Exploring reactivity and mechanism of the reductive activation of O_2 by Fe-porphyrin for the oxygenation of indole derivatives

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Keywords: O_2 reductive activation, Fe(porphyrin)-superoxo, controlled potential electrolysis

Oxidation reactions are widely used in industry to introduce a functional group onto an organic backbone. They generally require harsh conditions (temperature, pressure, strong and/or polluting oxidant), and are often stoichiometric and poorly selective.[1] Oxygenases are enzymes capable of efficiently and selectively oxidise substrate under mild conditions through the reductive activation of O_2. Our aim is to mimic this activity by using Fe-porphyrins under aerobic conditions and electrochemistry to generate *in-situ* highly reactive O_2-intermediates, which will enable oxygenation of organic substrates. Previously, using an (spectro)electrochemical approach,[2] we reported on the O_2 activation mechanism by Fe-porphyrins (Fe(III)(F_{20}TPP)Cl, Figure 1) demonstrating that different O_2-intermediates can be generated depending on the value of the applied potential (Figure 1).[3] Fe(III)-OO$^{\bullet}$ intermediate is generated when a mild potential is applied to an aerated Fe(III) solution.

We now focus our studies on the reactivity of the Fe(III)-OO$^{\bullet}$ species towards indoles, relevant to indoleamine dioxygenase activity.[4] We will address the challenges of selecting superoxo reactivity toward the substrate and propose a mechanism that rationalizes the observed reactivity. Ultimately, we will highlight how our electrochemical approach can lead to novel electrosynthetic processes, advancing the development of more sustainable and efficient oxidation reactions.

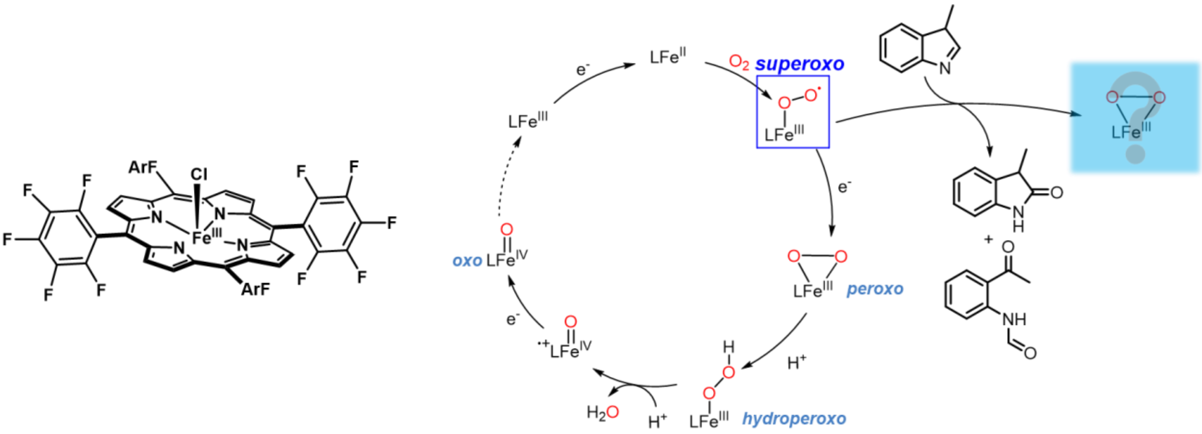

Figure 1 Fe-porphyrin studied Fe(III)(F_{20}TPP)Cl (F_{20}TPP: 5,10,15,20-Tetrakis-(2,3,4,5,6-pentafluorophenyl)-porphyrin) (left). Proposed catalytic cycle of O_2 reductive activation by Fe-porphyrin complex and reactivity with 3-methylindole (right).

[1]. a) J. H. Teles, W. Partenheimer, R. Jira, F. Cavani, G. Strukul, R. Hage, J. W. Boer, L. Gooßen, P. Mamone, O. A. Kholdeeva, Oxidation in Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook in Four Volumes, **2017**, *3rd ed*, Wiley. b) A. Timmins, S. P. de Visser, *Catalysts* **2018**, *8*, 314-339.
[2]. J.-M. Noël, N. Kostopoulos, C. Achaibou, C. Fave, E. Anxolabéhère-Mallart, F. Kanoufi, Angew. *Chem. Int. Ed.* **2020**, *59*, 16376–16380.
[3]. N. Kostopoulos, F. Banse, C. Fave, E. Anxolabéhère-Mallart, *Chem. Commun.* **2021**, *57*, 1198-1201.
[4]. a) P. Mondal, S. Rajapakse, G. B. Wijeratne, *J. Am. Chem. Soc.* **2022**, *144*, 3843-3854. b) J. J. D. Sacramento, D. P. Goldberg, *Chem. Commun.* **2020**, *56*, 3089-3092. c) P. Mondal, G. B. Wijeratne, *J. Am. Chem. Soc.* **2020**, *142*, 1846-1856.

Rare Earths-Based Coordination Polymers: Recent Innovations in Fabrication and Structural Design Techniques

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Keywords: Rare earths, coordination polymers, thermodynamic studies, core-shell particles

Text:

Over the past 20 years, our group has focused on researching lanthanide-based coordination polymers, valued for their unique optical properties that make them suitable for applications such as anti-counterfeiting markers.[1] These compounds consist of metal ions linked by organic ligands like 1,4-benzene-dicarboxylate, resulting in mono-, bi-, or three-dimensional network structures. For several years, we have synthesized molecular alloys by taking advantage of the similar chemical properties of lanthanides.[2] These alloys possess the notable characteristic of sharing a uniform structure while exhibiting varied emission colors. However, due to the random distribution and proximity of rare-earth ions, intermetallic transfer often occurs, leading to a decrease in luminescence intensity. To decrease this, we synthesized core-shell particles, which help reduce intermetallic transfer by forming a barrier between the core and the shell.[3] Recent thermodynamic studies[4] have provided greater precision in predicting optimal structures for the core-shell compounds under investigation in our group (Figure 1). In this work, we present our latest advancements in shaping lanthanide-based coordination polymers.[5]

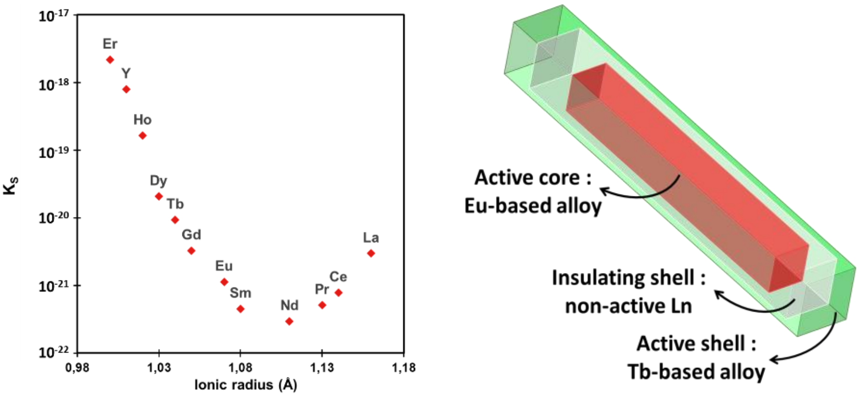

Figure 1 Left : Solubility product of homonuclear lanthanide-based coordination polymer $[Ln_2(bdc)_3(H_2O)_4]_\infty$ with Ln = La-Er plus Y and bdc = 1,4-benzene-dicarboxylate ligand, Right : optimized shaping of an emissive core-shell particle with terbium and europium.

1. O. Guillou, C. Daiguebonne, G. Calvez, K. Bernot, *Accounts of chemical research* **2016**, *49*, 844.
2. P. Dechambenoit, S. Ferlay, N. Kyritsakas, M. W. Hosseini, *Chemical communications* **2009**, 1559.
3. A. Abdallah, C. Daiguebonne, Y. Suffren, A. Rojo, V. Demange, K. Bernot, G. Calvez, O. Guillou, *Inorganic Chemistry* **2019**, *58*, 1317.
4. C. Blais, T. Morvan, C. Daiguebonne, Y. Suffren, G. Calvez, K. Bernot, O. Guillou, *Inorganic Chemistry* **2023**, *62*, 4495.
5. T. Morvan, C. Blais, A. Chang, C. Daiguebonne, Y. Suffen, N. Audebrand, G. Calvez, F. Le Natur, K. Bernot, O. Guillou, *Inorganic Chemistry Communications* **2024**, *170*, 113275.

