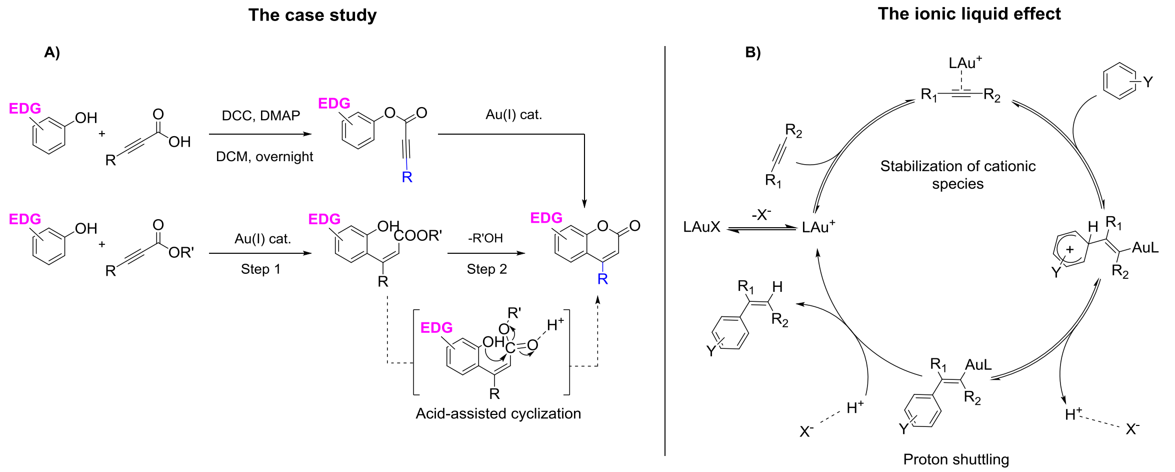
The case study **The ionic liquid effect**

Figure 1 **A)** Direct access of coumarins by hydroarylation of propiolic acid derivatives; **B)** Reaction mechanism and the ionic liquid effect;

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CO_2 CYCLOADDITION ONTO EPOXIDES WITH TRANSITION-METAL DERIVATIVES OF POLYOXOMETALATES

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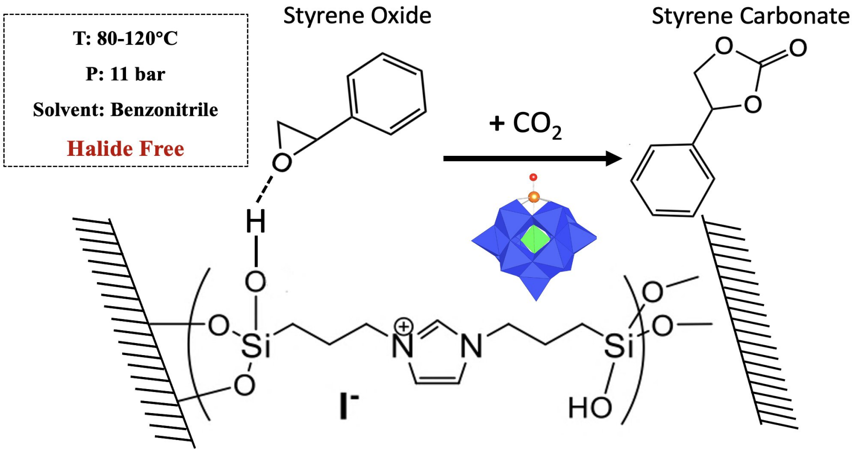
Keywords: Cycloaddition; Catalysis; Epoxides; Carbon dioxide; Polyoxometalates

Text: Cyclic carbonates are key compounds with a large scope of applications, such as monomers in plastics, solvents in paints or batteries, as degreasers or as organic intermediates for the synthesis of (poly)carbonates.[1] On the other hand, the large amounts of carbon dioxide released in atmosphere by human activities significantly contribute to the greenhouse effect. In this context, methods using CO_2 as a renewable, abundant C1-source to produce valuable chemicals, such as cyclic carbonates are regarded with large interest.[2] However, industrial production of cyclic carbonates/polycarbonates still uses C(IV) sources such as phosgene which is extremely toxic and gives rise to HCl.[3] A promising strategy to improve sustainability is the "one-pot" synthesis of cyclic carbonates from alkenes using oxidants and CO_2, referred as oxidative carboxylation cascade reaction which requires the successive use of oxidation (OxCat) and CO_2 cycloaddition catalysts (CyCat).[4] In this work, we focused in the conversion of epoxides into cyclic carbonates by reaction with CO_2. This process requires the use of efficient CyCat catalysts, among which transition-metal substituted polyoxometalates $[XW_{11}O_{39}M(H_2O)]n-$ (X = P, Si; M = Cr, Mn, Co, Ni, Zn) has been chosen. The main target was to find the optimal conditions to promote cycloaddition by controlling each factor separately during the reaction. Finally, in order to further improve the catalytic efficiency, immobilization of the transition metal substituted polyoxometalates CyCat onto silica support modified with cationic counter-ions was performed. Remarkably, this reaction was carried out in the absence of halides, the usual catalyst for CO_2 cycloaddition reactions. This opens up the possibility of coupling this reaction with a preliminary step of epoxidation of alkenes by H_2O_2 using the same catalyst, in an auto-tandem catalysis-type strategy.



T: 80-120°C
P: 11 bar
Solvent: Benzonitrile
Halide Free

Figure 1 Experimental conditions for CO_2 cycloaddition onto styrene oxide by $(R_4N)n[XW_{11}O_{39}M(H_2O)]$

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Group IV Complexes with Sterically Congested *N*-Aryl-adamantylcarbamidate Ligands

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Keywords: amidate; group IV metal; hydrofunctionalization reactions

Many researchers have shown keen interest in the amidate complexes of group IV metals because of their potential uses in polymerization and hydrofunctionalization reactions, including inter- and intra-molecular hydroamination.[1-3] This can be attributed to the ease of synthesis of amide proligands and the efficient preparation of group IV metal amidate complexes by a protonolysis method. Therefore, we were interested in synthesizing the proligand *N*-(2,6-dibenzhydryl-4-tolyl)adamantane-1-carboxamide (**HL**) and the corresponding group IV metal complexes.[4] Metalation with $M(NMe_2)_4$ (M= Ti, Zr, and Hf) led to $TiL(NMe_2)_3$ (**1**), $ZrL_2(NMe_2)_2$ (**2**), and $[HfL_2(NMe_2)_2]\cdot 5Tol$ (**3**). Indeed, compound (**1**) is the only example to date of an amidate complex with a tetracoordinate titanium metal center, whereas the metal centers in compounds (**2**) and (**3**) are both in distorted octahedral coordination environments. Interestingly, the amidate ligand shows a different coordination mode in the titanium complex (**1**) when compared to Zr and Hf congeners (Figure 1). Due to the unique structure of compound (**1**), we investigated the activity of this compound in metal-mediated intermolecular hydrofunctionalization reactions. Although the title compound has a weakly shielded titanium center, it undergoes decomposition when subjected to intermolecular hydroamination and hydrophosphorylation of alkynes via the preferred protonation of the adamantylamidato ligand (yielding HL) to release the intramolecular steric strain introduced by this bulky amidato ligand.

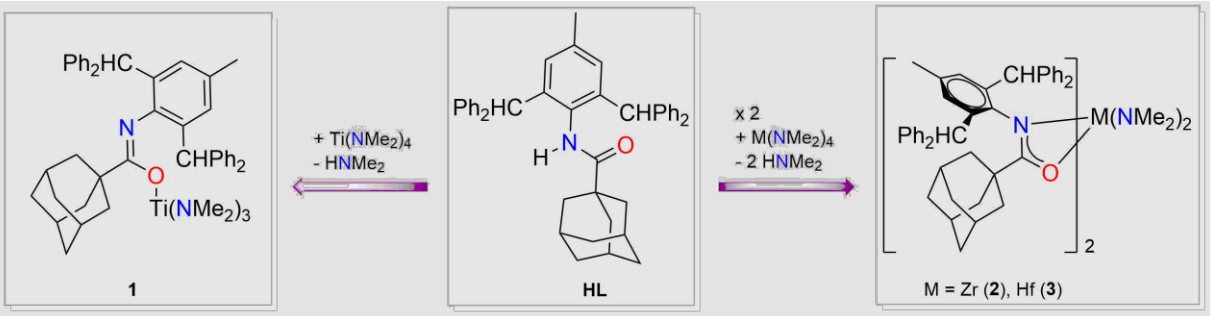

Figure 1 Synthesis route of the group IV complexes containing the bulky adamantylamidate ligand by metalation of **HL** with $M(NMe_2)_4$ (M = Ti, Zr, Hf)

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NHC-Au(I) complexes with long alkyl chains for catalysis in confined space

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Keywords: Gold, NHC, Catalysis, Alkyne, Supramolecular.

