



Book of Abstracts

Oral presentations

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Fournols

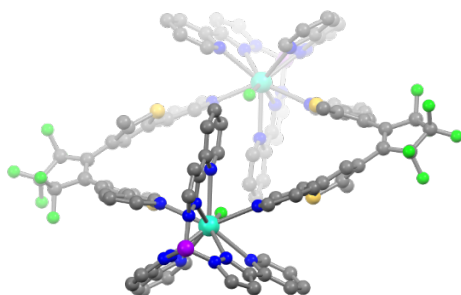
How to control SMM with light using photochromic ligands ?

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Molecules that exhibit slow magnetic relaxation resulting from a bistable ground state, called Single-Molecule Magnets (SMM) are attractive candidates for next generation information storage schemes.¹ Efficient control of their magnetization via an external stimulus could considerably increase the scope of application of these magnetic molecules. We are interested in using light to manipulate SMMs' characteristics in order to obtain fast and contactless control. Over the years, we have developed several strategies to reach such goal. First, we relied on spiropyran photoswitches and targeted discrete changes in a lanthanide complex coordination sphere in order to manipulate its magnetic anisotropy.² Then we used a supramolecular approach to assemble lanthanide based building units into photoswitchable chains³ and cycles (see Figure)⁴ by reaction of highly anisotropic dysprosium complexes featuring a short Dy(η^1 -F) bond⁵ and dithienylethene photoswitches. I hope to show that this two strategies are complementary to approach the challenging goal of photoswitchable SMM.



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Reductive Depolymerization of Oxygenated Plastics with Hydroboranes/La(III) or Hydrosilane/Zr(IV) Catalytic systems

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Plastics are ubiquitous in our modern society and their world annual production now reaches 368 Mt. Most household wastes accumulates in landfills or are burnt due to the absence of efficient and economical recycling and valorization processes. Such a situation causes severe damage to the environment and emissions of large amount of CO₂.¹

Today, while mechanical recycling is the most useful method to valorized the plastic bottle, chemical recycling, which is the depolymerization of materials into valuable monomers useful for the production of recycled virgin quality plastics or chemicals for industry, now emerged as a long-term strategy complementary to mechanical recycling.²

Recently, reductive catalytic depolymerization methods appeared as alternative approaches to access new value added products from oxygenated and/or nitrogenated plastics.³ Such ways are however scarce. Hydrogenolysis methods require noble metals (Ru, Ir) and high pressure and temperature.⁴ In contrast, the hydrosilylation of polyesters and polycarbonates took place under milder conditions with metal-based catalysts (Ir(III), Zn(II), Mo(VI)) or boron-based organocatalysts.⁴ We report here that the Schwartz's reagent, Cp₂Zr(H)Cl, traditionally used as a stoichiometric reagent for the reduction of unsaturated organic molecules, can be an efficient catalyst for the hydrosilylation of esters and polyesters.⁵

Inspired by the work of T. J. Marks *et al.*⁶ on the reduction of esters, we also reported the first use of hydroboranes as source of hydride when combined with a La(III) molecular catalyst. This system La[N(SiMe₃)₂]₃/Hydroborane depolymerize selectively a wide range of polyesters and polycarbonates into their corresponding borylated alcohols (Fig.1).⁷

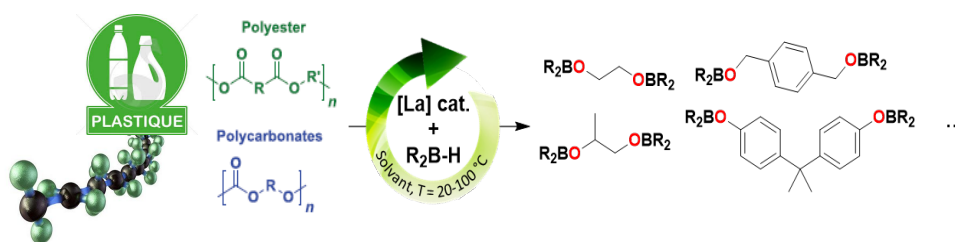


Fig. 1 Depolymerization of oxygenated plastics with the La(III)/HBpin catalytic system

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Chiral, L-shape N-heterobicyclic carbene ligands for asymmetric gold(I) catalysis

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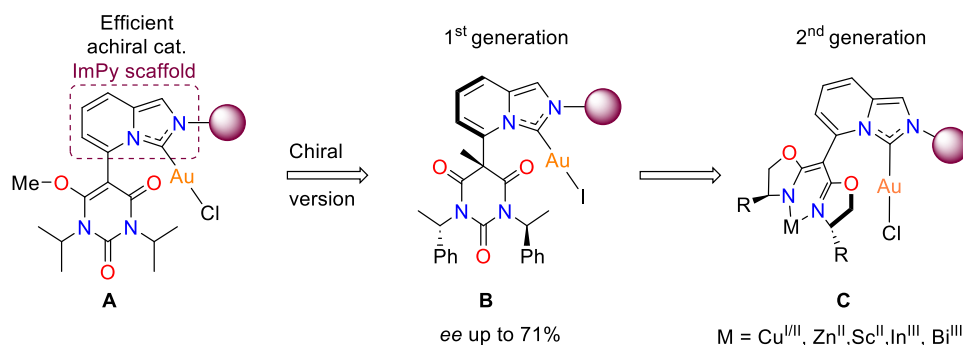
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Despite the outstanding advances realized in homogeneous gold(I) catalysis over the last two decades, the asymmetric version has not experienced the same growth.¹ The main challenge resides in the specific, linear coordination geometry of gold(I) complexes, which limits an efficient chirality transfer from the ligand to the substrate. In 2019, our groups reported that the “achiral”, tunable catalysts **A**, supported by a “L-shape”, bicyclic imidazo[1,5-a]pyridin-3-ylidene (ImPy) ligand laterally-functionalized by a barbituric heterocycle, are highly efficient in gold(I)-catalyzed C-N, C-O, and C-C bond formations.²

We present herein our progresses towards efficient chiral catalysts based on this privileged ImPy platform.³ The first generation is composed of chiral ImPy-Au(I) complexes **B** featuring a chiral lateral barbituric heterocycle obtained from enantiopure (*S*)-1-phenylethylamine. The use of the chiral pre-catalysts **B** in the domino cycloisomerisation/nucleophilic addition of 1,6-enynes with various nucleophiles gave excellent yields and good enantioinduction (up to 72% ee), resulting in functionalized heterocycles.⁴ As a second generation, the ImPy-Au(I) complexes **C** functionalized with a chiral, lateral bis-oxazolinane moiety was developed in order to improve the transfer of the chiral information.



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4. Unpublished results.

Charge And Discharge Of Electrons In Metal Complexes Of A Hybrid Polyoxotungstate

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Polyoxometalates (POMs) are nano-sized molecular oxides whose main property lies in their ability to store and release electrons with no or minor rearrangements. In the context of innovative energy materials development, POMs are therefore ideal redox candidates as component of model systems for exploring electron and protons transfer, including photocatalyzed hydrogen production.¹

Despite numerous works over the years, the mechanism leading to hydrogen evolution onto polyoxometalates is rather undefined. We are thus interested in studying the reaction of protons on reduced polyoxotungstates and in particular, on hybrids synthesized in our group.^{2,3} These studies are prerequisite for a more general work that deals with the coupling in a single system of the photochemical capacity of POM framework to promote hydrogen atom transfer, when irradiated under UV light, in tandem with the single electron transfer (SET) chemistry of early transition metal from the first row.⁴ The system will then be use for the oxidation of alkanes into alkenes.

In this presentation, we will discuss our recent results on the discharge of reduced POMs under protonation *stimuli* and on the transient species formed *in situ*, which have been highlighted by electrochemistry, chemical reduction or photocatalysis (Figure).⁵

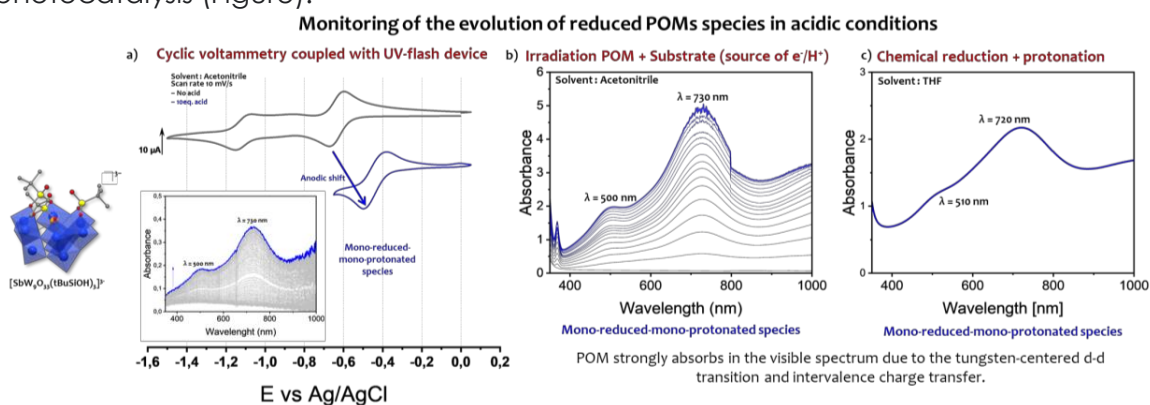


Figure. a) Cyclic voltammetry of hybrid POM coupled with UV-flash acquisition. b) UV-Vis monitoring of irradiated solution of POM in presence of an organic substrate. c) UV-Vis spectrum of synthesized mono-protonated-mono-reduced species.