Exploring the reactivity of Pd^{IV} alkyl species

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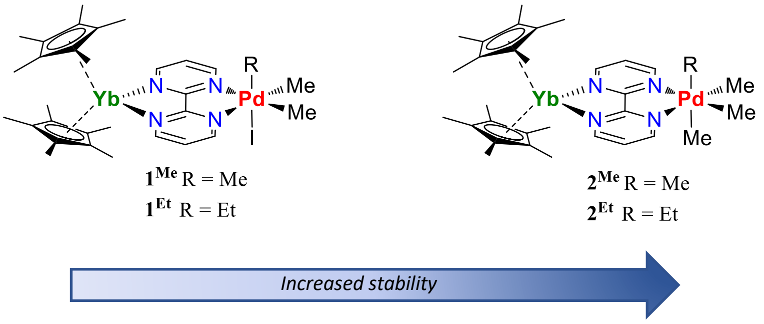
Keywords: palladium^{IV}, radical reactivity, light-induced homolysis

Palladium-mediated transformations are dominated by Pd^{0} and Pd^{II} species. In contrast, the reactivity of higher oxidation states such as Pd^{III} and Pd^{IV} are far less explored because of the low accessibility and stability of these species.[1]

One possibility to stabilize electrophilic Pd^{IV} species is to combine them with an electron-rich fragment that can donate electron density to the Pd center, such as a Yb-bipyrimidine fragment. [2,3] Yet, these compounds are still susceptible to undergo reductive elimination if labile ligands are coordinated to the Pd metal center.[4]

Intending to further increase the stability of these complexes, herein we present the synthesis of several Yb-stabilized Pd^{IV} tetraalkyl complexes (**2**^{Me}, **2**^{Et}), with a half-life time that is considerably longer than their tris-alkylated counterparts (**1**^{Me},**1**^{Et}). Mechanistic studies and various reactivity paths have been studied and will be presented.

Additionally, after studying the behavior of **2**^{Me} and **2**^{Et} in solution, we explore their photo-reactivity. This will give rise to a novel Pd^{IV} alkyl species resulting from the light-induced homolyses of the Pd-alkyl bond.



1^{Me} R = Me
1^{Et} R = Et

2^{Me} R = Me
2^{Et} R = Et

1. Sehnal, P.; Taylor, R. J. K.; Fairlamb, I. J. S. *Chem. Rev.* **2010**, 110 (2), 824.
2. Schultz, M.; Boncella, J. M.; Berg, D. J.; Tilley, T. D.; Andersen, R. A. *Organometallics* **2002**, *21* (3), 460–472.
3. G. Nocton, W. W. Lukens, C. H. Booth, S. S. Rozenel, S. A. Medling, L. Maron, R. Andersen, *J. Am. Chem. Soc.* **2014**, 136 (24), 8626.
4. V. Goudy, A. Jaoul, M. Cordier, C. Clavaguéra, G. Nocton, *J. Am. Chem. Soc.* **2017**, *139* (31), 10633.

PROTON-COUPLED ELECTRON TRANSFER TO AND FROM POLYOXOMETALATES

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Keywords: Polyoxometalates; photocatalysis; dehydrogenation

Polyoxometalates (POMs) are nano-sized molecular oxides that are well-known photocatalysts, able to promote Hydrogen Atom Transfer (HAT) from an organic substrate. Due to their ability to behave as multi-electron acceptors, polyoxometalates are ideal candidates to address environmental and energy challenges, particularly photocatalyzed hydrogen production. [1],[2] Therefore, W and Mo derivatives of the Keggin and Wells–Dawson series have been widely employed in related studies but, to date, the mechanism leading to hydrogen evolution onto polyoxometalates remains rather undefined. Initial studies have shown that SiloxPOMs are able to store electrons (electrochemically or chemically) and react with protons to eventually promote the formation of hydrogen. We thus came interested in understanding how the addition of protons or dioxygen trigger the release of electrons from reduced polyoxotungstate hybrids (*Silox*POM) that we synthesized in our group (Fig. 1). [3]

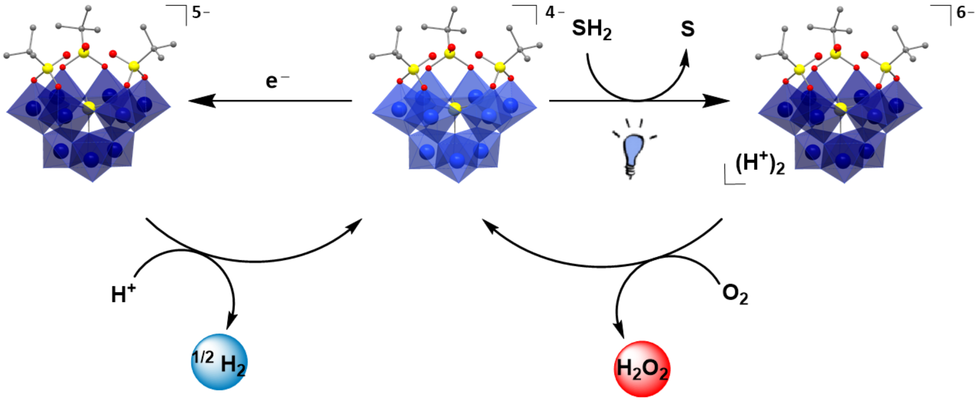

Figure 1. (left) spontaneous hydrogen release from reduced *Silox*POM upon protonation, and (right) hydrogen peroxide formation from aerobic solution of protonated / reduced cluster obtained by photo-oxidation of a suitable substrate SH_2.

Under photoirradiation, studies have shown that SiloxPOMs are able to promote HAT from non-functionalized alkanes. However, in the absence of a co-catalyst, dehydrogenation is not feasible under non-oxidative conditions. In order to carry out catalytic dehydrogenation reactions in these conditions, we developed Metala-SiloxPOMs. They represent unique entities that combine a photo- and redox-active platform, and a remote coordinatively well-defined metal center, thus able to tackle challenging catalytic reactions.

1. L. Hammarström, *Acc. Chem. Res*. **2015**, *48*, 840–850
2. H. Lv, W. Guo, K. Wu, Z. Chen, J. Bacsa, J. D. G. Musaev, Y. V. Geletii, S. M. Lauinger, T. Lian, C. L. Hill, *J. Am. Chem. Soc.* **2014**, *136*, 14015–14018; B. Matt, J. Fize, J. Moussa, H. Amouri, A. Pereira, V. Artero, G. Izzet, A. Proust, *Energy Environ. Sci.* **2013**, *6*, 1504−1508.
3. T. Zhang, A. Solé-Daura, S. Hostachy, S. Blanchard, C. Paris, Y. Li, J. J. Carbó, J.–M. Poblet, A. Proust, G. Guillemot, *J. Am. Chem. Soc*. **2018**, *140*, 14903–14914; L. K/Bidi, A. Desjonquères, G. Izzet, G. Guillemot, *Inorg. Chem.* **2023**, *62*, 1935–1941.

Photoactive Ruthenium(II) Bipyridyl Complexes Containing Phosphonium Ylide Ligands

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Keywords: Phosphonium Ylide, Photoluminescence, Photocatalysis.

Polypyridyl Ru(II) complexes exhibit unique photophysical properties that allow them to be involved in a large variety of photocatalytic applications.[1] The common method to manipulate excited state properties of such photocatalysts relies on modifying the ligand scaffold around the metal center. In this concern, the introduction of strongly σ-donating ligands such as *N*-heterocyclic carbenes (NHCs) has demonstrated beneficial effects.[2] However, and despite their rich coordination chemistry with transition metals, phosphonium ylides (P-ylides) of donor ability even superior to that of the NHCs,[3] have not yet been considered in the design of molecular photoactive Ru complexes.