The capability of NHC-gold(I) complexes to activate alkynes towards several transformations is well known.[1] The interaction of transition metal complexes with supramolecular structures could enable new catalytic performances compared to traditional homogenous systems, taking advantage from the spatial confinement of the catalyst, which imparts enzyme-like selectivity (i.e. substrate selectivity, regioselectivity and stereoselectivity).[2] For example, it was previously reported that NHC-gold complexes inside resorcinarene capsule showed different selectivity for alkynes with similar electronic properties, but with different shape and steric hindrance.[3] In this contribution we synthesize two types of complexes bearing on the NHC ligand a long alkyl chain able to interact with either resorcinarene capsule or monolayer-protected gold nanoparticles (AuNP) (Fig. 1). In the first case the catalyst interacts with the capsule through weak non-covalent bonds, while in the second case the complex is grafted on the nanoparticle's surface thanks to a thiol group. In the latter catalytic system, the forced proximity between the metal centres is expected to also favour the cooperativity phenomenon. The long alkyl chain is of interest because it can assume more conformations thanks to its flexibility.

Finally, the catalytic results of these systems in the hydration reaction of alkynes will be discussed in terms of activity and selectivity for substrates and products.

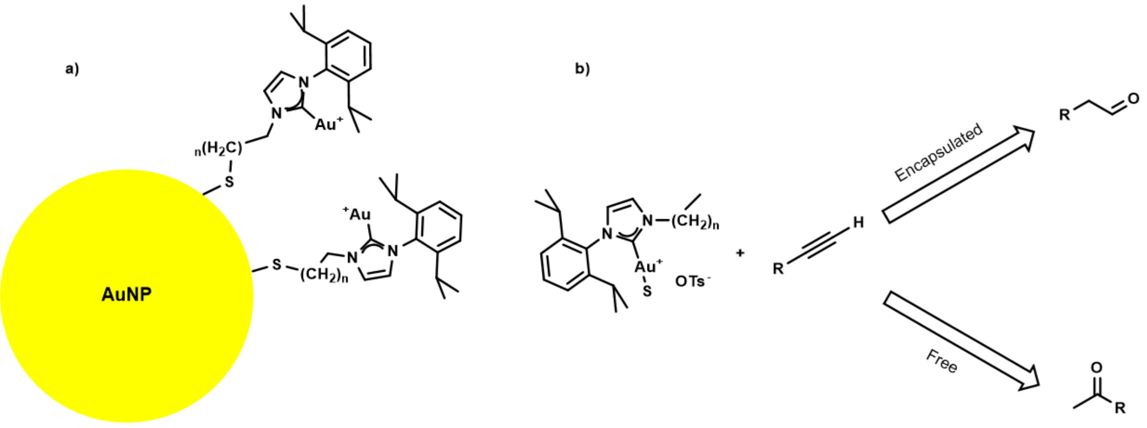

Figure 1. a) Gold complexes grafted to nanoparticle's surface. b) Hydration reaction of alkynes with encapsulated and free catalyst.

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Kinetic study: the dehydrocoupling of hydrosilanes and terminal alkynes with alkaline earth catalysts

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Keywords: dehydrocoupling, catalysis, rate of reaction, polymers, solvent-dependent reactions

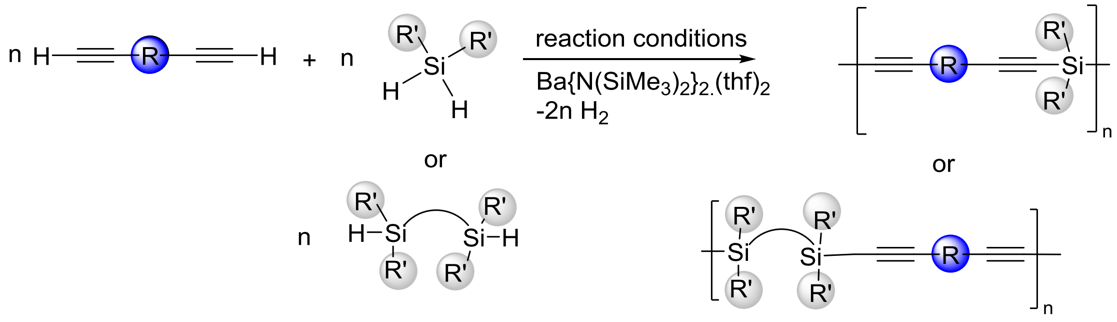
Based on this approach, the synthesis of dehydrocoupling reactions began with two benchmark substrates which are phenyl acetylene and dimethylphenylsilane. While the optimization of reaction parameters, dehydrocoupling between those substrates in the presence of $Ba\{N(SiMe_3)_2\}_2.(thf)_2$ catalyst was successfully achieved but we faced few challenges as well in the beginning it observed the reactions was sluggish even with 10% mol catalyst concentration and it came up that this type of dehydrocoupling is solvent dependent. Among all the solvents were used to make the dehydrocoupling faster, pyridine was the best all of them. However, S. Harder reported, about the reactivity of pyridine with hydrosilanes [1], to overcome this challenge we use all the possible spectroscopic methods to identify the reactivity of pyridine in our reaction for instance ^1H NMR, ^{29}Si NMR and Mass spectroscopy to make sure about the desirable product and not formation of side products. We also tried the benchmark reaction with several pre-catalysts in kinetic scale and compare their rate constants. It noticed that $[Ba\{N(SiMe_3)_2\}_2.(thf)_2]$ was the most active and efficient catalyst among all.

Moreover, to get the best reactivity in pyridine, we test via changing the various external parameters of the reaction for instance concentration of catalyst, temperature and reaction time. The best reaction conditions according to experimental data were 86% conversion in 16H with 5% mol concentration of catalyst.

The kinetic data tells, this dehydrocoupling reaction follows first order kinetics with respect to both substrates and Barium catalyst as well.

$$\text{rate}= k\,[\text{phenyl acetylene}]^{1}\,[\text{hydrosilane}]^{1}\,[\text{Ba}]^{1}$$

Eventually, the main objective of this project to synthesis of polymers, very few examples are already in literature [2] and study the applications of those polymers.



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Spectroelectrochemical mechanistic insights of CO_2 reduction to CO by an Fe porphyrin

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Keywords: CO_2 reduction; mechanism; iron porphyrin; spectroelectrochemistry

The in-depth study of the electrochemical reduction of carbon dioxide (CO_2) to carbon monoxide (CO) and other C1 products provides efficient ways to better control the CO_2 reduction reaction (CO_2RR) and to further develop the production of fuels and of chemical feedstocks. Molecular catalysts based on earth-abundant metals are the focal point of attention at the Laboratoire d'Electrochimie Moléculaire (LEM) for achieving these goals. Decades of electrochemical research have proven iron porphyrins to be exceptional homogeneous catalysts for the electrochemical reduction of CO_2 to CO.[1] Among them, [Fe(pTMA)Cl]Cl_4 is one of the most efficient and selective catalyst (Fig.1, A) to date.[2],[3] Despite noticeable advances provided by electrochemical studies for understanding the mechanistic aspects of the process, the lack of spectroscopic signatures prevents from catching the structures of intermediates along the catalytic cycle. In this connection, spectroelectrochemistry (SEC) is a powerful tool to collect data to further elucidate this mechanism.[4]

We will present our most recent results obtained in closed collaboration with Uppsala University. The combination of mid-infrared and UV-Visible SEC has enabled us to successfully detect Fe^n-CO intermediates (n = II, I, "0", Fig. 1, B). The nature of these intermediates has been carefully explored by comparing experiments carried out under CO atmosphere, then allowing to establish a detailed catalytic cycle.