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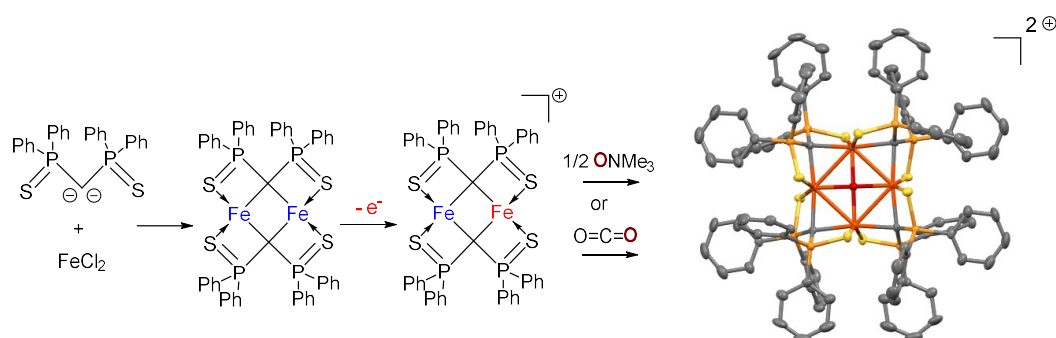
Versatility of iron complexes for biomimetic CO₂ reduction

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Nitrogenase cofactors are intensively studied for their ability to reduce N₂ to ammonia. Its structure is however extremely complex, with a central carbide surrounded by two iron sulfur cubanes. Numerous synthetic models have been proposed, in order to find the simplest structure with relevant reactivity, the carbide ligand being the hardest to model.^[1]

In recent years, it has been shown that their strong reducing capacity can be directed to CO₂ reduction. Indeed, a slightly modified version of an Fe/Mo nitrogenase could reduce CO₂ to methane at room temperature^[2]. The conversion of CO₂ into value-added chemicals is a major concern in today's issues. Nature's ability to reduce CO₂ into more complex molecules (mainly via photosynthesis) has inspired the bioinorganic chemistry community to find model compounds for the selective conversion of CO₂^[3]. Nevertheless, only a few multinuclear complexes (Mo/Cu^[4], Ni/Fe^[5]) inspired by enzymes specified in CO₂ fixation, are reported so far in the literature and can catalyze CO₂ electroreduction. From nitrogenase reactivity, efficient activation of CO₂ towards total hydrogenation by a carbon/sulfur stabilized iron cluster should be an interesting route. We propose to use bis-diphenylthiophosphinoylmethanediide as a versatile ligand for the preparation of a variety of tightly bound iron clusters. This gem-dianionic ligand (SCS)²⁻^[6] allowed us to prepare a set of bimetallic^[7] and tetrametallic structures, all exhibiting C²⁻-Fe interactions reminiscent of the structural role of the carbide ligand in FeMo-co. Moreover, their behavior in different redox situations, highlighted by cyclovoltammetry, shows the stability of this interaction. As a proof of concept, we showed that the mixed valence iron dimer **3** reacts with CO₂, liberating CO and a tetrameric iron oxo complex, in which the (SCS)²⁻ is bridging each iron centers. This pattern confirm the structural role of this ligand.



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Magneto-Chiral Dichroism in helicene based Dy(III) coordination polymer

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Résumé

Magneto-Chiral Dichroism (MChD) is the differential absorption of unpolarised light by a chiral medium in the presence of a magnetic field collinearly aligned to the propagating wavevector of light (**1**). Introducing chirality into Single molecule Magnets (SMM), the ultimate systems for magnetic data storage, and hopefully observing MChD in them, could allow optical readout of magnetic data using unpolarized light. The large spin-orbit coupling in chiral lanthanide complexes make them good candidates to observe both MChD and SMM behaviours. In recent studies, strong MChD has been observed in helicene-based, discrete (**2**) and polymeric (**3**), Yb(III) complexes up to room temperature. In addition to this, MChD associated to the transitions of Dy(III) in a chiral bimetallic cluster of Dy(III) and Ni(II) has also been reported (**4**). Since, Dy(III) complexes can be considered as the state-of-the-art SMMs, we have undertaken the study of the MChD properties of a Dy(III) helicene based chiral coordination polymer. The aim of this talk is to present the synthesis, the magnetic and the MChD properties of this Dy(III) complex. Like the Yb(III) parent polymer, it shows sharp and intense signals in the UV-Visible and Near IR regions of the electromagnetic spectrum. These promising results paves the way to use chiral Dy(III) SMMs to trace their magnetic hysteresis using MChD.

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Mots-Clés: Magnetochiral Dichroism, Molecular Magnetism, Chirality, Lanthanide complexes

^{*}Intervenant

Small Molecule Activation by Uranium complexes : Examples of Synergistic Effects

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Résumé

In this presentation, we will focus on the performance of an efficient interplay between experience and theory to elucidate the reactivity of actinide-catalyzed small molecule activation reactions. Based on the theoretical description of N₂ activation to yield Ammonia or O₂ activation, we will demonstrate that synergistic effects between Uranium(III) and transition metal but also with non-metal, such as phosphorus, allow facile direct full activation of N₂ and O₂ under ambient conditions.

Mots-Clés: mechanism, uranium, activation, DFT

^{*}Intervenant

Fine tuning of the solid state luminescence properties of homoleptic copper(I) bimetallic complexes constructed with diphosphines ligands

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Copper as a strategic resource is abundant, cheap, presents a low toxicity and is readily accessible. The combination of copper(I) ions with donor ligands can allow the obtention of molecular and supramolecular polymetallic structures with attractive spectroscopic properties such as wide range of emission colours and various emissions intensities. These properties are adjustable by controlling the electronic environment around the metal centres. This adaptability allows a strong potential for innovation in devices such as OLED (organic light-emitting diodes) solar cells, but also luminescent sensors.¹ By using chelating diphosphine ligands and copper(I) salts, four new homoleptic bimetallic Cu(I) complexes **D1-4** were obtained displaying original “propeller shape” structure. The variation of the nature of the chelating diphosphine ligands (bis(diphenylphosphino)methane vs bis(diphenylphosphino)amine) as well as the nature of the copper(I) counter anion (PF₆⁻, BF₄⁻ or [Al{OC(CF₃)₃}]⁻) allow to observe changes in the copper-copper intermetallic distance and the general electronic density of the resulting structure. What might seem as innocent changes at first, resulted in the observation of rich luminescent properties in the solid state, including high quantum yield, and TADF behaviour. Finally, we embedded **D1-4** in polymer matrix to further study their processability in order to getting closer to their implementation in devices.

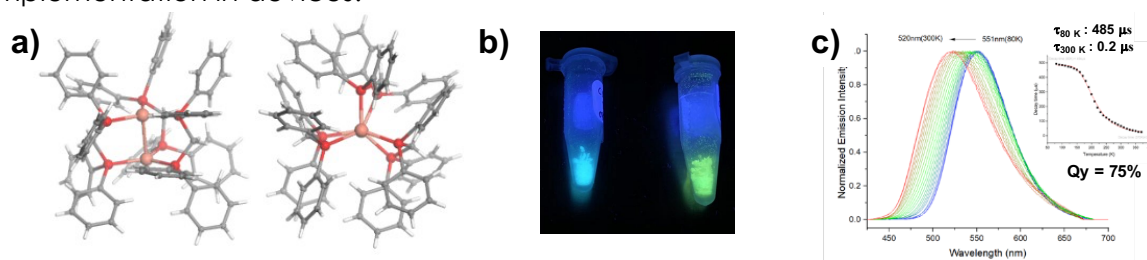


Figure. a) Views of the X-ray structure of the derivative **D1**, b) Photographs of **D1** and **D2** sample under UV-vis light, c) Normalized solid-state temperature dependent emission spectra of **D2** and plot of the emission decay lifetime against temperature.

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Polyurethane hybrid polymers based on (Mo₂O₂S₂)₂+ thiosemicarbazone complexes

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Résumé

The (Mo₂O₂S₂)₂+ thiosemicarbazone complexes are very promising molecules due to their biological proprieties. The shaping of these coordination complexes in organic polymers is an interesting way for the biomedical application. Here we present the synthesis and the characterisation of polyurethane hybrid polymers based on different (Mo₂O₂S₂)₂+ thiosemicarbazone complexes. The physical properties of obtained polymers are strongly related to the nature of the coordination complex which can be covalent-bond or not in the polymer matrix. These polymers have been characterized by various techniques as Differential Scanning Calorimetry (DSC), Energy-dispersive X-ray spectroscopy (EDX), NMR, TGA, IR which will be discussed focusing on the structure-physical properties correlation.