In this contribution, we report the straightforward preparation of the first photoluminescent Ru(II) bipyridyl complexes containing *C,N*-chelating pyridine-phosphonium ylide ligands from readily available 2-(diphenylphosphino)pyridine. Their photophysical and redox properties have been studied and exploited in visible light photocatalysis for reactions taking place by means of simple electron transfer (SET) and energy transfer (EnT) processes.[4] Moreover, we have also developed a new method for the efficient synthesis of Ru(II) complexes featuring three different bidentate ligands that are difficult to prepare by conventional methods. In these complexes, the specific impact of the third ligand on the photophysical properties will be discussed.[5]

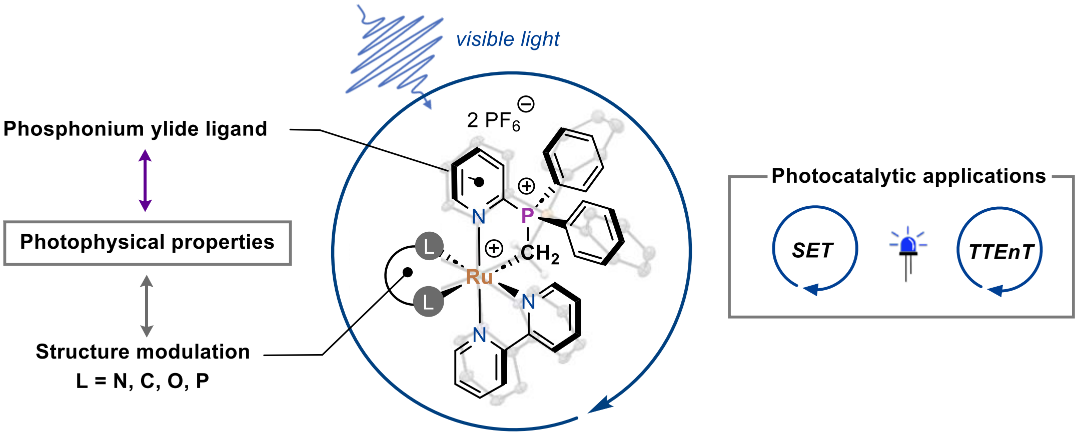

Figure 1: Phosphonium ylide ligands in photoluminescent Ru(II) complexes

1. S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini, V. Balzani, Photochemistry and Photophysics of Coordination Compounds: Ruthenium. In Photochemistry and Photophysics of Coordination Compounds I; Balzani, V., Campagna, S., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, **2007**; *Vol. 280*, pp 117–214.
2. a) S. U. Son, K. H. Park, Y. S. Lee, C. H. Choi, M. S. Lah, Y. H. Jang, D. J. Jang, Y. K. Chung, *Inorg. Chem.* **2004**, *43*, 6896; b) D. Schleicher, H. Leopold, H. Borrmann, T. Strassner, *Inorg. Chem*. **2017**, *56,* 7217.
3. Y. Canac, C. Lepetit, M. Abdalilah, C. Duhayon, R. Chauvin, *J. Am. Chem. Soc*. **2008**, *130*, 8406.
4. O. Fayafrou, E. Lognon, C. Duhayon, J.-B. Sortais, A. Monari, O. Baslé, Y. Canac, *Chem. Comm*. **2024**, DOI: 10.1039/D4CC05050A.
5. O. Fayafrou, C. Duhayon, J. B. Sortais, O. Baslé, Y. Canac, Manuscript in preparation.

EMISSIVE CHIRAL AND ACHIRAL HEXACOORDINATE Si(IV) COMPLEXES FROM VERSATILE PINCER-TYPE O^C^O AND O^N^O LIGANDS FOR OPTOELECTRONIC APPLICATIONS

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Keywords: fluorescence; silicon complexes; NHC ligands, Deferasirox, ECD, OLEDs, TD-DFT

Despite the widespread use of silicon and its derivatives, coordination compounds of this earth-abundant element are rarely investigated with regards to their optoelectronic properties, with most research focused on elemental Si, Si-phthalocyanines, silanes and siloxanes.[1]

Inspired by our previous results on versatile *pincer*-type O^C^O *N*-heterocyclic carbenes (NHCs)[2] and Deferasirox-inspired O^N^O ligands we attempted their coordination on Si(IV). We hereby report the synthesis, photo- and electro-luminescence characterization of the first example of a stable, homoleptic, neutral, hexacoordinate luminescent Si(IV)-NHC complex, namely **Si(OCO)$_2$** that displays an intense narrow blue emission in the solid state peaking at λ_{em} = 418 nm with a photoluminescence quantum yield (PLQY) of 32% (Figure 1).[3] Predictably, the **Si(ONO)$_2$** analogue was obtained as a racemic mixture of R_a/S_a atropisomers, which were isolated via chiral HPLC and possess similar photophysical behaviour to **Si(OCO)$_2$** with emission at λ_{em} = 420 nm and PLQY of 11% in the solid state[4]. This fluorescence, ascribed to an intraligand charge transfer (^{1}ILCT) transition enhanced by the rigidity of the 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) that show peak external quantum efficiency (EQE) of 1.3% (0.8 $cd \cdot A^{-1}$), maximum luminance of 2566 $cd \cdot m^{-2}$ and saturated true-blue emission.

In conclusion, this study will provide a taste of the untapped potential behind the chemistry of phenolate-stabilized Si(IV) complexes for the design of emitters with application in electroluminescent devices.

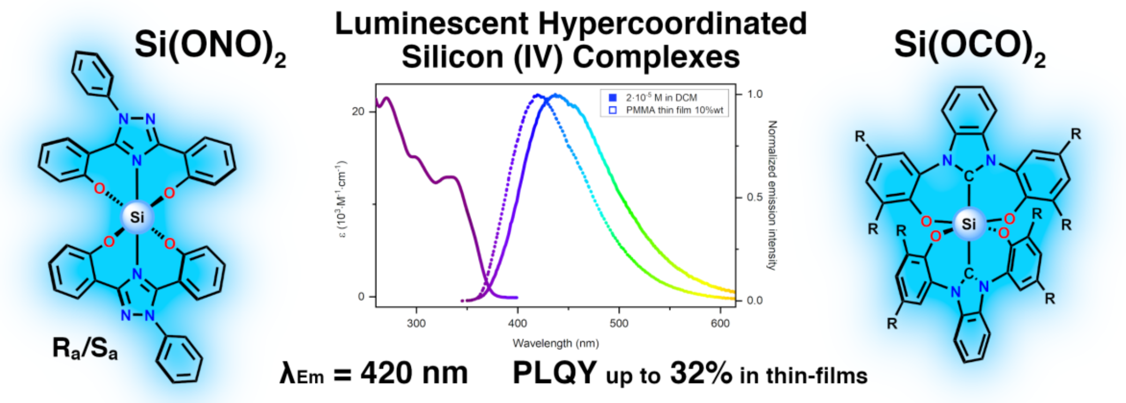

Figure 1 – Complexes **Si(ONO)$_2$** and **Si(OCO)$_2$** show intense blue emission peaking in the 420-430 nm range.

1. N. Auner, J. Weis, Organosilicon Chemistry III - From Molecules to Materials, Wiley-VCH, **2008**.
2. C. Romain, S. Choua, J.-P. Colin, M. Heinrich, C. Bailly, L. Karmazin-Brelot, S. Bellemin-Laponnaz and S. Dagorne, Redox and Luminescent Properties of Robust and Air-Stable N-Heterocyclic Carbene Group 4 Metal Complexes *Inorg. Chem.* **2014**, *53*, 7371.
3. T. Thierry, V. Giuso, F. Polo, P. Mercandelli, Y.-T. Chen, C.-H. Chang, M. Mauro and S. Bellemin-Laponnaz, A stable and true-blue emissive hexacoordinate Si(IV) N-heterocyclic carbene complex and its use in organic light-emitting diodes, *Dalton Trans.,* **2024**, *53*, 6445.
4. V. Giuso, T. Thierry, P. Mercandelli, N. Vanthuyne, M. Mauro and S. Bellemin-Laponnaz, A chiral Si(IV) complex bearing a 1,2,4-triazole-2,2'-diphenol ligand: synthesis, (chiro-)optical properties and computational investigation, *manuscript in preparation*

Synthesis and reactivity of reduced NHC-CO_2-Borane adducts

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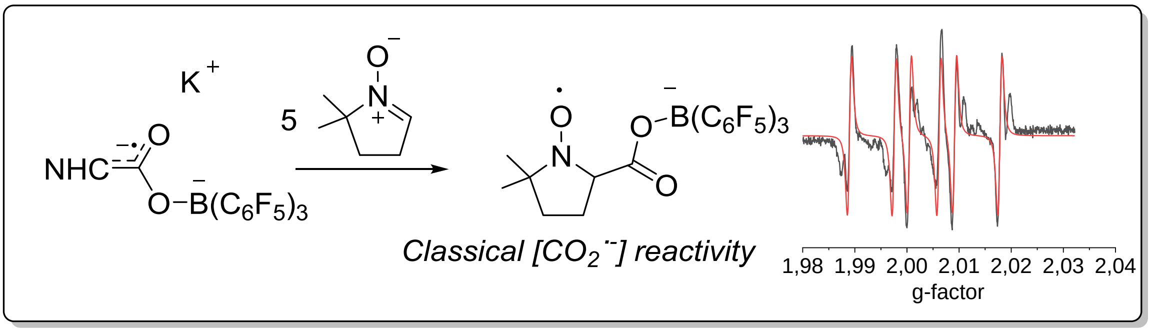
In the context of utilizing CO_2 as a sustainable carbon source, there is a compelling interest in identifying CO_2 activation methods facilitating a more accessible one-electron reduction to obtain $[CO_2^{\bullet -}]$. Our focus was on the single electron reduction of Frustrated Lewis Pair (FLP)-type activated CO_2 molecules, achieved through a bifunctional activation involving both Lewis basic and Lewis acidic entities. N-Heterocyclic Carbenes (NHCs) were selected for their significant electronic and steric modularity, along with their known ability to stabilize radical species.[1] We thus studied the reduction of NHC-CO_2-BR_3 species. We showed that these species undergo monoelectronic reduction at a less negative potential compared to free CO_2 and exhibit similar reactivity as $[CO_2^{\bullet -}]$, nonetheless.[2]