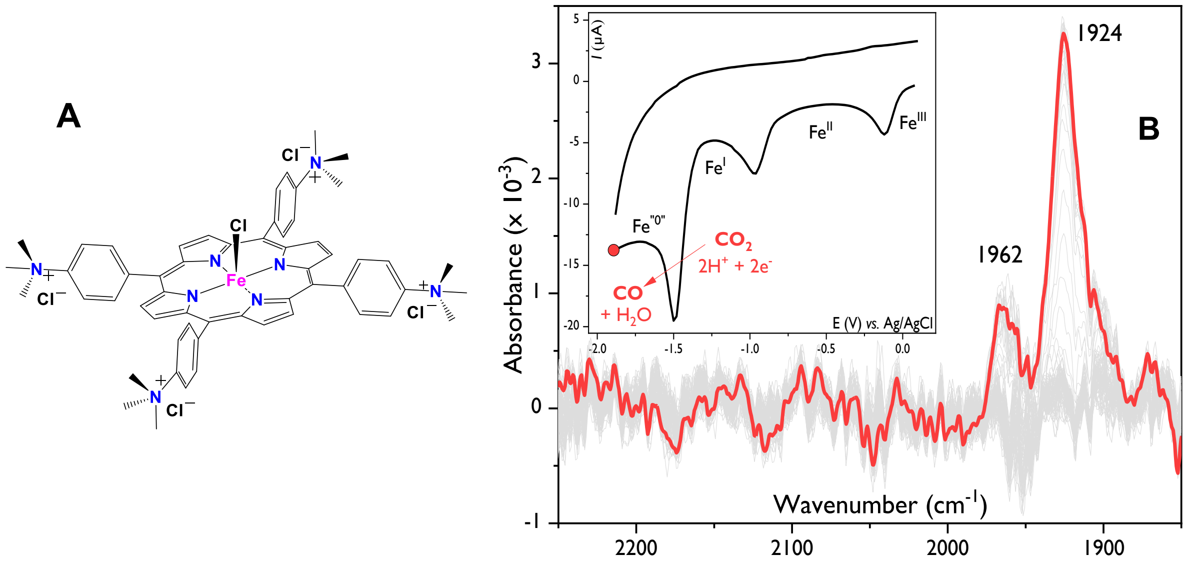

Figure 1. **A**) Structure of [Fe(pTMA)Cl]Cl_4. **B**) MIR spectrum obtained under *operando* conditions during the CO_2RR to CO catalyzed by FepTMA. Solvent = DMF/$TBAPF_6$, atmosphere = CO_2, applied potential = -1.85 V *vs.* Ag/AgCl.

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IRREVERSIBLE THERMAL ALTERATION OF SOLID STATE LUMINESCENCE IN POLYMETALLIC COPPER(I) COORDINATION POLYMER

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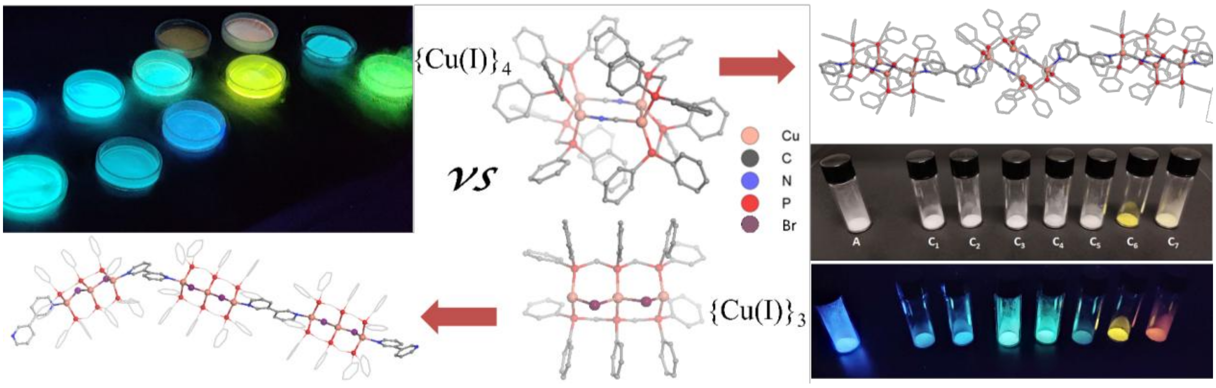
Keywords: Cu(I), Luminescent materials, Coordination polymers, Thermal transition

There is a growing focus on exploring Cu(I) ion assemblies, which have emerged as promising and innovative luminescent materials suitable for a wide range of applications, such as illumination and stimuli-responsive sensor technology taking advantage of both the various photophysical properties, and the large flexibility of the coordination sphere exhibited by this ion.[1] By using specific pre-assembled luminescent $\{Cu(I)\}_n$ polymetallic precursors (n = 3,4), two distinct series of photoactive Cu(I) coordination polymer [3] will be presented. These polymeric assemblies present, in particular, an original and general irreversible non-destructive solid-state transition of their luminescence properties that opens appealing perspectives for innovative solid-state temperature sensors' design.[4]



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Copper(II) complexes of chloro-oxo-dihydroquinoline-hydrazones ligands as effective cytotoxic agents

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Keywords: Cu(II) hydrazone complexes; X-ray-structures; biological activity; cytotoxicity tests

Hydrazones represent an important class of compounds in medicinal chemistry with great potential for chemotherapeutic applications due to the great variety of functional groups in the X-C(Z)=N-NH-C(=O)-Y structure, thus modulating chemical, physical, and coordination properties.[1,2] In recent years, a wide variety of mononuclear and polynuclear copper complexes containing aroylhydrazone-based ligands have been described and their biological activity investigated. Among them, significantly low IC50 values were observed for the derivatives with 2,6-dimethyl-phenyl aniline as Y moiety and halogen atoms in the aroyl X group.[3]

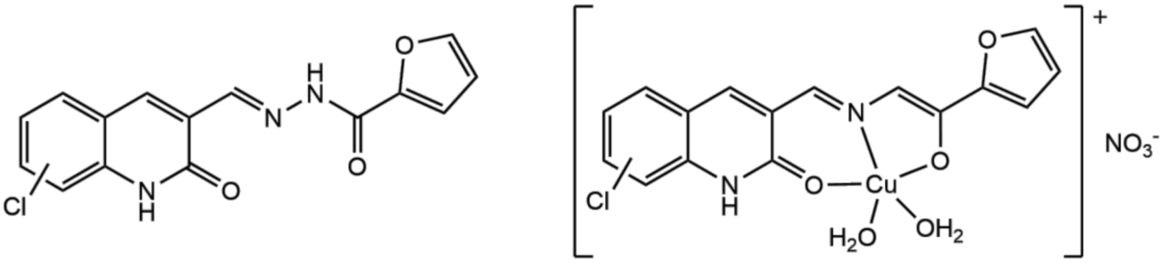

Figure 1 General structure of the dihydroquinoline-hydrazone ligands and their copper(II) complexes.

We report the preparation of the new 6- and 7-chloro-2-oxo-1,2-dihydroquinoline-3-hydrazone derivatives bearing a furane Y moiety, and the corresponding Cu(II) complexes. They have been characterized in terms of X-ray structure and solution behavior with the support of DFT calculations. The new complexes showed very promising cytotoxic activity against human colon (HCT-15), lung (H1573), pancreatic (BxPC3 and PSN-1), ovarian (A2780), and colorectal (LoVo) cancer cell lines and their resistant sublines.