Mots-Clés: polyurethane, thiosemicarbazone complexes, (Mo₂O₂S₂)₂+ cluster, biomedical application

*Intervenant

Development of New Iron Based Pre-catalysts: Synthesis, Characterization and Trend in Selective Catalytic Oxidation of Unprotected Carbohydrates

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Résumé

Sustainability concerns and challenges, have incited the development of eco-friendly methodologies for synthesis and catalysis using earth-abundant catalysts based on first-row transition metals (e.g.- Mn, Fe, Co, Ni, etc.).^{((1),(2))} In this context, Knölker's complex⁽⁽³⁾⁾ and its variants have been promising due to their robustness, straightforward synthesis and performance in catalysis such as hydrogenation, reductive amination, alkylation, oxidation etc. of alcohols and amines.^{((4),(5))} Recently, we have developed an efficient transfer hydrogenation strategy for the chemoselective oxidation of the anomeric position of unprotected hexose and pentose sugars to corresponding sugar lactones, by using the Knölker catalyst in the presence of acetone as a formal hydrogen acceptor.⁽⁽⁶⁾⁾ Our focus is now to extend our methodology to selectively oxidize an hydroxyl group of sugars. We envisioned that an improved catalyst design which could promote the substrate-catalyst approach via secondary interaction (e.g.- H- bonding), could direct the oxidation of the hydroxyl moieties in sugars. To achieve such pre-organization, modified side chains with heteroatoms (N, O) were introduced on the cyclopentadienone moiety leading to various new catalysts. In this work, we will present the synthetic routes and characterizations of these new Knölker type catalysts with chosen substituted side arms (pyridyl, O-alkyl), potentially capable of secondary interactions with the substrate. The catalytic activity of these complexes will also be presented and compared to the results obtained with common Knölker catalyst.

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Mots-Clés: Iron, Knölker type catalysts, Catalysis, Oxidation, Unprotected sugars

PHOTOINDUCED ISOMERIZATION OF CYCLONONATETRAENYL ANION LIGAND IN LANTHANIDE SANDWICH COMPLEXES

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The cyclonatetraenyl (Cnt) anion is a nine-membered ring aromatic molecule that was first synthesized in 1963 by Katz and Garrat.¹ This compound features two isomers: the *cis,cis,cis,cis*-Cnt and the *cis,cis,cis,trans*-Cnt as depicted in Figure 1. At that time, scientist observed spontaneous isomerization from the *trans* form to the *cis* one. Given the aromatic character of the fully *cis* form, it was considered as the stable form. Unfortunately, the high sensitivity of the Cnt[−] ligand toward protonation and reorganization into 8,9-dihydroindene precluded further analysis.

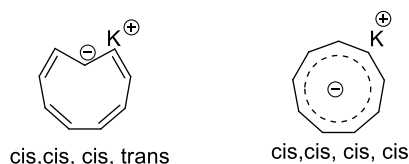


Figure 1: Cyclonatetraenyl anion isomers

Despite all these challenges, the Cnt ligand has regained interest in organometallic chemistry to form sandwich complexes.^{2,3} Our group have expanded this result to a series of lanthanides-containing complexes, where it was shown that a mixture of the *cis* and *trans* isomer complexes were observed.⁴ After careful evaluation of the different stimuli that could cause such species to be isolated, we came to the conclusion that, in certain cases, the isomerization is photo-induced. Thus, this work focuses on how to control the isomerization of the Cnt[−] ligand and its complexes using light.

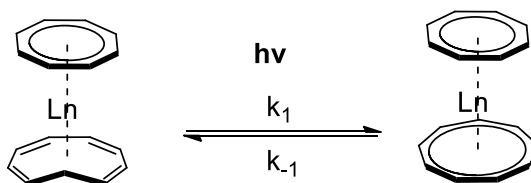


Figure 2: Photoinduced isomerization of Cnt in lanthanide complexes

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Molybdenum Polyhydride Complexes: Synthesis and Reactivity Towards Small Molecules

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Transition metal hydride complexes are key intermediates in a large variety of stoichiometric and catalytic processes. They are commonly invoked along catalytic cycles relevant to environment- and energy-associated issues, such of H₂ evolution^[1] and CO₂ reduction reactions^[2]. In these reactions, they typically act as hydride donors. Some transition metal hydrides, however, are also capable to behave as proton donors^[3] or even as HAT reagents^[4] (Hydrogen Atom Transfer). The chemistry of molybdenum polyhydrides containing mono- and bi-dentate phosphine ligands has been the subject of significant investigations, notably due to the ability of such species to support mixed coordination modes associating η^2 -H₂ ligands and hydride ligands. By contrast, the reactivity of these species towards common small molecules still has to be explored and understood.

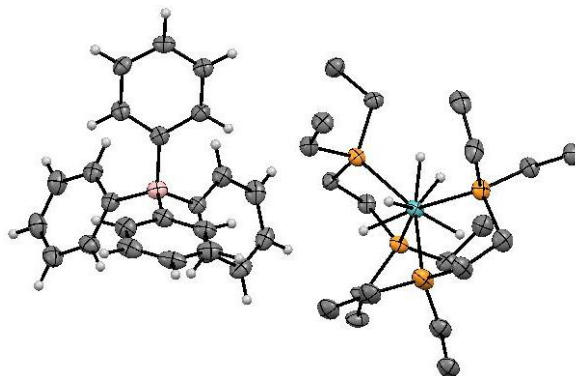


Figure. Molecular structure of [MoH₅(depe)₂]⁺, a Mo(VI) pentahydride complex.

In this communication, preparations of a rare 9-coordinate cationic pentahydride Mo(VI) complex will be reported and its various reactivities towards small molecules (CO₂, CS₂, CO, C₂H₄) described.

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Design of Frustrated Lewis Pair related to the active site of [FeFe]-Hydrogenases for the activation of H₂

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Metalloenzymes are proteins containing one or several metals in their active site.¹ Among them, a family of enzymes called hydrogenases is able to catalyse the reversible conversion of dihydrogen into proton and electron according to the reaction $\text{H}_2 = 2\text{H}^+ + 2\text{e}^-$.² In a context of energy crisis and development of a decarbonized energy resource, such metallic systems were the focus of much research as these are based on abundant transition metals and allow the production of H₂.

Numerous studies³ have been carried out on dinuclear complexes bio-inspired by the [Fe-Fe]-hydrogenases active site. However, these studies have more focused on the reduction of proton than on the activation of H₂. In literature,⁴ the reported diiron dithiolate complexes, able to oxidize H₂, feature a ligand (dithiolate or diphosphine) carrying an amine function playing the role of a Lewis base in the second coordination sphere of the diiron site acting as a Lewis acid. Such a functioning is reminiscent of Frustrated Lewis Pair devices in which, due to steric hindrance, the Lewis base and the Lewis acid cannot form an adduct; the use of FLP to perform the activation of hydrogen has been firstly developed with phosphine-borane couple.⁵

Very recently, a study in our group designed a diiron complex which, associated to a borane B(C₆F₅)₃, can cause the heterolytic cleavage of the H-H bond, forming a protonated diiron complex and a hydroborate anion.⁶ In this design, B(C₆F₅)₃ has the role of the Lewis acid and the diiron center behaves as a Lewis base, as it is in a low oxidation state and coordinated to strong electron donating phosphine ligands.

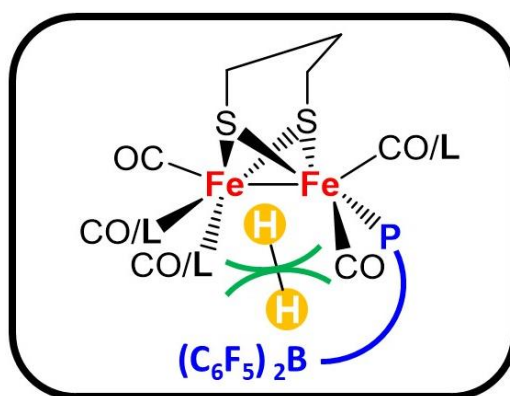


Figure 1 – Schematic representation of the complexes designed for the activation of H₂.

The work presented in this communication is based on a similar strategy of combining a borane entity with an electron-rich diiron complex to form an intramolecular and non-biomimetic Frustrated Lewis Pair in view to activate H₂ (Figure 1). A series of complexes has been prepared with different phosphines in order to modulate the basicity of the diiron

Lanthanide-based coordination polymers: from molecular alloys to core-shells, shaping study of heteronuclear luminescent materials

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Since few decades, lanthanide-based coordination polymers have been studied for their interesting optical properties that make them suitable for several applications such as anti-counterfeiting.^[1] Coordination polymers are composed with metallic ions that are linked by organic ligands to form infinite one-, two- or tri-dimensional molecular networks. Because of the hypothesis that lanthanides ions have similar chemical behavior, iso-structural homo- and hetero-lanthanide compounds can be prepared as microcrystalline powders.

When hetero-lanthanide compounds present a random repartition of the metallic ions over the metallic sites they behave as actual "molecular alloys".^[2] If this repartition is organized, core-shell particles can be synthesized (**Figure**).^[3] Herein, we report the synthesis of homonuclear and molecular alloys with two different ligands and various lanthanide ions to understand how to optimize the syntheses to finally obtain the desired core-shell particles.^{[4],[5]}

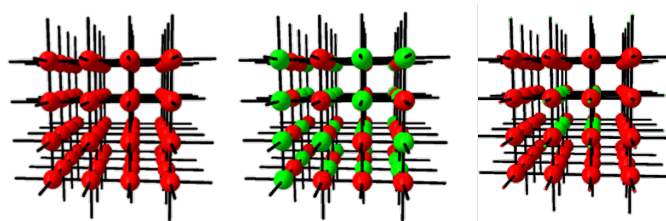


Figure. Schematic representation of homonuclear (left), molecular alloy (centre) and core-shell (right) coordination polymers.