[1] L. A. Freeman, A. D. Obi, H. R. Machost, A. Molino, A. W. Nichols, D. A. Dickie, D. J. D. Wilson, C. W. Machan, R. J. Gilliard, Chem. Sci. 2021, 12, 3544–3550.
[2] A. Morales, C. Gonçalves, A. Sournia-Saquet, L. Vendier, A. Lledós, O. Baslé, S. Bontemps, Chem. Sci. 2024, 15, 3165–3173

Expending the family of cobalt tetraaza-macrocyclic complexes through ligand substitution to modulate catalytic performances

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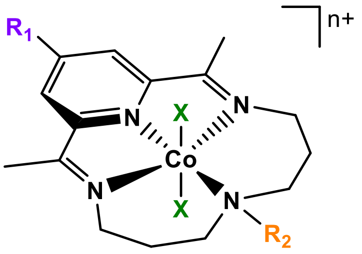
Keywords: cobalt tetraaza complexes; electrochemistry; catalysis; HER; CO2RR

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



X = Cl, MeCN

R_1 = Electron-withdrawing/donating groups

R_2 = Proton relay

Figure 1 Possible ligand substitutions for the modulation of catalytic properties of tetraaza-macrocyclic cobalt complexes

1. a) E.-I. Ochiai, K. M. Long, C. R. Sperati, D. H. Busch, *J. Am. Chem. Soc.*, **1969**, *91*, 3201-3206. b) K. M. Long, D. H. Busch, *Inorg. Chem.*, **1970**, *9*(3), 505-512.
2. a) C. C. L. McCrory, C. Uyeda, J. C. Peters, *J. Am. Chem. Soc.*, **2012**, *134*, 3164-3170. b) S. Varma, C. E. Castillo, T. Stoll, J. Fortage, A. G. Blackman, F. Molton, A. Deronzier, M.-N. Collomb, *Phys. Chem. Chem. Phys.* **2013**, *15*, 17544-17552.
3. a) A. H. A. Tinnemans, T. P. M. Koster, D. H. M. W. Thewissen, A. Mackor, *Recl. Trav. Chim. Pays-Bas*, **1984**, *103*, 288-295. b) D. C. Lacy, C. C. L. McCrory, J. C. Peters, *Inorg. Chem.*, **2014**, *53*, 4980-4988. c) E. Boutin, L. Merakeb, B. Ma, B. Boudy, M. Wang, J. Bonin, E. Anxolabéhère-Mallart, M. Robert, *Chem. Soc. Rev.*, **2020**, *49*, 5772-5809.
4. S. Roy, M. Bacchi, G. Berggren, V. Artero, C*hemSusChem*, **2015**, *8*, 3632-3638.
5. a) W. Nie, D. E. Tarnopol, C. C. L. McCrory, *J. Am. Chem. Soc.*, **2021**, *143*, 3764-3778. b) C. H. Lee, D. Villágran, T. R. Cook, J. C. Peters, D. G. Nocera, *ChemSusChem*, **2013**, *6*, 1541-1544.

Mixed-ligand, radical, gold bis(dithiolene) complexes: from single-component conductors to controllable NIR-II absorbers

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Keywords: Metal bis(dithiolene), Mixed-ligand.

Radical species such as neutral gold dithiolene complexes are excellent precursors of single-component molecular conductors. [1] So far, all such Au complexes reported in the literature are homoleptic complexes involving two identical dithiolene ligands. The formation of heteroleptic bis(dithiolene) complexes associating two different dithiolene ligands in the gold coordination sphere makes it possible to modulate not only the structures of materials as single-component conductors but also their intrinsic molecular properties, such as their redox characteristics and their strong absorption in the Near Infrared (NIR).[2] Herein, we wish to present a straightforward synthesis of mixed-ligand gold bis(dithiolene) complexes and the consequences of two different ligands on the NIR absorption and on the organization of the molecules in the solid state compared to the symmetrically substituted complexes as well as on their transport properties.[3]

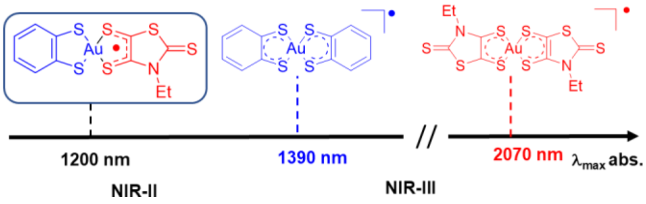

Figure 1 : NIR absorption of radical gold dithiolene complexes.

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1. Y. Le Gal, T. Roisnel, P. Auban-Senzier, N. Bellec, J. Íñiguez, E. Canadell, D. Lorcy, J. *Am. Chem. Soc.* **2018,** *140,* 6998−7004.

2. R. Perochon, F. Barrière, O. Jeannin, L. Piekara-Sady, M. Fourmigué, *Chem. Comm.* **2021,** *57,* 1615-1618.

3. H. Kharraz, E. Canadell, T. Roisnel, H. Cui, M. Fourmigué, D. Lorcy, *Chem. Sci.* **2024,** *15*, 11604-11616.

Unveiling the mechanism of the super-reduction of Dawson-type Polyoxometalate

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Keywords: Polyoxometalates, Electrochemistry, X-ray Absorption Spectroscopy

Electrochemical energy storage can be realized through batteries or the conversion into chemical fuels. Nevertheless, integrating redox mediators can pave the way for energy storage solutions that can operate both as batteries and fuel generators, thus transforming the application of renewable energy. Polyoxometalates (POMs), a fascinating class of inorganic molecules built from transition metals in their highest oxidation states, are known for their ability to exchange massively electrons in aqueous solution. In context, Cronin's group has highlighted that the Wells-Dawson $[P_2W_{18}O_{62}]^{6-}$ can be used as a groundbreaking electron reservoir to develop high-performance electrolyte in redox flow batteries, exceeding the energy density of redox flow batteries by six times.[3][4] In such devices, the POM undergoes a reduction and protonation process involving the transfer of 18 electrons and protons; however, the mechanism of the super-reduction is currently unknown.

Our research group has recently demonstrated that several POMs can store massively electrons within metal-metal bonds.[1][2] In this communication, we will unveil the mechanism of the super-reduction of Dawson-type POMs $[P_2W_{18}O_{62}]^{6-}$ in an acidic solution, up to the injection of 18 electrons (see **Figure A/**). This presentation will be supported by i) *in-situ* measurements (XANES/EXAFS (see **Figure B/**), UV-vis, and voltammetry) and ii) *ex-situ* measurements (^{31}P and ^{183}W NMR, Raman, single-crystal X-ray diffraction).

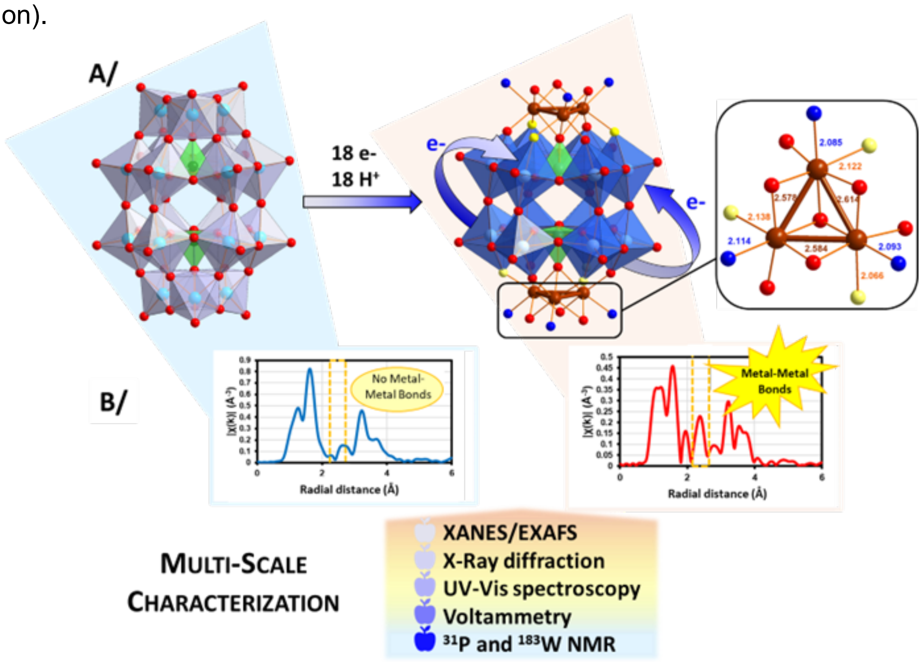

Figure A/ Schematic representation of the 18-electron-reduction of Dawson-POM $[P_2W^{VI}_{18}O_{62}]^{6-}$ revealed by **B/** in situ XANES/EXAFS techniques as part of a multi-scale characterization approach.