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Azaullazine Ligands toward Panchromatic Iron(II) Complexes

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Keywords: Azaullazines, Iron complexes, N-heterocyclic carbenes

Over the past decades, there has been a growing interest in using Iron(II) complexes as potential chromophores and sensitizers, mainly due to the abundance and cost-effectiveness of iron. Unfortunately, most iron(II) polypyridines have proven to be ineffective chromophores, as their excited photoactive metal-to-ligand charge transfer (MLCT) states quickly decay into non-photoactive metal-centered (MC) states.[1] Various approaches have been developed to enhance their photophysical properties, such as broadening the absorption spectrum, increasing molar extinction coefficients and prolonging the excited state's lifetime. One promising strategy involved substituting the pyridine ring with N-Heterocyclic carbenes, which possess a robust σ-donating effect, resulting in destabilization of the MC states over the MLCT states.[2] Additionally, achieving panchromaticity, which is essential for photophysical applications, would be attained upon increasing the conjugation within the ligand.[3] Recently, our research group successfully developed the synthesis of azaullazine derivatives, which consist in a fused and planar heterocycle isoelectronic to pyrene. [4-5] Herein, we report for the first time, the synthesis and photophysical characterization of homoleptic Fe(II) complexes involving azaullazine as new ligands and displaying a remarkable broad absorption spectrum (Fig 1).

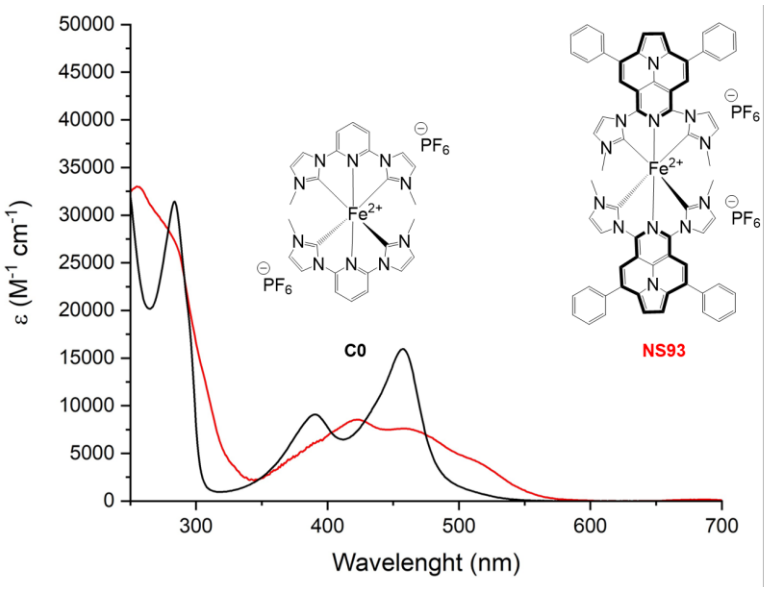

Figure 1. *UV-vis spectrum of azaullazines-based complex NS93 in comparison with the pyridine-based analog C0*

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SYNTHESIS AND EVALUATION OF NEW LEAD-212 CHELATORS

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Keywords: lead-212; acyclic chelators; DACH;NMR; theranostics.

Text: In cancer treatment, receptor-targeted image-guided radionuclide has gained recognition as a promising approach. In particular, for cancer therapy, the use of α emitters shows several advantages over β^- ones, in fact the short range of αradiation in tissue (<0.1 mm), together with their high energy and high linear energy transfer allow a selective and effective cancer cells killing and the consequent reduction of side effects in the surrounding environment [1]. Generator-produced lead-212 ($t_{1/2}$ = 10.6h), which decays via β^- particle emission to ^{212}Bi that itself can be used as *in-situ* generator for αparticles, is a promising radionuclide for alpha-therapy. Interest in ^{212}Pb is also encouraged by another imaging radioisotope, ^{203}Pb ($t_{1/2}$ = 10.6h), that undergoes decay via an electron capture suitable for SPECT imaging. Therefore, this offer a possible theranostics pair combining the capability of both isotopes [2].

The development of lead chelator has primarily focused on macrocyclic ligands, including the well-established DOTA, known to coordinate Pb^{2+} with high thermodynamic stability, but prone to acid catalyzed dissociation, and TCMC, whose complex with Pb^{2+} remains stable under acidic conditions[3]. However, there has been an increasing interest in alternative ligands that can better satisfy the stringent demands on the metal chelator for its application with lead isotopes in nuclear medicine. Recent works have focused on developing nonmacrocyclic ligands which are capable of forming rapidly complexes with the metal of interest, while rigid enough to remain inert in vivo.

In the present study, new chelators for Pb^{2+} complexation have been synthetized and thoroughly characterized. This new class shows as scaffold (1R,2R)-N,N'-**b**is(**p**yridin-2-ylmethyl)-1,2-**c**yclohexanediamine (H_2bpc), which allows to maintain rigidity within the structure. The amine position has been differentially functionalized to give the desired chelators.

In the present study, the synthesis of new potential chelators for lead is reported, together with their complete characterization. The acid/base behavior of the new chelators, the kinetics and the thermodynamics of metal-complexation have been investigated by UV-vis spectroscopy and ^{1}H/^{13}C NMR.

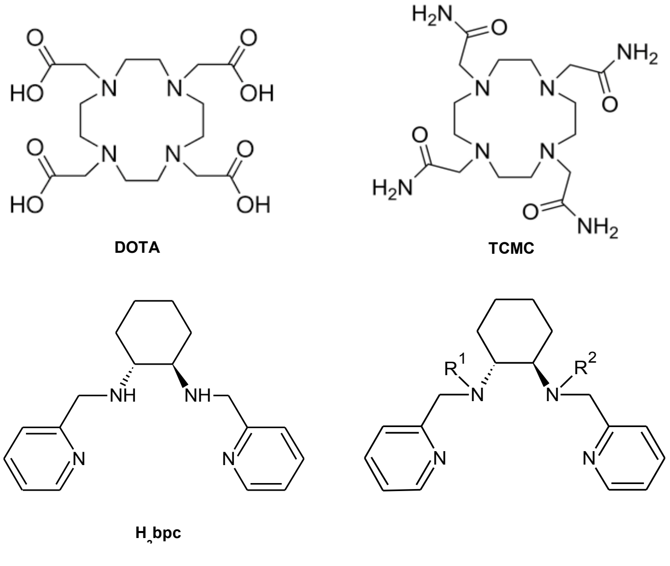

Figure 1 Structure of the ligands reported in this work.

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Impact of Deep Eutectic Solvents on Metal-Organic Framework Synthesis and Properties

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Keywords: Metal-organic frameworks, Deep Eutectic Solvents, Porous materials, Crystal morphology

Deep Eutectic Solvents (DESs) represent an emerging class of solvents featuring some characteristics of their ionic liquid cousins - low vapor pressure, relatively wide liquid range, non-flammability and the ability to dissolve polar species - along with unique specificities, such as their limited toxicity and an improved biocompatibility [1]. Their use as media for the ionothermal preparation of Metal-Organic Frameworks (MOFs) has been recently explored, showing that not only DESs represent green and less toxic alternatives to solvents commonly used in the synthesis of these porous crystalline materials, but also that they may play different roles in the MOF construction [2]. Aiming at further investigating the potential of DESs for MOF synthesis and their impact on the properties of the materials, we are exploring their use for the preparation of prototypical MOFs as well as of new architectures [3-4]. For example, we have recently reported that the choline chloride/urea (1:2) DES and its analogue based on ethylene-urea can be used for the preparation of Mg-MOF-74 as well as of novel Ca-based MOFs. Interestingly, these mediums were shown to have an impact on the crystal morphology and textural properties, and were demonstrated to allow the preparation of otherwise water-sensitive materials [4]. These results and more recent efforts will be presented in this contribution.