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Zincate-Mediated Remote Functionalisation of *p*-iodobenzyl Derivatives Through Metallotropy

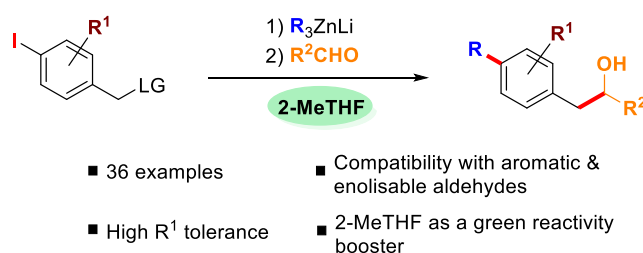
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Metal-promoted remote functionalisation through internal induction is an efficient synthetic concept to swiftly access added-value molecular architectures with a high degree of structural diversity from simple and readily available substrates.¹ If perfectly implemented, such an approach leads to the selective functionalisation at a site away from a functional group initially interacting with the used reagent or catalyst. In this context, through-space metal migration² or intrinsic migration of the metal along a flexible carbon via unidirectional positional isomerisation sequence of a double C-C bond³ are the most popular used internal communication processes between initiation and functionalisation sites. By contrast, metallotropic rearrangement⁴ received very little attention from the synthetic community.

We will present you the remote functionalisation of diversely decorated 4-iodobenzyl derivatives through metallotropy by using lithium tributylzincate as reagent and 2-MeTHF as solvent. The process leads to the selective formation of both a C(sp³)-C(sp²) and a C(sp³)-C(sp³) bond at sites localised at five atoms away from one another in a single operation and with a unique organometallic reagent. Compared with the literature precedent,⁵ our reaction conditions allow us to reach an unprecedented synthetic scope, both in terms of compatible substrates and electrophiles.⁶ The influence and the role of the eco-friendly solvent on key elementary steps of the overall transformation will be discussed, namely (i) metalation step through I/Zn exchange, (ii) Bu 1,2-migration and (iii) generation of a benzyl zinc intermediate after dearomatisation / rearomatisation / metallotropy chain.



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Mechanistic studies of hydroalkylation of 1,3-enynes with ketones by cooperative catalysis: a joint experimental/computational approach.

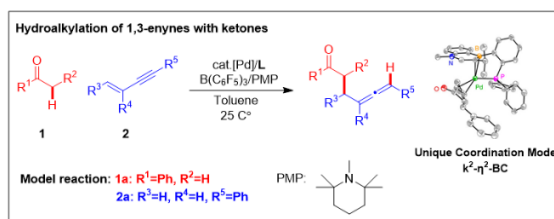
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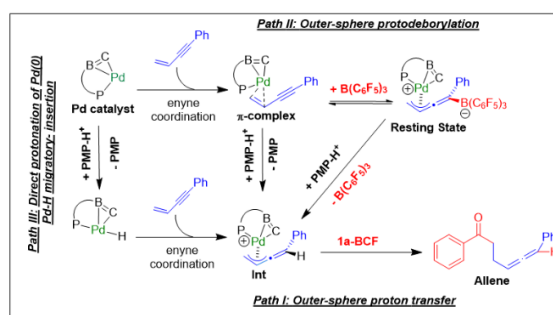
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Palladium-catalyzed hydrofunctionalization of conjugated enynes and in particular, hydroalkylation of 1,3-enynes is a way to synthesize allenes, which are common structural motifs in natural products, bioactive small molecules, materials and also versatile synthetic intermediates.^[1] Some enantioselective processes catalyzed by transition metal complexes (Cu, Rh, Ir, Ni, Pd) have recently been developed.^[2] However, these reactions occur under drastic conditions (high temperatures, strong acid or strong base).^[3] Recently, Liu research group, described an efficient Pd-catalyzed hydroalkylation of 1,3-enynes with simple ketones via (B,N)Pd(0)/B(C₆F₅)₃/PMP catalysis affording allenes in high yields under mild conditions (RT) and tolerating a wide range of both enynes and ketones.



To support experimental data (NMR, kinetic studies) and provide information on the mechanism, Density Functional Theory (DFT) calculations were carried out. Acetophenone **1a** and 1,3-enyne **2a** were used as model substrates. Different pathways were considered theoretically: path I: outer-sphere proton transfer; Path II: outer sphere protodeborylation; Path III: direct protonation of Pd followed by Pd-H β -migratory insertion.



In this communication, we will present the different energy profiles in addition to the experimental mechanistic investigations. We will show how the joint experimental/computational approach allowed to elucidate the mechanism of this reaction and highlight the key role of the Pd/borane/amine combination on the feasibility of the process.

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Circularly Polarized Luminescence in Lanthanides complexes.

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Lanthanide-coordination complexes exhibit fascinating optical and chiroptical properties, intimately related to the symmetry of the first coordination sphere due to the so-called crystal-field splitting effect (CFS). This CFS is also the key factor that governs the magnetic anisotropies at the origin of single-molecule magnets properties. As a consequence, both (chir)-optical and magnetic properties of metalorganic complexes are strongly correlated.

In this contribution, we will illustrate the interplay between these (chir)-optical and magnetic properties thanks to the design of chiral Yb(III) complexes featuring functional dipicolinamide ligands. Absorption, emission, circular dichroism and circularly polarized luminescence will be described. Since magnetic properties are only recorded at low temperature, a particular effort has been devoted to determine the (chir)-optical properties at low temperature to evidence de CPS correlation.

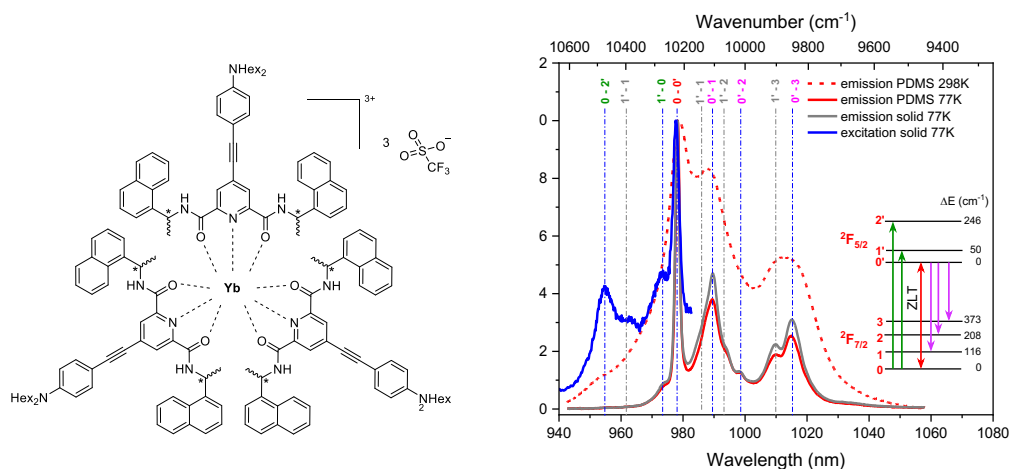


Figure : Helicoidal Yb(III) complexes and related optical properties.

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Nucleophilic Addition on Coordinated N₂: Fact or Fiction ?

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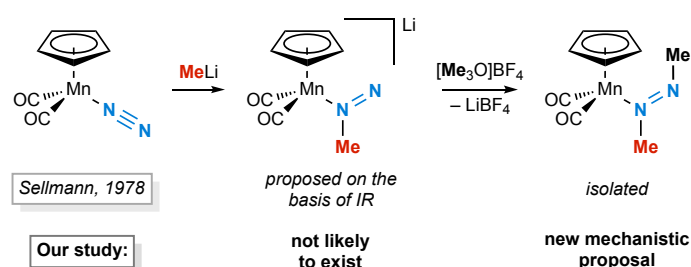
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Nitrogen is a life-sustaining element primarily sourced from the widely available, inexhaustible but commonly non-bioavailable N₂ allotrope. Coordination to transition metals is the way Nature has chosen to achieve the transformation of this abundant but inert molecule: within the active site of the nitrogenase enzymes, an FeS cluster can activate N₂ towards its reduction to NH₃. Taking inspiration thereof, chemists have achieved N₂ activation within coordination complexes, eventually culminating in catalytic reduction of N₂ to NH₃ under ambient conditions. The reactivity of N₂-complexes may also extend beyond NH₃ synthesis, with the production of more complex N-containing molecules.¹ The large majority of N–C bond formation reactions between coordinated N₂ and an organic substrate relies on its reaction with a C-electrophile. Yet, a unique example of functionalization by a C-nucleophile stands out in the literature and involves the complex [CpMn(N₂)(CO)₂]² (Figure). Intrigued by this particular reactivity, we have carried out a mechanistic study combining experiment and DFT. We have disclosed a previously undetected intermediate that seems crucial for obtaining an N₂-derived nitrogen-containing compound. Besides, our data suggest that the direct attack of the C-nucleophile (RLi) on coordinated N₂, initially proposed as a key step for N₂ functionalization, is not likely to take place.