[1] C. Falaise and al. *Inorg. Chem.* **2023**, *62*, 2494
[2] G. Mpacko Priso and al. *Angew. Chem. Int. Ed.* **2023**, e202312457
[3] L. Cronin, and al. *Nature Chem* **2018**, *10*, 1042
[4] L. Cronin, and al. *J. Am. Chem. Soc.* **2022**, *144*, 8951

Low-valent Iron(II)-Complex for Catalytic Alkene Isomerization: From Mechanistic understanding to Applications

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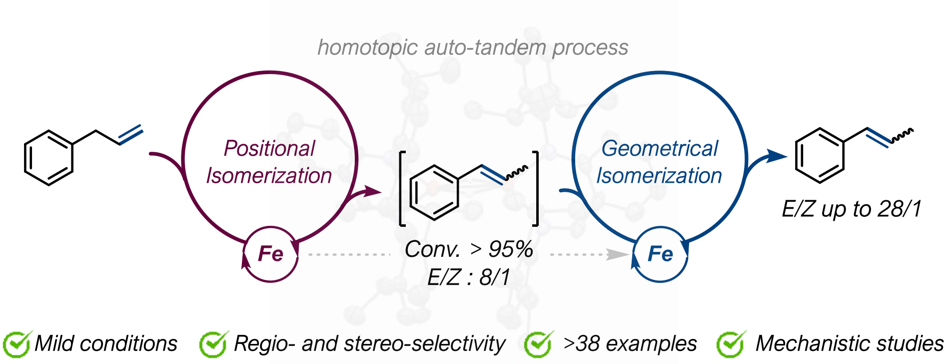
Keywords: alkene, catalysis, iron, isomerization, mechanism.

Metal-catalyzed isomerization of alkenes is a strategic route, providing value-added or synthetically relevant alkene-containing compounds from more readily available and/or easily accessible analogues.[1] Major challenges associated with the development of such a method are the control of the carbon-carbon double bond relocation over the carbon scaffold and/or the control of the configurational geometry of the re-formed alkene. For decades, precious metals have been at the forefront to address selectivity issues and to enrich the reaction applications.[2] However, environmental, and economic concerns about these metals, coupled with opportunities for new modes of reactivity and potential expansion of the reaction scope, have prompted the exploration of sustainable 3d TMs as potential catalysts for this transformation. Although considerable progress has been made in this area, most notably with cobalt, nickel and more recently with the cheapest and less toxic iron-based catalysts, the applicability of these protocols has been impeded by lack of generality, selectivity issues and limited availability of catalyst design/or tailor-made ligand that support the metal along the reaction pathway.[3] Therefore, the establishment of an efficient and highly selective alkenes transposition methodology is still a sought-after goal.

Leveraging our expertise in iron catalysis,[4] we have achieved, through a mechanistically driven approach combining extensive experimental (NMR, EPR, kinetic studies, control experiments) and computational studies, a highly regioselective and stereoselective method for alkene transposition using a novel low-valent iron(II)-based complex. This bespoke catalyst demonstrates a unique behavior to mediate positional and geometrical isomerization in an auto-tandem fashion via two state reactivity (e. g. scheme 1). Our methodology has been directly and efficiently applied to a range of both functionalized and unfunctionalized alkenes, including industrially and synthetically relevant targets and can be further expanded to perform regiodivergent or stereoconvegent isomerization.



Scheme 1 Overview of iron(II)-catalyzed isomerization of allylbenzene

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1. J. J. Molloy, T. Morack, R. Gilmour, *Angew. Chem. Int. Ed.* **2019**, *58*, 2.
2. a) E. Larionov,H. Li, C. Mazet, *Chem. Commum* **2014**, *50*, 9816; b) I. Massad, I. Marek, *ACS Catal*. **2020**, *10*, 5793.
3. a) X. Liu, B. Li, Q.Liu, *Synthesis* **2019**, *51*, 1293 ; b) S. Zhang, M. Findlater, *Synthesis* **2021**, *53*, 2787 ;c) A. -H. Obeid, J. Hannedouche, *Adv. Synth. Catal.* **2023**, *365*, 1100.
4. a) E. Bernoud, P. Oulié, R. Guillot, M. Mellah, J. Hannedouche, *Angew. Chem. Int. Ed*. **2014**, *53*, 1; b) C. Lepori, E. Bernoud, R. Guillot, S. Tobisch, J. Hannedouche, *Chem. Eur. J*. **2019**, *25*, 835; c) C. Lepori, R. Guillot, J. Hannedouche, *Adv. Synth. Catal*. **2019**, *316*, 714; d) C. Chen, C. Lepori, R. Guillot, R. Gil, S. Bezzenine, J. Hannedouche, *Angew. Chem., Int. Ed.* **2024**, *63*, e202408419.

Photo-dehalogenation reaction by reductive quenching mechanism with homoleptic copper(I) complexes: mechanistic study and scope

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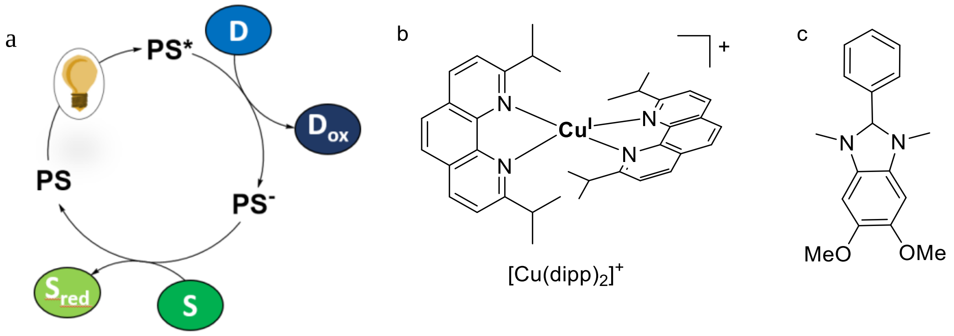
Keywords: reductive quenching • homoleptic copper(I) complexes • photochemistry • Hydrogen Atom Transfert (HAT) • sacrificial donors

Text: Photo-driven reactions have been widely explored since recent years and represent a very powerful tool in organic synthesis. Indeed, this type of reaction (involving, in particular, reactive radicals) enable unique reaction pathways and products compared to classical methods. Moreover, radical chemistry has to face different challenges: among others, be conducted in green and sustainable manner and have a high tolerance towards functional groups. In a previous contribution,[1] we have reported a reductive quenching cycle with a simple, strongly colored homoleptic copper(I) complex $[Cu(dipp)_2]^+$ (Scheme 1b, dipp = 2,9-diisopropyl-1,10-phenanthroline) as photosensitizer (PS). Complexes of this family being weak photo-oxidants,[2] we specifically designed and synthesized powerful, recyclable sacrificial electron donors D based on a benzimidazoline molecular skeleton (Figure 1c). We have demonstrated that, during irradiation with LED in presence of D, the strong reductant $[Cu(dipp)_2]^{(0)}$ is efficiently photo-generated and we used this strong reductive power to realize the photo-induced hydrogenation of a series of aryl halides and compare the photochemical performances of $[Cu(dipp)_2]^+$ vs. other classical photosensitizers. Using a set of chemical and physical techniques, we propose here to unravel the mechanism of this reaction and explore the scope of this reaction.

In order to confirm the supposed mechanism pathway, we performed different tests. EPR and radical trap experiments show that the reaction involves radical species. Moreover, the on/off light cycles have no influence on the reaction. This evidences that the reaction is not a radical chain. Kinetic studies and preliminary deuteration of specific position of the sacrificial donor converge towards the involvement of a hydrogen atom transfer step (HAT). The scope of the reaction is explored and demonstrates that the outcome of the photocatalytic reactions is substrate-dependent. Indeed, the most easily dehalogenated substrates are electron-poor aromatic bromides (bearing ester, ketone, halogen, amide on the phenyl ring) compared to electron-rich ones (methoxy, amine) as expected and so confirm that the reaction involves radical and/or anionic species stabilized in presence of electron withdrawing groups. Nevertheless, the scope of the reaction was successfully extended to more challenging chlorinated aromatics with high yields and in a short time. These results highlight the relevance of implementing reductive quenching of the excited state of homoleptic Cu(I) complexes in organic photochemistry.