Figure 1. Examples of MOFs prepared in DES [4]

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N-heterocycles Reduction Catalysis under Hydroboration conditions by Using well-defined anionic Al-H complexes

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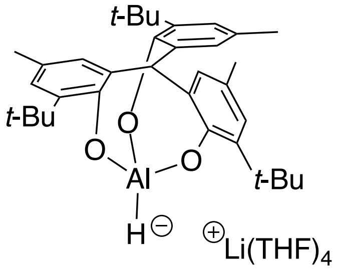
Keywords: Hydroboration; Pyridines reduction; Aluminum hydride complexes; Main group catalysis

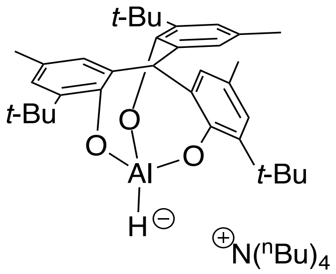
Synthetic methods for *N*-heteroarenes reduction have been accomplished by various catalytic reactions (hydrogenation, transfer hydrogenation, hydrosilylation, and hydroboration).[1] Among these methods, one of the most worthwhile organic synthons for various applications are organoboranes afforded by dearomative hydroboration of pyridines under mild conditions. Such approach has been gaining intensive studies.[2]

Aluminum species have long been known to mediate various chemical transformations in a catalytic manner, including reduction processes.[3] Since Al is the third most abundant metallic element and a cheap metal source, Al complexes have recently drawn considerable attention for novel catalytic applications.[4] To date, the use of Al-based complexes as catatysts for *N*-heteroarenes hydroboration catalysis, with the exception of a recent report by Nembenna in 2020.[5] Herein, we detail the first use of well-defined anionic aluminum hydride complexes (**A** and **B**, Figure 1) for the highly selective hydroboration catalysis of a wide range of *N*-heteroarenes (14 examples) under a low catalyst loading and neat conditions (solvent-free).

Catalyst **A**



Catalyst **B**



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STIMULI-RESPONSIVE PORPHYRIN TWEEZERS AND CAGES

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Keywords: Tweezer, cage, allostery, multi-switching, porphyrin

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

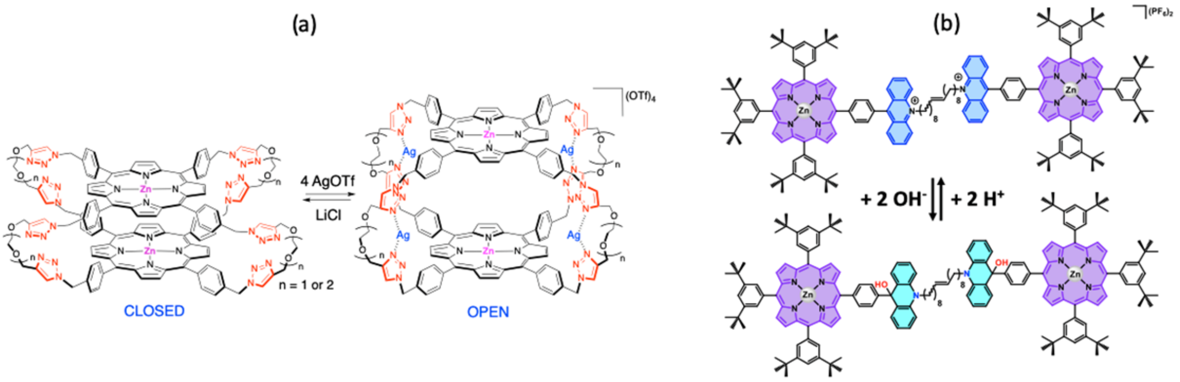

Figure 1. Stimuli-responsive (a) cages and (b) tweezers.

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INTERMOLECULAR BIMETALLIC COOPERATION FOR HIGHLY EFFICIENT AMINE-BORANES DEHYDROGENATION CATALYSIS

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Keywords: Manganese; *N*-heterocyclic carbenes; Homogeneous catalysis; Hydrogen production; DFT calculations

Cooperative bimetallic activation of inert bonds in organic molecules is one of fundamental principles of coordination chemistry largely exploited in metalloenzymes and related biomimetic systems. While these transformations mostly proceed in *intramolecular* fashion within well-defined binuclear metal complexes, few examples of *intermolecular* cooperative reactivity based on two monometallic species have been recently reported for heterobimetallic Frustrated Lewis Pairs[1] and Fe/Al radical couple.[2] We present herein a novel type of intermolecular bimetallic cooperativity observed in Mn-catalyzed dehydrogenation of amine-boranes (Figure 1), in which the concomitant activation of N−H and B−H bonds of the substrate proceeds by a synergetic action between cationic (**2^+**) and hydride (**3**) metal species generated *in situ* from the corresponding Mn(I) bromide precursors **1**, halide abstractor and bifunctional substrate as hydride donor.[3] According to spectroscopic, kinetic and theoretical data the formation of the ternary adduct **4^+** represents a key step of this process allowing to form dihydrogen and regenerate starting **2^+**/**3** couple by a sequence of proton and hydride transfers.

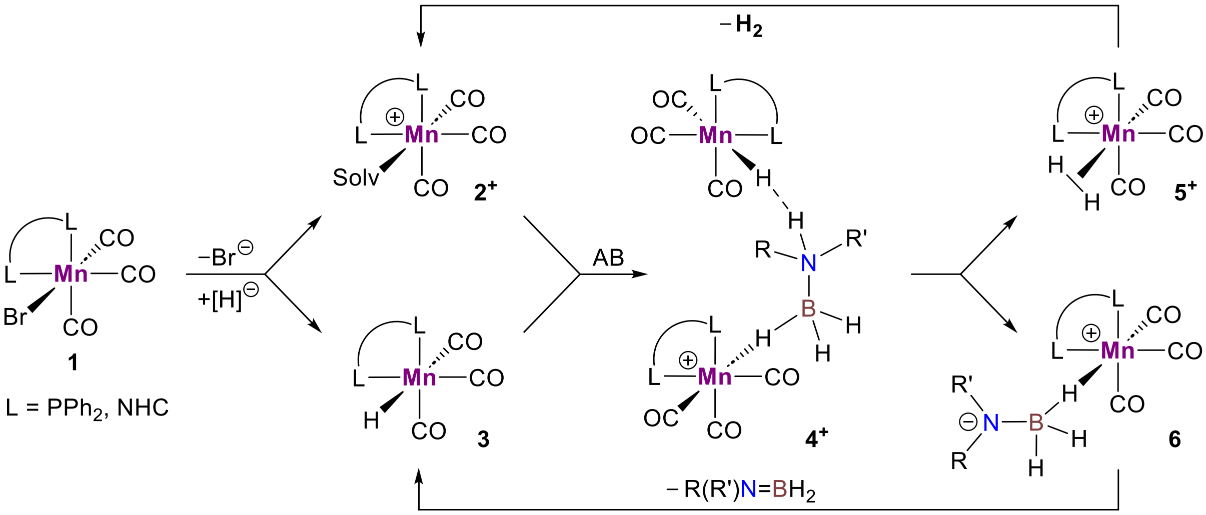

Figure 1. Reaction mechanism for amine-borane dehydrogenation catalyzed by Mn(I) complexes **1** bearing bidentate ligands

The catalytic system based on air-stable Mn(I) bis(NHC) complex **1** and $NaBPh_4$ shows state-of-the-art performance for a wide variety of amine-boranes at low loading (0.1 mol% to 50 ppm, TON up to 18200) and does not require the activation by strong bases or UV-irradiation typical for other 3d metal catalysts, thus making an important step towards the potential applications in the area of hydrogen storage.

The work was financially supported by CNRS and Russian Science Foundation (grant no. 22-73-00072). E.S.G. is grateful to the French Embassy in Moscow for a joint PhD fellowship (Vernadski program). Computational studies were performed using HPC resources from CALMIP (grant no. P18038).