Figure. The unique reactivity of [CpMn(N₂)(CO)₂].



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Silylformates as hydrosilane surrogates:

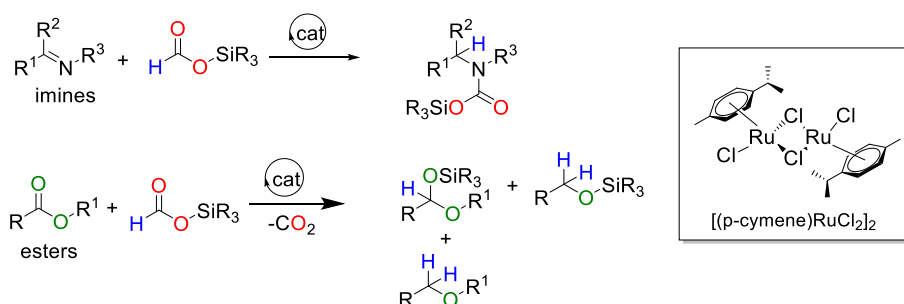
Catalytic reduction of imines and esters

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Hydrosilylation is an important reaction for the reduction of various organic compounds. Transfer hydrosilylation has emerged as a substitute for the hydrosilylation process owing to the difficulty in handling some hydrosilanes which can be toxic or pyrophoric (SiH_4 , SiMe_3H). In this regard, silicon substituted cyclohexa-1,4-dienes have been used as hydrosilane surrogates by Studer[1] and Oestreich[2] for the reduction of alkenes, alkynes, aldehydes and ketones. The main drawback of such surrogates is that their preparation involves a Birch-reduction, which is energy-intensive and results in quantitative arene derivatives as by-products after reduction. Our group has recently demonstrated the use of silyl formates as hydrosilane surrogates [3]. They are easy to produce and the only by-product after reduction is CO_2 . Silyl formates have already been utilized for the ruthenium-catalyzed transfer hydrosilylation of aldehydes and ketones. In this work, we focus on the extension of this application for the reduction of more challenging substrates such as imines and esters. We present here a ruthenium-based catalytic system that enables the conversion of imines to the corresponding carbamates in high yields (>90%) and with CO_2 incorporation. The more challenging transfer hydrosilylation of esters will also be discussed, especially in terms of selectivity.



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Development of red absorbing photosensitizer for reactive oxygen species generation

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Antibacterial resistances are a concern since the 70's. With the lack of new antibiotics, an increase of untreatable infections is forecast in a few decades. Nowadays, Trojan horse^{1,2} combined with photodynamic therapy² are exhibiting promising properties. Here, we are presenting our preliminary results on the development of red absorbing photosensitizer for oxygen reactive species generation.

Our new photosensitizers based on cationic iridium complexes bearing di-pyridylamine or bipyridine ligands as ancillary ligand with various cyclometallated ligands have been fully structurally, photophysically and physico-chemically characterized.

All these properties allowed us to rationalize their photo-enhanced antibacterial activities against Gram positive and negative bacteria under various irradiation wavelength.²

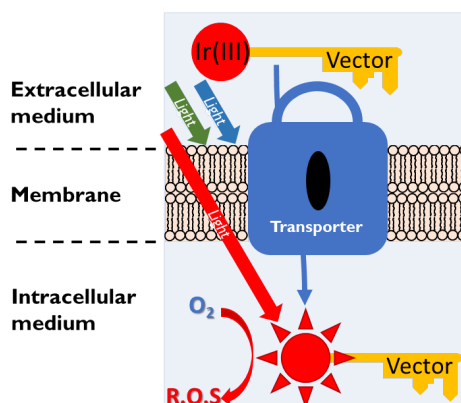


Figure. Antibacterial activity by R.O.S generation of red absorbing complexes

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Main group (r)evolution: C-H activation with Antimony(III)

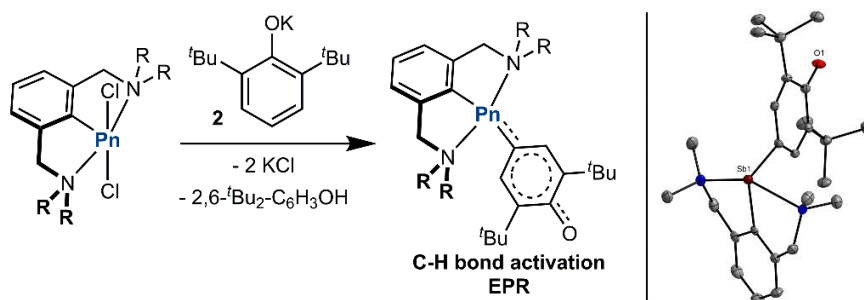
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C-H bond activation processes have classically been a domain of late transition metal chemistry. Yet, main group compounds have also successfully entered this field of research in recent years.¹ Several examples include the activation of C-H bond in aryl, allylic, and benzylic positions and in α -positions of cyclic thio-ethers.^{2,3} Albeit antimony(III) Lewis acids are used for formal C-H functionalisation of aldehydes, examples of C-H bond activation mediated by antimony(III) are still extremely scarce. Prompted by the exciting features reported for bismuth congeners by Evans *et al.*,⁴ we have investigated the unique formation of pnictogen(III) complexes, more particularly Sb(III), supported by different NCN⁻ pincer scaffolds and containing the oxyaryl, formally dianionic ligand (C₆H₂^tBu₂-3,5-O-4)²⁻. This remarkable family of complexes is produced upon a Sb-mediated process of C-H activation in *para* position of the phenolate. The intricacies of the mechanism of formation, bonding properties and reactivity of these complexes will be presented.⁵ Their ambivalent radical/ionic nature will be discussed on the grounds of XRD, 2D solution NMR, ESR and DFT investigations.

**Formation of unique oxyaryl pnictogen(III) complexes via C-H bond activation.**References

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Novel luminescent polymetallic assemblies of pyridylidene bricks with π -extended assembling ligands

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Among luminescent transition metal complexes, cyclometalated platinum(II) and iridium(III) complexes have increasingly attracted much attention as a result of their outstanding photophysical and luminescent properties.¹ In these complexes, an important role is played by the chelating ligand which defines the stability of the complex. An intriguing poorly explored class of C[^]N chelating ligands is pyridylidenes²; this non-classical NHC carbenes exhibit stronger σ -donating and π -acidic properties compared to Arduengo's type NHCs³. On the other hand, π -extended polytopic assembling ligands constitute a valuable building block for the construction of discrete and polymeric structures from one- (1D) to three-dimensional (3D) metallosupramolecular assemblies⁴.

In this presentation, a novel class of bimetallic assemblies incorporating π -extended and pyridylidene ligands will be presented. π -extended ligands are based on pyridine or 2-picolinate moieties (Figure 1a). Then, their coordination with platinum(II) pyridyl-pyridylidene bricks led to unprecedented bimetallic architectures. In addition, the formation of assemblies from Ir(III) pyridylidene building blocks is currently underway, with the recent development of an unprecedented efficient preparation of mono- or bis-cyclometallated pyridylidene iridium(III) bricks (Figure 1b). These novel platforms are currently under investigation for their luminescence and biological activities.

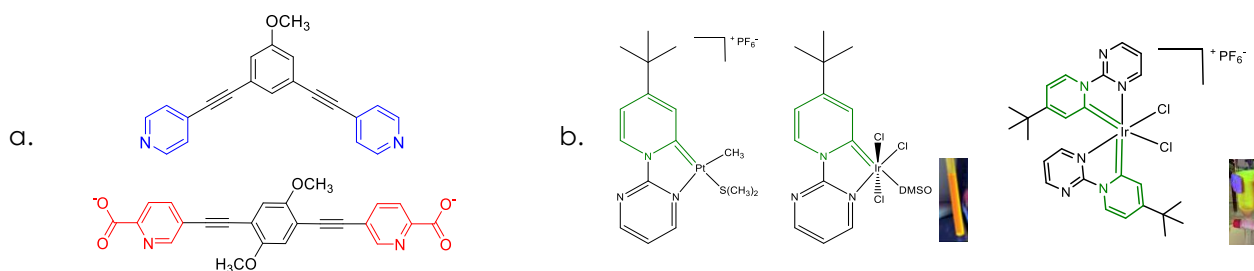


Figure 1 a. π -extended assembling ligands; b. Platinum(II) and iridium(III) pyridylidene bricks

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Solid-State ^{19}F NMR Chemical Shift in Square-Planar Nickel-Fluoride Complexes Linked by Halogen Bonds

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Although the halogen bond is widely explored by experimental and computational studies, its NMR signature has attracted little attention.