Figure 1 (a) Illustration of the reductive quenching cycle. Structures of (b) $[Cu(dipp)_2]^+$ and (c) the benzimidazoline donor used in this study



1. Gimeno, L.; Queffélec, C.; Mall Haidaraly, K.; Blart, E.; Pellegrin, Y. *Catal. Sci. Technol.* **2021**, *11*, 6041-6047
2. Gushurst, A. K. I.; McMillin, D. R.; Dietrich-Buchecker, C. O.; Sauvage, J. P. *Inorg. Chem.* **1989**, *28*, 4070-4072. Cunningham, K. L.; McMillin, D. R. *Inorg. Chem.* **1998**, *37*, 4114- 4119

TETRATHIAFULVALENE AND DITHIOLENE SCHIFF BASE LIGANDS AND COMPLEXES

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Keywords: Tetrathiafulvalene; dithiolene complexes; Schiff bases; chirality; transition metal complexes

Text: Chirality is a fundamental property found in chemistry, biology and physics. In chemistry, chirality produces unique properties in materials, such as circularly polarized luminescence, circular dichroism, spin polarization (Chirality Induced Spin Selectivity, CISS), or electrical resistance variations (electrical Magnetochiral Anisotropy) depending on the presented enantiomer[1].
Tetrathiafulvalene (TTF) is a non-aromatic system capable of reversible oxidation to its radical cationic and dicationic states at relatively low oxidation potentials. The large majority of TTF derivatives are known as excellent precursors for organic conductors[2]. Nowadays, TTF derivatives are getting the attention as scaffolds for electroactive ligands and complexes,[3] including coordination polymers[4]. Other important families of electroactive materials are metal dithiolene complexes, which are interesting in the context of chiral single component conductors[5]. Introducing chirality into electroactive TTF derivatives and dithiolene complexes can lead to molecular materials that exhibit coexistence or synergy of two distinct properties[6].
Our strategy is to synthesize functional ligands containing the chiral TTF moiety and donor atoms that form Schiff base coordination pockets for complexation to access novel complexes provided with multifunctionality. Herein, we present the synthesis and characterization of new Schiff base ligands containing electroactive TTF unit, and also dithiolene counterparts (Figure 1). The coordination of these compounds with Cu(II), Ni(II), Pd(II), Pt(II), Au(III) has been investigated.

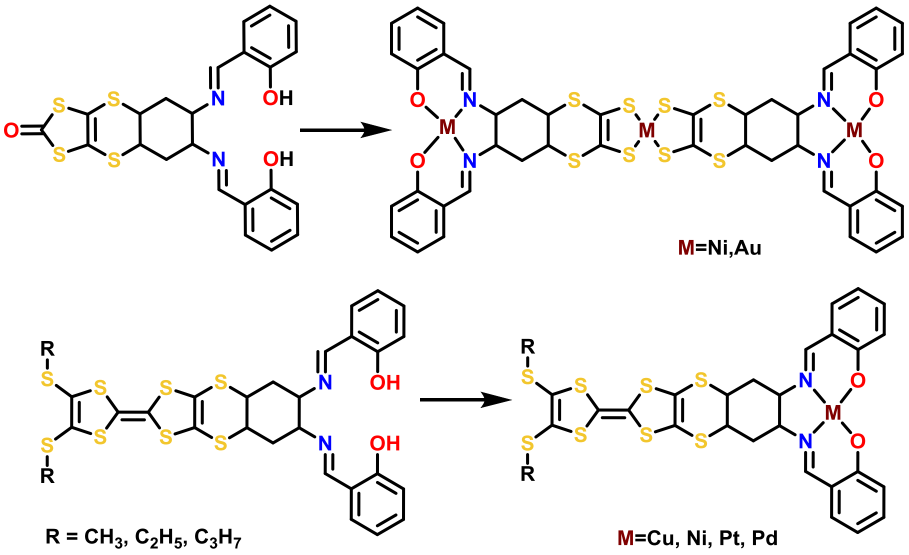

Figure Schematic synthesis of complexes with TTF and dithiolene ligands.

1. F. Pop, N. Zigon, N. Avarvari, *Chem. Rev.,* **2019**, *119*, 8435–8478.
2. J.-I. Yamada, TTF Chemistry: Fundamentals and Applications of Tetrathiafulvalene., *Berlin and Heidelberg, Springer-Verlag*., **2004**.
3. C. Schreck, S. Schönfeld, P. Liebing, G. Hörner, B. Weber, *Dalton Trans*., **2024**, *53,* 9092–9105.
4. F. Solano, P. Auban-Senzier, I. Olejniczak, B. Barszcz, T. Runka, P. Alemany, E. Canadell, N. Avarvari, N. Zigon, *Chem. Eur. J.* **2022**, *29*, 8, e202203138.
5. F. Pop and N. Avarvari, *Coord. Chem. Rev.*, **2017**, *346*, 20–31.
6. F.Pop, P. Auban-Senzier, E. Canadell, G.L. J. A. Rikken, N. Avarvari, *Nature Commun.* **2014**, *5*, 3757.

Coordination of NNN iminophosphorane ligands to Mn^{II}, Co^{II} and Fe^{II} and application in catalytic transfer hydrogenation of ketones

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Keywords: Iminophosphorane; coordination chemistry; abundant metals; catalytic transfer hydrogenation of ketones

In coordination chemistry, suitable ligands must be chosen in order to tune the steric and electronic properties of a metal. Thus, ligand design is essential in order to achieve good catalytic performances, especially when attempting to replace rare and noble metal complexes by first row earth abundant metal ones.

Three tridentate NNN ligands (L) containing three different types of N coordinating groups; an iminophosphorane, a secondary amine and a pyridine functions, a rather unprecedented combination, [1] were designed in our group. Iminophosphoranes are electron rich [2] and exhibit a good affinity for earth abundant metals. That is why L ligands were coordinated to Fe^{II}, Co^{II} and Mn^{II} centers leading to [LMX_2] complexes (Figure 1). Moreover, depending on the R substituent, some differences in the solution behavior of these complexes can be observed.

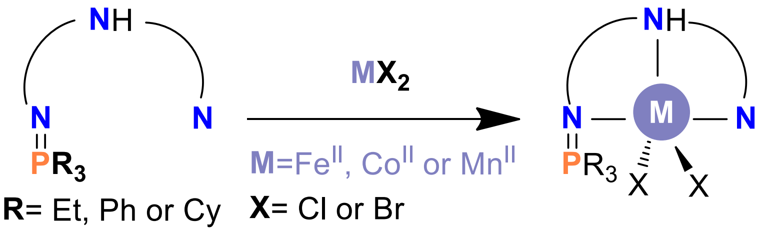

Figure 1 Synthesis of [LMX_2] complexes

Our focus relied on transfer hydrogenation reactions in order to test the catalytic abilities of the [LMX_2] complexes because it is a convenient and very user-friendly manner to reduce polar bonds. [3]
Moreover, examples of iminophosphorane supported catalysts for such reactions are restricted to a family of Fe^{II} complexes, [4] while iminophosphorane Co^{II} and Mn^{II} were almost unexploited in most catalysis reactions.
Furthermore, there are only a handful of examples of Co^{II} catalysts for the transfer hydrogenation of ketones and only one Mn^{II} complex that has this reactivity. [5] These NNN supported complexes have comparable properties to some reported Co^{II} catalysts and represent only the second example of Mn^{II} catalyst for the transfer hydrogenation of ketones.

In this communication the synthesis of the NNN ligands, their coordination to earth abundant metals as well as the influence of the R substituent of the iminophosphorane on their behaviors in solution will be discussed firstly. Then, the catalytic performances in the transfer hydrogenation of ketones of the Co^{II} and Mn^{II} complexes will be explored.