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Modification of the terminal functionality of desferrioxamine B for the synthesis of new Zr4+ chelators for applications in PET imaging

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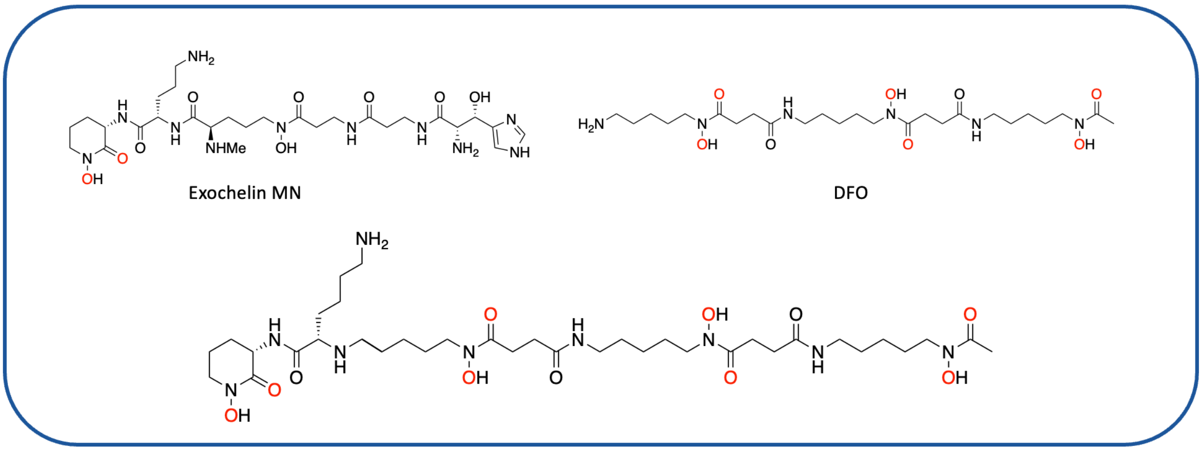
Keywords: Zirconium, siderophore, PET

Text: Positron emission tomography (PET) is an imaging technique used to detect and monitor the progression of cancer by administering a pharmaceutical compound containing a positron-emitting isotope. When this isotope is linked to an antibody that allows it to reach its target, this method is called immuno-PET. [1] ^{89}Zr is a radionuclide of interest for immuno-PET because its half-life time of 3 days is in accordance with the time required for the antibody to reach its target. [2] Nevertheless, the current chelators based mainly on desferrioxamine B (DFO) cause a release of ^{89}Zr which is found in the bones *in vivo*. [3] The synthesis of a new ligand composed of two siderophore chelating units from exochelin MN and DFO was considered but a modification of the terminal amine of the DFO was necessary to link these two parts. An enantiomerically pure chelator was synthesized from modified DFO bearing an aldehyde. This ligand is composed of 4 hydroxamate functions including a cyclic one allowing to complete the coordination number of Zr^{4+}.



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PARAMAGNETIC CHELATES EMBEDDED IN NANOGELS AS MRI PROBES

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Keywords: paramagnetic chelates, nanogels, contrast agents, relaxometry, MRI applications

Text: Nanogels (NGs) offer a promising strategy for highly sensitive MRI probes because of their exceptional biocompatibility, versatility in synthesis, and hydrophilic properties. Notably, when contrast agents (CAs) are confined within NGs, their relaxivity is significantly boosted. This enhancement results from the constraints imposed on the rotational dynamics of the encapsulated CA, the abundance of confined water within the NGs, and the increased viscosity of the entrapped water molecules within the polymer network. In an initial investigation, we prepared nanogels (NGs) through the use of electrostatic interactions between biocompatible chitosan and hyaluronic acid. These NGs were designed to incorporate Gd^{3+}-chelates with varying hydration state and charges.[1] Of particular interest were the NGs functionalized with the $[Gd(DOTP)]^{5-}$ complex, which, despite lacking water molecules coordinated to Gd^{3+}, exhibited an impressive relaxivity value of 78.0 mM^{-1} s^{-1} at 0.5 T and 298 K.[2] However, an *in vivo* MRI study revealed the limited stability of the NG formulation, as the complex was completely released within 24 hours in solutions with high ionic strength. To address this limitation, an alternative, more stable nanogel was proposed. This nanogel is based on chitosan covalently functionalized with a bisamide-derivative of *t*-CDTA, which can effectively coordinate paramagnetic Mn^{2+} ions (Figure 1).[3] The new nanogel offers several advantages: i) it provides r_1 values seven times higher than typical monohydrated Mn(II) chelates at clinical field strengths, ii) it maintains high stability of the formulation over time at both pH 5 and 7.4, thus preventing metal leaching or particle aggregation, iii) it demonstrates good extravasation and accumulation, with the maximum contrast achieved 24 hours after injection in mice bearing subcutaneous breast cancer tumors, and iv) it delivers high T_1 contrast (at 1 T) within the tumor 24 hours post-injection. Building on these promising outcomes, the same synthetic approach employed in the creation of the Mn(II)-based nanosystem was utilized to develop innovative nanogels that incorporate Gd(III)-based chelates. The aim was to produce nanoprobes for MRI applications with T_1 shortening capabilities (Figure 1). In this system, chitosan chains are interconnected using an octacoordinated bifunctional Gd-1,7-$DOTAGA_2$ chelate. The r_1 value of the nanogel, measured at 30 MHz and 298 K, is notably higher than that of the free chelate, approaching 30 $mM^{-1}s^{-1}$, and it enhances MRI contrast at both 7.1 and 1 T compared to commercially available contrast agents.

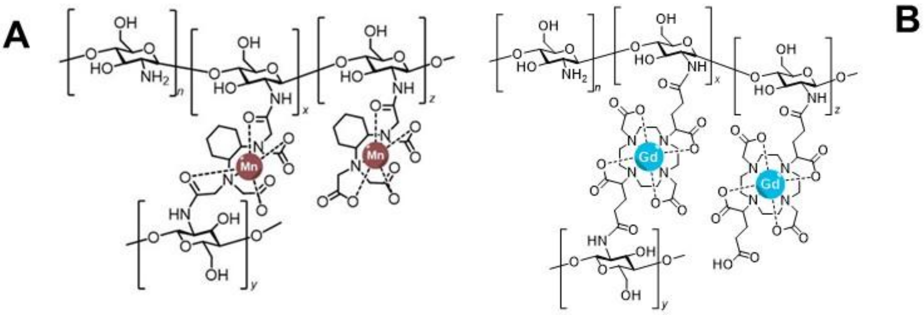

Figure 1. Schematic illustration of nanogel functionalized with Mn(II) (A) and Gd(III)-chelates (B).

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Mitochondrial DNA G-Quadruplexes and their interaction with novel Ruthenium(II) polypyridyl complexes

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Keywords: G-quadruplexes, mitochondrial DNA, synthesis, ruthenium complexes, anti-cancer agents

G-quadruplexes (G4s) are secondary DNA structures that play roles in various biological processes, including transcription, translation, genome stability, and cancer. G4s are notably abundant in significant portions of the human genome, such as oncogene promoters and telomeres.[1] Only very recently it has been observed that G4 formation can also occur in mitochondrial DNA (mtDNA), suggesting a potential regulatory role of the mitochondrial functions.[2] It is worth noting that mitochondria play a pivotal role in cellular metabolism, and their dysfunction has been closely linked to several cancer hallmarks. On the other hand, recent developments have seen the integration of ruthenium-based anticancer drugs into advanced clinical trials, revealing highly promising results. Ruthenium complexes offer a wide array of potential actions and targets. For instance, some ruthenium compounds bearing polypyridyl ligands, can target mitochondria, inducing apoptosis or necrosis in cells.[3] Metal complexes containing the dipyrido[3,2-a:2',3'-c]phenazine (dppz) ligand have already demonstrated the capability to interact with G4 *in vitro*.[4] Additionally, the inclusion of the triphenyl phosphonium moiety is specifically used for mitochondrial targeting. To evaluate the potential influence of G4-interacting compounds on mtDNA G4s, we synthesized new Ru(II) complexes of the type [Ru(bipy)$_2$(L)] and [Ru(phen)$_2$(L)], with 'L' representing a dppz moiety modified with a triphenyl phosphonium salt (**Fig. 1**). Furthermore, considering the promising anticancer properties of metal complexes with oxadiazole ligands,[5] which remain relatively unexplored in the literature, we conducted investigations into the G4 interaction of new complexes featuring 1,2,4-oxadiazoles ligands with Ru(II). Our assessment of their interaction with mitochondrial G4 sequences involved the use of spectroscopic techniques, including UV-Vis absorption, fluorescence, circular dichroism, and FRET.