In this work, we modelled and analysed the previously measured ^{19}F solid state NMR chemical shifts in a family of trans trans $\text{Ni}^{\text{II}}-(\text{PEt}_3)_2$ -iodoaryl-fluoride complexes, capable of forming self-complementary networks held together by a $\text{NiF}\cdots\text{I}(\text{C})$ halogen bond.¹ To understand how the ^{19}F NMR resonances of nickel-bonded fluoride are affected by the halogen bond, we investigate the origin of the shielding in trans- $[\text{NiF}(2,3,5,6\text{-C}_6\text{F}_4\text{I})(\text{PEt}_3)_2]$, trans- $[\text{NiF}(2,3,4,5\text{-C}_6\text{F}_4\text{I})(\text{PEt}_3)_2]$, and trans- $[\text{NiF}(\text{C}_6\text{F}_5)(\text{PEt}_3)_2]$ in the solid state, where an halogen bond is present in the two former systems, but not in the latter. The ^{19}F NMR chemical shift calculations and analysis, both in periodic and molecular models, highlight the factors controlling the shielding characteristics of square-planar nickel-fluoride complexes, as well as the experimentally observed deshielding of fluoride in halogen-bonded systems.

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Cu(II) complexes for white Light-emitting Electrochemical Cells

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Cationic copper complexes with bidentate pyridine ligand $[\text{Cu}(\text{L})(\text{N-N})][\text{PF}_6]$ (L = NHC or diphosphine) have been developed for lightening applications.^{1,2} The influence of the electronic properties on the N-N ligands were investigated, giving a wide range of wave length emission from blue to red. We established some structure – properties relationships, supported by structural, photo physical and TD-DFT studies. Thermally Activated Delayed Fluorescence was highlighted as the specific luminescence of these cationic copper complexes. Based on these results, blue to red and white LEC were developed.



Figure. Design of copper complexes for rainbow emission and white LECs application

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HOMOGENEOUS METAL-CATALYSED CHEMO-SELECTIVE TRANSFORMATION OF UNPROTECTED SUGARS AND POLYOLS

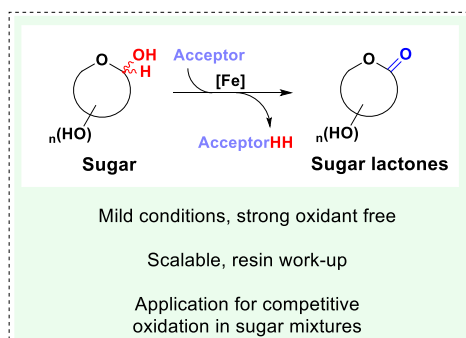
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Sébastien Comesse* and Laure Benhamou***

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Oxidation of sugars and polyols traditionally relies either on protection/deprotection strategies or on the use of a stoichiometric amount of halogenated reagent. Catalytic strategies have also been reported, but they are relying on precious metals such as palladium, platinum, rhodium or ruthenium.²⁻⁵

We recently developed a straightforward catalytic method for the anomeric oxidation of fully unprotected carbohydrates using an iron complex.⁶ Our approach relies on a transfer hydrogenation mechanism, where dihydrogen is formally transferred from the anomeric carbon of the sugar to an external hydrogen acceptor (e.g. ketone) without the use of strong oxidant or base. Knölker type complexes, which have been previously described for simple alcohols⁷ and diols oxidation, proved to be an excellent catalyst for this transformation.⁸

After optimisation, our procedure allows the selective oxidation of the anomeric position of a wide range of unprotected monosaccharides, to form quantitatively the corresponding lactones (either *delta*- and/or *gamma*-lactones). Noticeably, the products were obtained without using any chromatographic techniques. Moreover, by taking advantage of the kinetic discrepancy of oxidation between hexoses and pentoses, we achieved selective oxidation of a pentose in a hexose-pentose mixture.



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Trifluoroborate azamacrocyclic chelators as an innovative approach to theranostic radiopharmaceuticals design

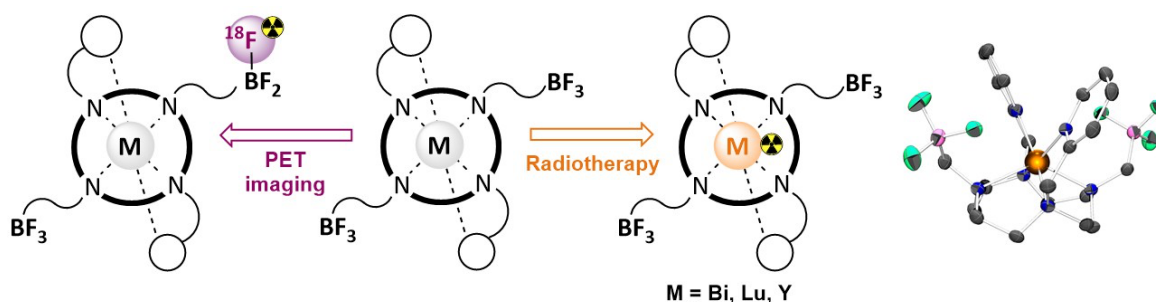
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In oncology, one of the main challenges is the development of theranostic tools whose objective is to combine therapy and diagnosis. Ideally, in nuclear medicine, therapy and diagnosis can be performed with a single entity to provide identical biodistribution during imaging and therapy, which facilitates dosimetry calculations and allows to monitor the effectiveness of the treatment. Currently theranostic radiopharmaceuticals used clinically possess a single molecular site that can be radiolabelled with two different isotopes, one useful for imaging and the other for radiotherapy. Isotopes can come from the same element ($^{64}\text{Cu}/^{67}\text{Cu}$)¹ or two different ($^{68}\text{Ga}/^{177}\text{Lu}$).² However, elements presenting two complementary isotopes are scarce, and a single coordination site for different elements often results in non-optimal chelation of the radioisotopes. The most used and available element for PET (Positron Emission Tomography) imaging is fluorine (^{18}F isotope), whereas for radiotherapy, metallic elements are mainly used (Bi, Lu, Y...). Our objective is therefore to synthesize an innovating family of tracers with two distinct radiolabelling sites, one dedicated to fluorine and the other for metallic cation, providing optimal stability for both elements. Thus, we present herein a proof-of-concept cyclen-based chelator, functionalized by two trifluoroborate units that allow easy $^{19}\text{F}/^{18}\text{F}$ isotopic exchange.³ Its coordination chemistry was studied and its ^{18}F -radiolabelling was successfully achieved. Current development of a second generation of ligands will also be discussed, in order to optimize chelation of metals of interest in radiotherapy (Bi, Lu, Y),⁴ bringing these compounds towards the preparation of innovative theranostic radiopharmaceuticals.



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center. Those phosphines have been post-functionalized to include a borane group in the second coordination sphere of the metal center. By using different lengths for the hydrocarbon chain carrying the borane entity, it can influence the flexibility of the ligand and therefore the positioning of the borane group relative to the iron center. The influence of those changes on the reactivity of those complexes toward the activation of H₂ will be considered.

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Original Photoactive Cerium-Based Catalyst for Photoinduced Electron Transfer

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Résumé

Catalysis is a fascinating opportunity for chemists to unbolt new reaction pathways in mild conditions. Among promising fields of catalysis, photoredox catalysts have shown good reactivity. However, the mostly-used photocatalysts are still mainly based on precious metals such as iridium and ruthenium. Efforts to develop more abundant metals photoactive complexes brought some examples using iron, copper, and chromium complexes as photocatalysts. However, they remain only mildly reductive. Among other abundant metals, cerium is an interesting candidate: as abundant as cobalt (66.5 ppm) and cheaper, its comprehensive photochemical behaviour has been recently highlighted both as a powerful Single-Electron Transfer (SET) reagent in +III oxidation state, and as a Hydrogen Atom Transfer (HAT) reagent, even capable of activating light alkanes (including methane).

Nevertheless, the widespread use of CeCl₃ as the photocatalyst hampers the progress in cerium photocatalysis. Indeed, its low solubility in apolar solvents significantly narrows the scope of possible reactions in mild conditions, and non-tunable redox potential complicates using this species in a multicatalytic system. Moreover, the mechanism of HAT reactions of cerium is still discussed, mainly the nature of the HAT agent. This is particularly due to the high coordination number of lanthanide complexes, which renders the intermediates more difficult to ascertain.

To overcome those issues, we synthesized a highly soluble cerium complex: Ce(N(CH₂CH₂NSiPr₃)₃) CeTRENTIPS, which displays SET reactivity with aryl and alkyl halides (Cl, Br, I) under +III oxidation state. Having a single open apical coordination position, CeIIITRENTIPS can be easily oxidized in corresponding CeIV mono-halides.

Mots-Clés: Photocatalysis, Lanthanides, Single Electron Transfer

^{*}Intervenant

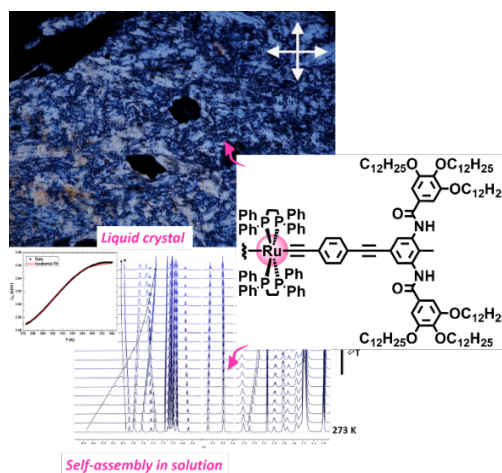
New insights into the self-assembly processes of Ru^{II} bis-acetylide compounds

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Small molecules self-assembly through non-covalent interactions is ubiquitous not only in natural but also in artificial systems and is particularly central to achieve high charge transport.¹⁻² While self-assembly may occur in the solution state leading to the formation of supramolecular polymers,³ assemblies of molecules may also appear at the solid state and has been well-developed since the discovery of liquid crystals (mesogens) for display technologies.⁴ In those fields, organometallic molecules have shown their superiority compared to purely organic compounds because introducing a metal into the molecular backbone has brought about a wealth of new properties such as (chiral)luminescence,⁵ complementary weak metallophilic interactions that have strengthened and guided the supramolecular process⁶ to name a few.