1. T. Tannoux, A. Auffrant, *Coord. Chem. Rev.* **2023**, *474*, 214845.
2. I. Popovici, C. Barthes, T. Tannoux, C. Duhayon, N. Casaretto, A. Monari, A. Auffrant, Y. Canac, *Inorg. Chem.* **2023**, *62 (5),* 2376.
3. D. Wang, D. Astruc, *Chem. Rev.* **2015**, *115* (13), 6621-6686.
4. A. Buchard, H. Heuclin, A. Auffrant, X. F. Le Goff, P. Le Floch, *Dalton Trans.* **2009**, *No. 9*, 1659.
5. R. T. Kumah, F. K. Migwi, M. Schmitz, W. R. Thiel, S. O. Ojwach, *ChemCatChem* **2023**, *15 (23).*

Molecular photocatalysis for small molecule activation

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Keywords: Photocatalysis; CO_2 reduction, O_2 activation, Fe complexes

Text:

Nature teaches us great lessons, one in particular is the harvesting of solar energy to transform it into a readily available form of energy, such as sugars. In an epoch marked by the energy crisis and the need to abandon fossil fuels, scientists are looking back to this highly engineered machine trying to capture some of these teachings and translate them into artificial systems, capable of using sunlight to perform chemical reactions. In these works[1,2] we aimed to study molecular systems specifically tailored for different photocatalytic reactions, such as CO_2 reduction and O_2 activation. The presentation here will focus on the photocatalytic CO_2 reduction by a homogeneous molecular system. As catalyst, we implemented an iron porphyrin with urea groups modifications on the second coordination sphere that facilitate CO_2 binding and therefore enhance the catalytic activity[1,3,4]. This study also involves investigation of the reaction mechanism by different spectroscopic techniques. We then turned our interest towards integrating the same molecular catalyst into a surface to build a photocathode for CO_2 reduction. This approach, despite its potentialities of an increased stability and recyclability still needs substantial optimizations in terms of materials assembly to prove the overall catalytic activity. Another example of photocatalytic reaction displayed here involves O_2 activation for oxygen atom transfer reactions. Here too, mechanistic investigations were carried out on the system that relies on a non-heme iron complex[2].

[1] E. Pugliese, P. Gotico, I. Wehrung, B. Boitrel, A. Quaranta, M. Ha- Thi, T. Pino, M. Sircoglou, W. Leibl, Z. Halime, A. Aukauloo, *Angew Chem Int Ed* **2022**, *61*, e202117530.
[2] E. Pugliese, N. T. Vo, A. Boussac, F. Banse, Y. Mekmouche, J. Simaan, T. Tron, P. Gotico, M. Sircoglou, Z. Halime, W. Leibl, A. Aukauloo, *Chem. Sci.* **2022**, *13*, 12332–12339.
[3] P. Gotico, B. Boitrel, R. Guillot, M. Sircoglou, A. Quaranta, Z. Halime, W. Leibl, A. Aukauloo, *Angew. Chem. Int. Ed.* **2019**, *58*, 4504–4509.
[4] D. H. Cruz Neto, E. Pugliese, P. Gotico, A. Quaranta, W. Leibl, K. Steenkeste, D. Peláez, T. Pino, Z. Halime, M. Ha- Thi, *Angew Chem Int Ed* **2024**, *63*, e202407723.

Möbius ring with photoswitchable configuration

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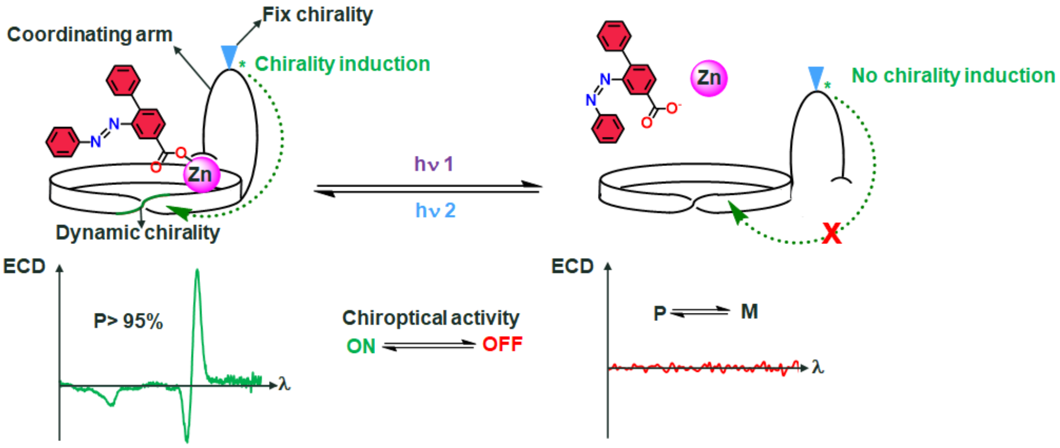
Keywords: Zinc coordination; Chiroptical activity; Möbius aromaticity; Hexaphyrin ligand

These past few decades, control of the inherent chirality of Möbius hexaphyrins has posed a real challenge. To take advantage of this dynamique scaffold,[1] our lab has focused on synthesizing new hexaphyrin-based platforms, comprising notably a chiral coordinating arm. Through the cooperative complexation of Zn(II) to the N-core with the chiral arm and an exogeneous ligand, impressive chirality induction was reached and allowed the formation of Möbius stereoisomers with a diastereomeric excess of over 95%.[2,3] Furthermore, this induction was fully reversible by protection/deprotection of one of the exogeneous ligands. Building on these results, the aim of this work is to achieve not only a reversible chirality induction of the complexes but also to propose a non-invasive way using exogeneous azobenzene ligands which are able to isomerize from *trans* to *cis* configuration solely by UV/Vis irradiation. The tuning of chirality induction should proceed by a coordination/decoordination process respectively with the *trans*/*cis* isomers, where the decoordination is induced by an enhancement of the steric hindrance.[4] Up to now, the new hexaphyrin zinc complexes obtained show a strong signal on circular dichroïsm for both *trans/cis* isomers of the azobenzene ligands. A diastereomeric excess of over 95% and the perfect orientation of the *cis* azobenzene ligand pointing toward the hexaphyrin core were determined through 1D/2D NMR analysis.



1. A. Osuka *et al*, J. *Am. Chem. Soc.* **2008**, *130*, 13568.
2. S. Le Gac *et al*, *J. Am. Chem. Soc.* **2023**, *145*, 27067.
3. S. Le Gac *et al*, *Angew. Chem. Int. Ed.* **2022**, *61*, e202113844.
4. E.W. Meijer *et al*, *Angew. Chem. Int. Ed.* **2013**, *52*, 304.

Luminescent Cu(I) Assemblies with High-Temperature Solid-State Transitions for Advanced Thermic History Tracing

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Keywords: Copper(I), Luminescence, Molecular Material, Metallacycle, Stimuli-responsive thermal tracers

Copper(I)-based luminescent materials are increasingly sought after for a variety of applications, including everyday lighting, displays, and sensor technologies. Owed to copper's abundance, low toxicity, and accessibility, Cu(I) complexes offer an affordable source of luminophores, with a high flexibility of their coordination sphere and tunable photophysical properties that make them ideal for responsive applications.[1] Here, we report a synthetic strategy for creating new polycyclic luminescent Cu(I) assemblies, based on bimetallic precursors assembled by dppm ligand to facilitate controlled copper-copper interactions. Reacting these precursors with a range of pyridyl or nitriles-capped organic linkers led to the formation of two distinct highly emissive Cu(I) coordination assemblies ranging from discrete molecular structure incorporating a very unusual bridging aqua ligand up to multidimensional coordination polymers. These assemblies exhibit irreversible, non-destructive, solid-state luminescence transitions in response to thermal stimuli, paving the way for innovative thermally responsive sensors based on Cu(I) coordination polymers.[2,3]