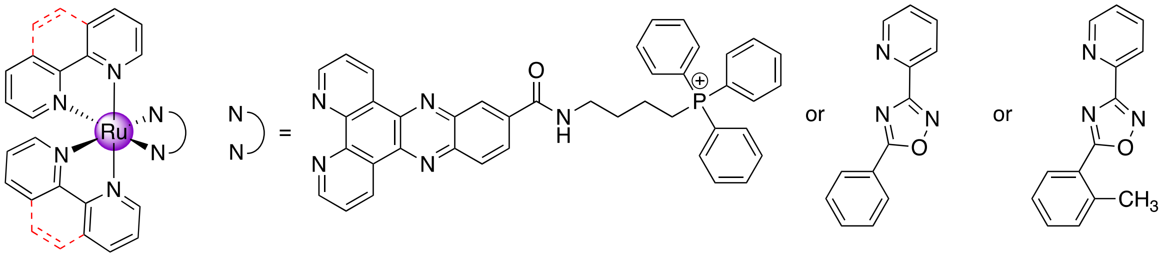

Figure 1 Structure of the synthesized ruthenium compounds with the general formula [Ru(bipy)$_2$(L)] and [Ru(phen)$_2$(L)].

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COUNTERION INFLUENCE ON THE N-HETEROCYLIC CARBENE GOLD-CATALYZED CYCLIZATION OF PROPARGYL AMIDES

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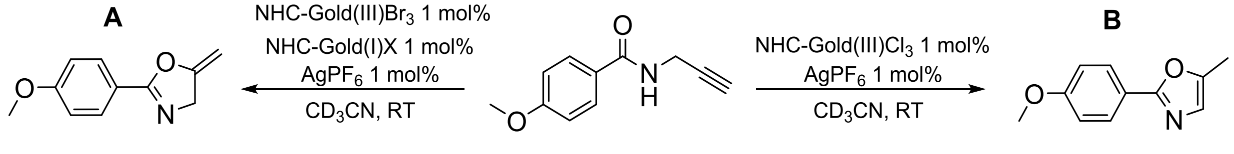
Keywords: Gold Catalysis, N-Heterocyclic Carbenes, Oxazole Synthesis

Over the last decades, gold catalysis has become a robust synthetic method for the activation of π-bonds towards nucleophilic attacks in order to approach many organic transformations.[1] The effects of both the ligand (L) and the counterion (X^-) are considered fundamental factors in homogeneous gold catalysis.[2] In this context, N-heterocyclic carbenes (NHCs) have demonstrated to be ideal ligands in combination with gold. The stereo-electronic properties of both NHC-gold(I)X and gold(III)X_3 complexes (X = Cl, Br or I) can be modulated by changing the carbene structure or the substituents at the N-positions.[3] On the other hand, despite being usually regarded as innocent partners, the metal counterions, for example halides (Cl^-, Br^-, and I^-), also proved to be highly influential in both the reaction mechanism and the regioselectivity.[4] Last but not least, the oxidation state of the gold center has some influence too on the regioselectivity and switching from gold(I) to gold(III) may have extreme outcomes, even leading to different reaction products.[5] A rational understanding of all these factors is still lacking and uncertainties still exist regarding the actual importance of the oxidation state of the catalytic species since the presence of a highly donating counterion, more than the oxidation state,[6] seems to be responsible for the observed selectivity.

In this work, the influence of both the oxidation state and the counterions was considered toward the gold oxidation-state-dependent cycloisomerization of 4-methoxy-N-(prop-2-yn-1-yl)benzamide to 2-(4-methoxyphenyl)-5-methylene-4,5-dihydrooxazole (**A**) or 2-(4-methoxyphenyl)-5-methyloxazole (**B**) ("Oxazole Synthesis", Scheme 1).[7] Thus, starting from 1,3-dimethyl-NHC-gold(I) chloride and 1-benzyl-3-methyl-NHC-gold(I) chloride, the NHC-gold(I)iodide and NHC-gold(I) bromide analogs were achieved by metathesis reactions with large excess of sodium iodide or sodium bromide. Finally, iodobenzene dichloride, liquid bromine and solid iodine were employed as oxidizing agents to get, respectively, the NHC-Au(III)Cl_3, NHC-Au(III)Br_3 or $[(NHC)_2AuI_2]Y$ (Y = I_3^-, AuI_2^- or AuI_4^-) and NHC-Au(III)I_3 series. All complexes were isolated as crystals and characterized by elemental analysis, ^1H and ^{13}C-NMR, IR-ATR and X-ray diffraction spectroscopies. The catalytic behavior of these complexes was ultimately studied in the cyclization reaction of the N-propargyl carboxamide. All the reactions were done at room temperature in NMR tubes in d_3-acetonitrile with a catalyst load of 1 mol%, with or without the addition of 1 mol% of $AgPF_6$, and the conversion was monitored by ^1H NMR. The analysis of the results underlines a larger impact of the counterion than of the oxidation state at the metal center.



Scheme 1: The cyclization of N-propargyl carboxamide as benchmark reaction to study the gold catalysts in this work.

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Exploring the spectroscopic wonders of Ytterbium(III)-based complexes

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Keywords: Ytterbium complex; Near-Infrared luminescence, Bioimaging.

The development of emissive optical probes is essential to the progress of cell biology and biochemistry research.[1] Lanthanide(III) complexes have attractive properties as optical probes, such as long emission lifetimes that allow the use of time-gated acquisition methods to enhance signal/noise, minimizing interference from light scattering or autofluorescence. As for Ln(III)-based luminescent probes design, it is important to take into account several requirements, such as high thermodynamic stability and kinetic inertness. Apart from designing a suitable chromophoric ligand capable of protecting the lanthanide ion from the aqueous medium and of sensitising its luminescence, one additional important task is to ensure a suitable excitation wavelength to the system. Usually, to excite the *antenna* chromophore ligand, UV light is used, despite its drawbacks as the small penetration depth in tissues and the hazard for cell life. An elegant solution to overcome this problem is the use of near-infrared light as excitation source.

During these last years, we focused our attention on the possibility of designing new potential bioprobes based on NIR emitting Ln(III) complexes. Our study started from the synthesis and characterization of a UV-excitable Yb(III) complex (Yb**1**),[2] which being not water soluble, needed to be encapsulated into water dispersible poly lactic-co-glycolic acid (PLGA) nanoparticles to be considered for bio application. Later, we went on by modifying the ligand to shift the excitation wavelength towards the vis region (Yb**2**),[3] less toxic for cells. Finally, in order to have a species excitable in further less dangerous regions of the spectral range, we designed an Yb(III) complex (Yb**3**), which could be two-photon excitable and which, thanks to the presence of polyethylene glycol (peg) fragments, was also directly soluble in water. The results obtained were promising and the applicability of these NIR-to-NIR probes will be further tested in biphotonic imaging experiments.

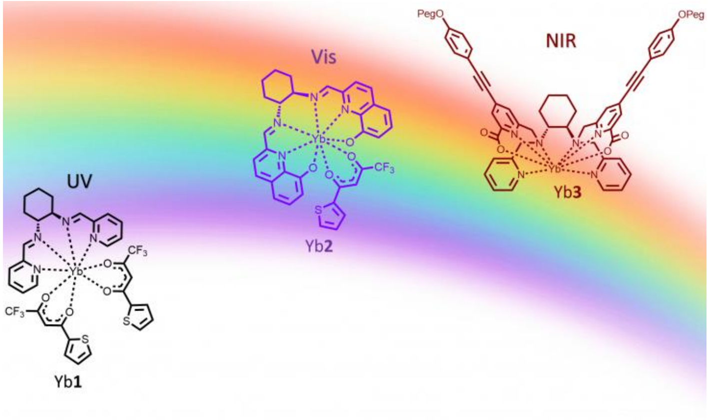

Figure 1 Yb(III)-based complexes discussed in this contribution, with their excitation range.