We recently reported the preparation of a new Ru^{II} bis-acetylides complex equipped with a mesogenic ligand,⁷⁻⁸ which was able to form micrometer long ribbons that eventually trapped aromatic solvent molecules to form a gel. Inspired by those outcomes, we have explored new scaffolds⁷ and investigated their self-assembly behaviour at the solid state and in solution. In this communication, we will disclose our conclusions on the molecular parameters driving their self-assembly.

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Mechanosynthesis: Green Chemistry applied to the design of copper-based photoinitiators

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Photoinitiated polymerization plays a more and more important role in industry as reflected by the continuously growing number of applications of this technique in conventional areas such as coatings, inks, and adhesives but also in high-tech domains, like optoelectronics, laser imaging, stereolithography and nanotechnology. Indeed, photopolymerization presents several advantages such as very short reaction time even at room temperature and the absence of solvents avoiding the formation of volatile organic compounds (VOC). Moreover, the possibility to irradiate with high precision specific zones allows the spatial control of the polymerization.[1] Since 2011, photoinitiating systems able to initiate polymerization under soft light irradiation sources have been the subject of intense efforts to minimize the risks and the costs related to the conventional UV irradiation. However, even if some results are promising, so far the reported systems still present low to moderate reactivity and can hardly compete with actual UV systems.

In the search for new photoinitiating systems, copper (II) complexes have been identified as promising candidates for the development of photoinitiating systems usable in industrial processes for coating applications and the production of thick epoxy/glass fiber composites. Parallel to high photoinitiating efficiencies, the mechanosynthesis of copper complexes has been identified as a promising approach for the design of photoinitiators.

In this presentation, a comparison of copper complexes with reference photoinitiating systems is also provided. The development of photoredox catalysts based on copper complexes provides a means for creating photoinitiating systems with unprecedented reactivity. Currently, no photoredox catalysts exist on the market and the design of photoinitiators by mechanosynthesis is not under use in industry yet.

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Nitrogen electroreduction in aminoboranes electrocatalyzed by a molybdenum coordination complex

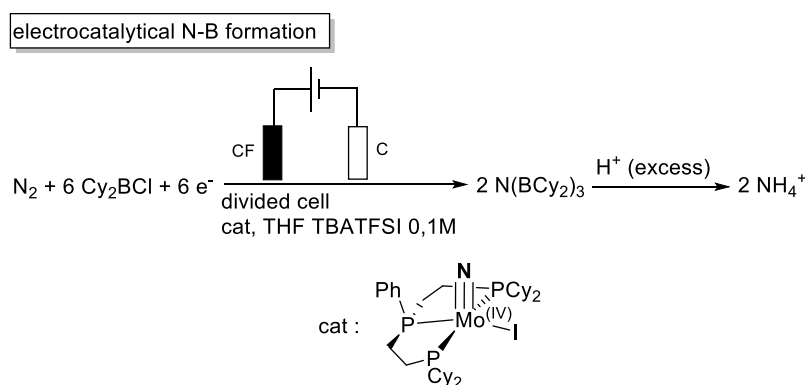
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The electrocatalytic reduction of N_2 (eN₂RR) by homogeneous metal complexes is currently considered as a promising alternative to the Haber-Bosch process, which is both too energy intensive and too polluting. It opens up the possibility of replacing the harsh conditions used today in this industrial process with milder conditions involving clean electricity sources.¹ Despite all these advantages, very few molecular catalysts have so far proven effective for the electrochemical reduction of N_2 , facing problems such as secondary reaction and low reactivity of N_2 .^{2,3} To date, the most efficient example has been reported by Peters *et al.* with a faradaic yield of 44.5 %.⁴ In this presentation, we will present our recent work on the electrocatalytic reduction of N_2 using a (PPP)Mo(\equiv N)(I) catalyst developed by our group (see scheme below).⁵ We will show that chloroboranes can be used as a source of electrophile to activate the nitrogen atom bound to the Mo(IV) center. The properties of the catalyst and its role in the electrocatalytic transformation of N_2 into borylamine will be discussed on the ground of detailed electrochemical and spectroscopic data.⁶



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Coordination chemistry of ligands based on 2,1,3-benzothiadiazole

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

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

The work presented here will focusses on the synthesis and characterization, DFT and TD-DFT calculations of chelating ligands (Figure 1), bearing BTD unit and their transition metal complexes [3-5]. The photophysical and magnetic properties of the new compounds were investigated.

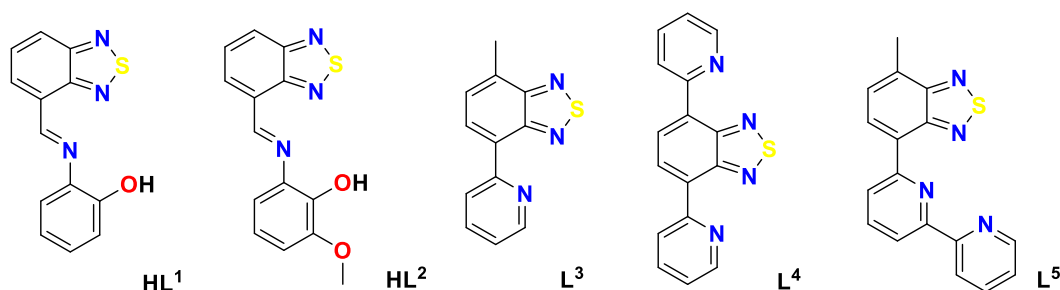


Figure 1. Ligands developed in this work.

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Combining Spectroscopies & *Ab Initio* Molecular Dynamics to Decipher the Structure-Activity Relationship of Cu-H Clusters

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Cu-H clusters occupy an important place in organic synthesis. A prime example is Stryker's reagent, a commercial, phosphine-stabilized, hexameric polymetallic copper(I) hydride $[(\text{Ph}_3\text{P})\text{CuH}]_6$ routinely used as a mild and selective reducing agent.¹ While the solid-state structure of Stryker's reagent and its derivatives has been clarified,² the mechanistic understanding of their role in reduction reactions is still a white page. This likely originates in the limited knowledge available on the structure of Cu-H clusters in solution, as well as in their large size which had so far limited computational exploration.³

A combination of *in situ* XANES, EXAFS, NMR, MS, cyclic voltammetry and EPR was used to investigate the structure of a series of $[\text{LCuH}]_n$ complexes in solution under reaction conditions. The spectroscopic data were interpreted with the assistance of *ab initio* molecular dynamics of $[\text{LCuH}]_n$ clusters in a solvent cage and spectroscopic prediction at the DFT level.

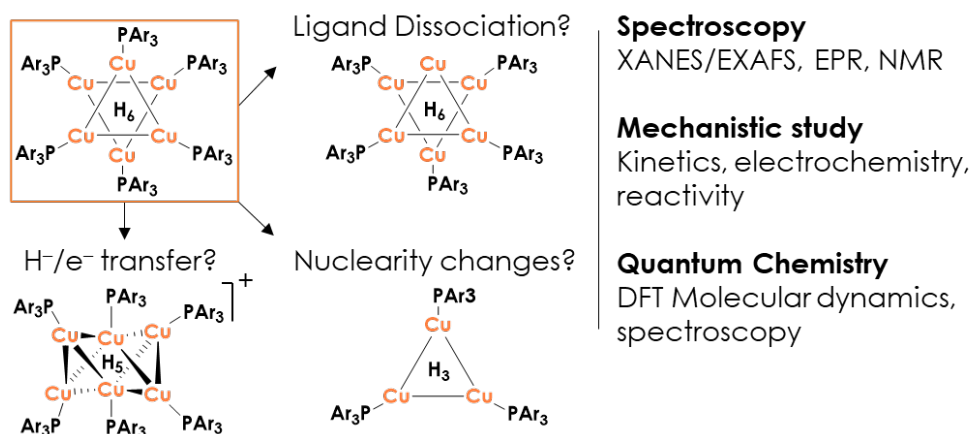


Figure – Spectroscopy, quantum chemistry and mechanistic studies were used to probe the structural changes of copper hydride clusters under reaction conditions

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Synthesis of Multi-metallic f-element Complexes with the Cyclononatetraenyl Ligand

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For many decades, the chemical reactivity of metals from the f-block were thought to be limited to their Lewis acid properties.¹ However, the end of the 20th century saw a renewed interest for the rare earth metals, first thanks to their use as single electron reductant² and quickly, for various application in material and molecular science.³ Most notably their magnetic properties have been extensively studied during the last twenty years.⁴

In depth investigation of their electronic structures have allowed for a better comprehension of their singularities, such as intermediate valent states. The rationalization of the electronic structure has shown the importance of the environment and the decisive role molecular chemistry can play.⁵

Particularly, aromatic ligand are very powerful ligands in terms of electronic and steric control. The small cyclopentadienyl ligand (Cp)⁶ and the cyclooctatetraenyl (Cot)⁷ have been studied in a variety of complexes. We recently studied the larger cyclononatetraene (Cnt), which displays higher flexibility⁸ as well as redox active properties in order to create unique complexes with f-elements. These multi-metallic species were investigated through several characterization including SC-XRD, magnetic studies, and CASSCF calculations.