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Mechanistic and reactivity studies of reductive activation of O_2 by Fe-porphyrin – Greener oxygenation inspired by nature

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Keywords: O_2 reductive activation; Fe(porphyrin)-superoxo; electrolysis, 3-methylindole; oxidation

Nature is able through enzymatic system to efficiently and selectively oxidise substrate in mild conditions using O_2 as an oxidant source. In the economic and environmental context, it is primordial to perform greener chemical reactions. Indeed, oxidation reactions are widely used in industry such as pharmaceutic for the incorporation of a functional group onto an organic backbone. However, they generally require harsh conditions (temperature, pressure, strong and/or polluting oxidant), and are often stoichiometric and poorly selective.[1] Getting inspired by nature and especially enzymes such as cytochrome P450, we used iron-porphyrin in presence of dioxygen and electrochemistry to generate *in-situ* highly reactive O_2-intermediate, to finally induce oxidation reaction of organic substrates.
Previously,[2] thanks to spectroelectrochemistry, we have reported the O_2 activation mechanism by Fe-Porphyrin complexes revealing that different O_2-intermediates can be generated depending on the value of the applied potential and the reaction medium (presence or absence of proton) (Figure 1).[3] The reactivity and mechanism will be emphasized on the first O_2-intermediate to be reach, i.e. Fe-superoxo, thus requiring lower potential to be generated.[4] By definition, trapping intermediate to elucidate mechanism necessitate to choose experimental conditions that do not favour high reactivity. I will present the challenges to overcome by changing the solvent conditions and how to drive the superoxo reactivity toward the substrate of interest.

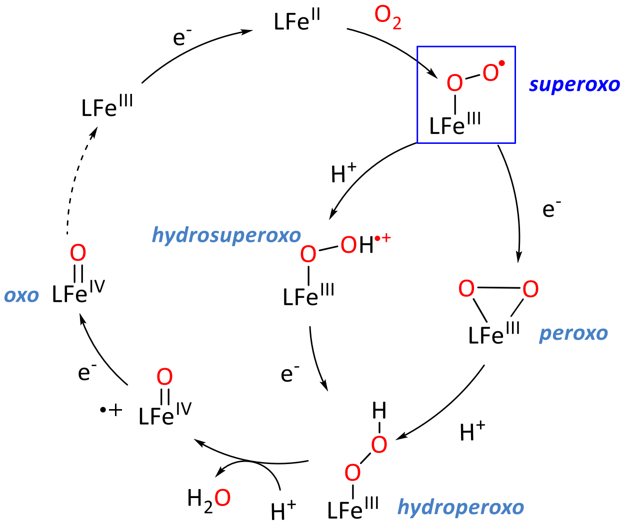

Figure 1 Proposed catalytic cycle of O_2 reductive activation by Fe-Porphyrin complex.

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PORPHYRIN AND CORROLE MACROCYCLEs-BASED POROUS MATERIALS FOR THE DETECTION OF VOLATILE MOLECULES

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Keywords: Metal-Organic Framework; Covalent Organic Framework; Corrole; Volatile Organic Coumpounds; Toxic gases

Text:
Volatile Organic Compounds (VOCs) and other gases can cause dramatic illnesses. These gases are present in the atmosphere.Thus, it is important to detect and monitor these small molecules (CO, CO$_2$ or NH$_3$) to keep the atmosphere as healthy as possible. In this regard, carbon monoxide (CO) can bind selectively to the Cobalt center of a metalated corrole, a macrocycle belonging to the porphyrin family (Fig. 1a).[1,2] Corrole macrocycles have demonstrated sorption hindering π-stacking interactions, when deposited as layer, which reduces their detection capacity when applied to sensor. Therefore, we prospect to introduce metallocorroles into porous materials such as Metal-Organic Frameworks (MOFs) or Covalent-Organic Frameworks (COFs)[3,4] to minimize the π-π interactions and enhance the accessibility of the Cobalt center to CO$_{(g)}$. Since the last decade, these organized porous compounds have received a great deal of attention due to their high surface area, their customizability, and their importance in the fields of gas detection. Herein, we explore the synthesis of a new MOFs containing cobalt corroles for CO detection, while paying attention to the stability of the material that must resist several cycles of reactivation. We focus on a new hybrid MOF with mixed porphyrin and corrole linkers (Fig. 1) with the expectancy to obtain a stable and sensitive crystallized material. The new materials we have prepared have been characterized by XRD, ^{1}H NMR, BET and SEM.

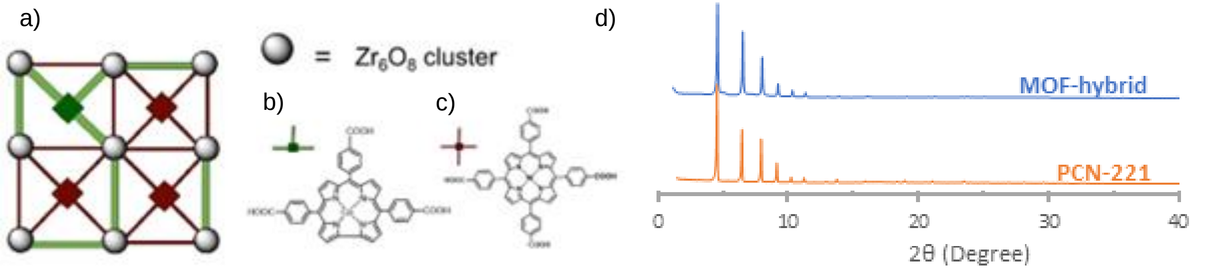

Fig. 1 – a) Scheme of the hybrid corrole-porphyrin MOF synthesized with b) Cobalt 5,10,15-tris(p-carboxylphenyl)corrole) c) Nickel 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin d) XRD of the hybrid corrole-porphyrin MOF

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Grafting Cobalt Corroles in Porous Material Networks for Carbon Monoxide Detection

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Text: Carbon monoxide (CO) is a colorless, odorless, flavorless and non-irritating gas responsible, every year, of serious intoxications that can lead to death. It is imperative to design new devices that can detect this imperceptible and deadly gas at low concentrations before it reaches harmful levels.[1] In this regard, cobalt corroles (a tetrapyrrole macrocycle of the porphyrinoid family) present a selective affinity for CO detection. Indeed, they have been shown to coordinate CO even in the presence of interferents such as dinitrogen (N_2) and dioxygen (O_2).[2] Moreover, Metal-Organic Frameworks (MOFs) are porous materials renowned for their high porosity and superior tunability. Following suit, our work is to use the porous MOFs structure that can host metallocorroles to synergistically combine their high sorption capacity with the corrole sensitivity for CO detection. In particular, porphyrin-based MOFs such as the PCN-222 (Fig. 1a) can present natural vacancies on their metal cluster which can then be used to graft cobalt corroles. 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 judiciously 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, ^1H NMR, and BET analysis.

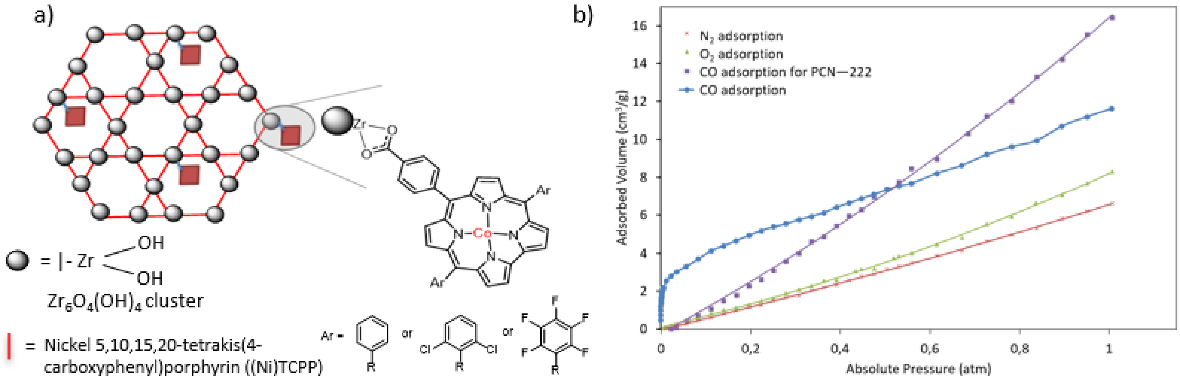

Fig. 1: a) Structure of a cobalt corrole grafted on PCN-222, b) N_2, O_2 and CO adsorptions of the grafting material

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