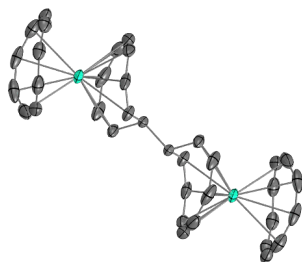


Figure X-ray structure of a dysprosium dimer with a coupled cyclononatetraenyl ligand. Carbon atoms are in grey, dysprosium in light blue, hydrogens are removed for clarity.

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Catalytic carbonylation of acrylic acid to succinic anhydride

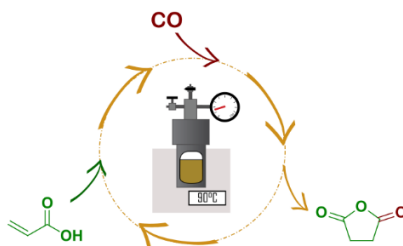
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Nowadays, the share of plastics reaches 90 % of the production of petrochemicals. To reduce our dependence on fossil feedstock for the synthesis of polymers, renewable starting materials could be used instead. In this context, we are targeting the formation of a monomer, succinic anhydride, from bio-based starting materials. The current industrial production of succinic anhydride relies on the oxidation and hydrogenation of petrosourced *n*-butane; another route consists in promoting the carbonylation of β -propiolactone, also a petrochemical.¹ As an alternative, we developed the carbonylation of acrylic acid, an isomer of β -propiolactone, which is not only a common platform chemical, but has also the potential of being biosourced.²

Early studies on the carbonylation of acrylic acid highlighted the difficulty of performing a selective, efficient and direct carbonylation reaction on acrylic acid.³ Yet, by designing a selective low-valent cobalt complex supported by phosphine ligands, the production of succinic anhydride from acrylic acid was unlocked, thanks to mild reaction conditions (90 °C, 16 bar).⁴ Screening of several reaction parameters such as gas phase pressure and composition, ligands and temperature, enabled us to propose some mechanistic hypotheses to rationalize the trends observed during this challenging carbonylative ring-closure.



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Counter-ion Effect on $\text{Ru}(\text{bpy})_3(\text{X})_2$ Complexes-Catalyzed Photocycloaddition through Energy Transfer

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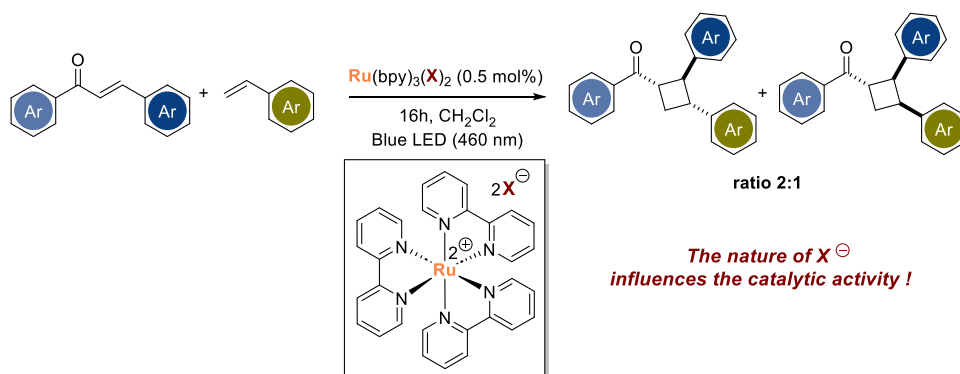
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Ruthenium tris(bipyridine) complexes have been widely used and studied over the past decades. These $\text{Ru}(\text{II})$ -based complexes are indeed well-known for their unique reactivity and their valuable photophysical and electrochemical properties.¹ In particular, they have been used as photocatalysts in a large range of organic transformations.² A recent report has brought to light counter-ion dependence in single electron transfer (SET) efficiency promoted by cationic ruthenium photoredox catalysts.³ Nevertheless, in energy transfer (EnT) photocatalysis,⁴ counter-ion effect has been to date completely neglected in the literature.

In this contribution, we report that the modification of the counter-ion X has a dramatic impact on the catalytic activity of $\text{Ru}(\text{bpy})_3(\text{X})_2$ complexes in intermolecular [2+2] cycloaddition reactions operating through triplet energy transfer. Experimental results were then rationalized by measuring different physicochemical parameters such as excited-state lifetime, photostability, quantum yield and excited-state energy of the $\text{Ru}(\text{bpy})_3(\text{X})_2$ complexes.

Thus, based on catalytic results, photophysical studies and a scope of substrates, we have demonstrated that a judicious choice of the counter-ion can modulate the reactivity of $\text{Ru}(\text{bpy})_3(\text{X})_2$ complexes in photocatalysis operated by energy transfer.⁵



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⁵ Publication submitted.

Rh-based molecular cages and gels for CO₂ photoreduction

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Having molecularly-defined active sites, porous macroligands^[1] have been found to drive the activity of heterogenized catalytic processes on a similar way as molecular ligands but with the advantage of the structuration in a three-dimensional framework and the confinement within a porous nanospace. Following this principle, organometallic Rh molecular complexes embedded within porous organic polymer and metal-organic frameworks used as macroligand showed a high productivity for the photoreduction of carbon dioxide into formic acid, selectively, using visible light as sole energy source. Recently we applied our strategy to more complex Rh-based metal organic polyhedra (MOP) as catalytic building units. Rh-MOP gels showed the highest activity reported so far for CO₂ to formic acid photoreduction using visible light, with a productivity of 3 g(formic acid)/g(catalyst)/h.^[2] The very high catalytic activity compared to other heterogeneous photocatalysts can be rationalized by the high number of Rh sites per gram of catalyst, but also by their very high accessibility inside the supramolecular cage. The coordination of the MOP by electron-donating N-ligands not only leads to a heterogenization of the active centre in a stable, and easily recyclable polymer. The present work opens new perspectives for the design of novel discrete molecular architectures with accessible metal sites for the production of solar fuels.

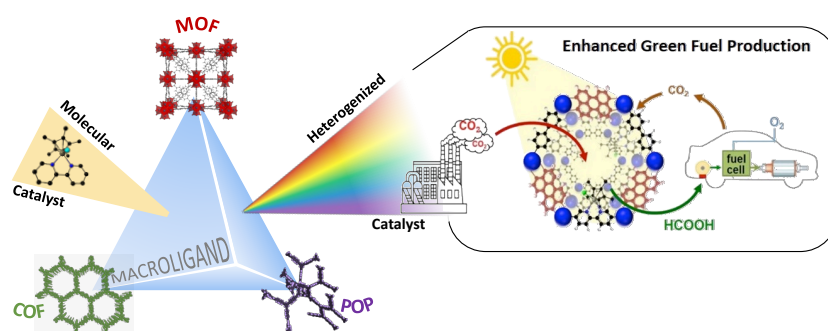


Figure. 1 Porous hybrid solids as macroligands for the photocatalytic CO₂ conversion.

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Synthesis and coordination of a diphosphine-[NHC-borane] compound: a new ligand framework for bimetallic structure featuring a boron-bridging moiety

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The development of ligand frameworks able to support multiple metal centres is a challenging task that is much less developed than ligand stabilising “only” one metal. Yet, these researches gave rise to very original structures featuring a multiplicity of reactive sites.¹

In this presentation, I will describe the synthesis of a diphosphine compound featuring a central (NHC-BH₃) unit. This compound can act as a ligand supporting two Au centres bridged by the NHC-borane fragment eventually giving rise to a rare Au₄²⁺ complex through reduction and dimerization processes upon loss of a molecule of H₂. I will present a combined experimental and theoretical investigations shedding light on i) the electronic description of this complex as well as on its formation via (μCl)-Au₂ and (μH)-Au₂ species. Furthermore, despite its sensitivity, the reactivity of the Au₄²⁺ complex was notably studied toward thiol, showing a clean oxidative reaction leading to the formation of a (μS(Ph))-Au₂ species.

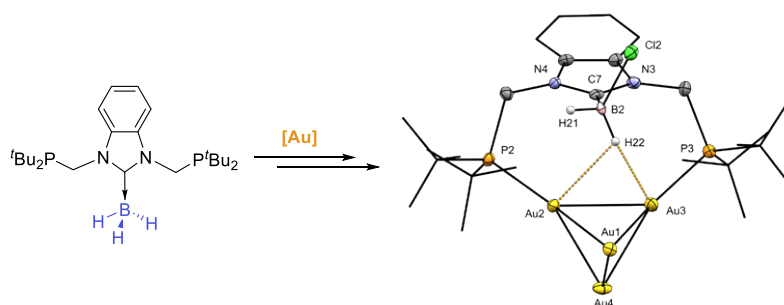


Figure: Truncated molecular structure of Au₄ complex

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