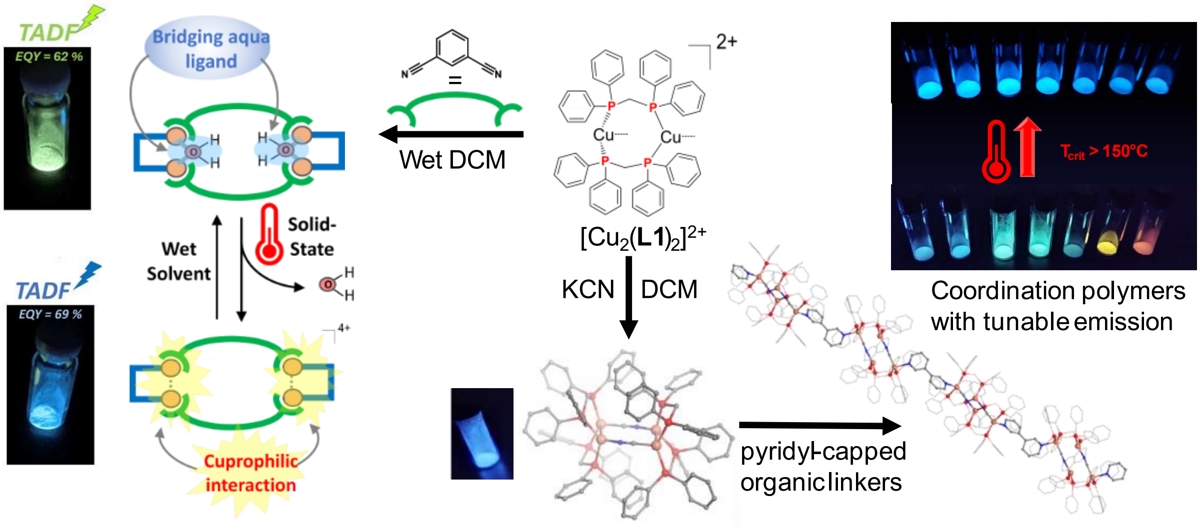

Figure 1

1. a) V. W.-W. Yam, V. K.-M. Au, S. Y.-L. Leung, *Chem. Rev.* **2015**, *115*, 7589–7728 ; b) R. Czerwieniec, M. J. Leitl, H. H. H. Homeier, H. Yersin, *Coord. Chem. Rev.* **2016**, *325*, 2–28 ; c) A. Kobayashi, M. Kato, *Chem. Lett.* **2017**, *46*, 154–162 ; d) S. Perruchas, *Dalton Trans.* **2021**, *50*, 12031–12044 ; e) C. Lescop, *Chem. Rec.* **2021**, *21*, 544–557.
2. A. Schlachter, F. Moutier, R. Utrera-Melero, J. Schiller, A. M. Khalil, G. Calvez, M. Scheer, K. Costuas, C. Lescop, *Adv. Opt. Mater.* **2024**, *12,* 2400347.
3. A. Schlachter, C. Xu, J. Schiller, R. U. Molero, S. Kerneis, G. Calvez, K. Costuas, M. Scheer, C. Lescop, *Angew. Chem* **2024**, e202413151.

Pyclen-based Gd^{3+} complexes for Zn^{2+} sensing by Magnetic Resonance Imaging

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Zinc homeostasis; Zn^{2+} detection; Gd^{3+} complexes; Relaxivity increase

Zinc, the second most abundant transition metal ion in human body, plays a crucial role in numerous physiological processes. However, its quantitative distribution and specific functions remain insufficiently understood. Zinc concentration is tightly regulated, and disruptions in its homeostasis are linked to various diseases, including cancers (prostate, pancreas and breast), neurodegenerative diseases, or diabetes.[1,2] Therefore, monitoring Zn^{2+} in vivo by non-invasive technique such as MRI is essential for advancing biomedical research, elucidating zinc's biological roles, and enabling earlier diagnosis of certain pathologies.[3]

In this study, we investigated the use of paramagnetic contrast agents, specifically Gd^{3+} complexes, for Zn^{2+} detection. The effectiveness of these contrast agents, defined as relaxivity, depends on several microscopic parameters, including the hydration number (q) of the Gd^{3+} complex. In the absence of Zn^{2+}, the Zn^{2+} targeting moiety coordinates with Gd^{3+}, resulting in low relaxivity. However, when Zn^{2+} is present, the targeting moiety binds preferentially to Zn^{2+}, allowing one or more water molecules in the first coordination sphere of Gd^{3+} and thereby increasing relaxivity.

We have previously developed contrast agents that respond to Zn^{2+} in the presence of Human Serum Albumin.[4,5] Here, we developed a new generation of Gd^{3+}-based systems using pyclen derivatives, chosen for their excellent thermodynamic stability and kinetic inertness. Dipicolylamine derivatives were selected as Zn^{2+} complexing units due to their high affinity and selectivity for Zn^{2+}.

Following a 15-steps synthesis, we obtained the GdL_1 complex (Figure 1) and assessed its Zn^{2+}-responsive behavior. A 240 % increase in relaxivity was observed with one equivalent of Zn^{2+} added. To further understand the response mechanism, we characterized both GdL_1 and its Zn^{2+}-bound form using NMRD profiles, ^{17}O NMR, potentiometry studies, and luminescence lifetimes measurements on the homologous Eu^{3+} complex.

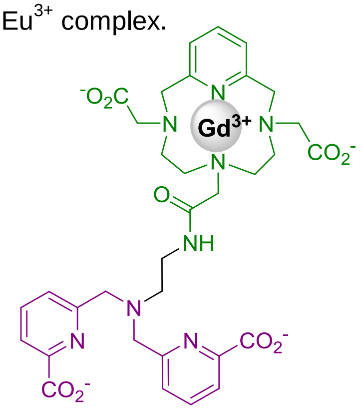

Figure 1 : GdL_1

1. Fukunaka, Y. Fujitani, *Int. J. Mol. Sci.*, **2018**, 19(2), 476.
2. L. C. Costello, R. B. Franklin, *Archives of Biochemistry and Biophysics*, **2016**, 611, 100-112.
3. Bonnet, C. S., *Coordination Chemistry Reviews*, **2018**, 369, 91-104.
4. Malikidogo, K. P., Isaac, M., Uguen, A., *Chem. Commun.*, **2023**, 59(86), 12883-12886.
5. Malikidogo, K. P., Isaac, M., Uguen, A., *Inorg. Chem.*, **2023**, 62(42), 17207-17218.

Copper peptide complexes as models for histidine-brace actives sites

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Keywords: LPMO, Enzymes, Copper, Bioinspired, DFT

Lytic Polysaccharide MonoOxygenase (LPMO) enzymes gained attention when they were discovered in the 2010s for their ability to degrade polysaccharides and their role in the conversion of plant biomass. LPMOs consist of a copper active site coordinated by two histidines with one being coordinated in a bidentate fashion to the metal center and denoted as the « Histidine brace ».[1] This unusual motif is rare in metalloproteins and is believed to give LPMOs their remarkable oxidative power. LPMOs have thus become a source of inspiration for the development of new catalysts. In this context, copper-based complexes with peptidic ligands have been synthesized in our laboratory[2,3] in order to mimick the histidine brace motif. Our objective is to better understand the mechanism of LPMO enzymes using bio-inspired models of the active site. With peptidic ligands, we aim to replicate the active site metal coordination, redox chemistry and catalytic ability of LPMO to target practical applications in bioengineering, namely biomass degradation and the biofuel synthesis. The first bio-inspired model, denoted His-Pro-His (HPH), closely mimics the histidine-brace motif and features potential electron donors with four nitrogen atoms from the N-terminal primary amide, the two imidazole rings and an amide on the peptide bond. The second model, denoted HMePH, is pretty similar to the first one but displays a methyl group on the imidazole ring of the histidine-brace, as observed in some fungal LPMOs. The purpose of this modification is to evaluate the functional role and the structural impact of this methyl group on the catalytic properties and stability of the active site. Activity studies and characterizations using EPR and UV-vis spectroscopic techniques were performed and combined with computational modeling using a methodology we developed in the laboratory to accurately predict EPR parameters[4] and identify unknown species in solution.[5] These DFT-based calculations are essential for correlating the experimental data obtained by spectroscopy with the probable structures of the peptidic complexes, thus providing detailed information on the influence of the methyl modification on the conformation and reactivity of the histidine-brace motif.

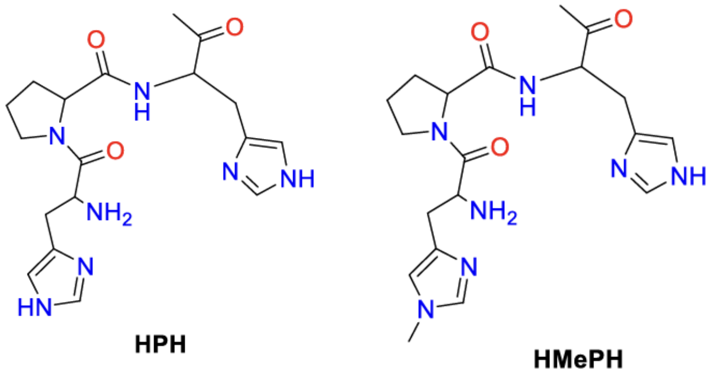

Figure 1 HPH and HMePH models

1. J. De Tovar, R. Leblay , Y. Wang , L. Wojcik, A. Thibon-Pourret, M. Réglier, A. J. Simaan, N. Le Poul, C. Belle *Chem. Sci.*, **2024**, 15, 10308
2. A. L. Concia, M. R. Beccia, M. Orio, F. Terra Ferre, M. Scarpellini, F. Biaso, B. Guigliarelli, M. Réglier, A. J. Simaan *Inorg. Chem.,* **2017**, 56, 1023.
3. A. A. Hassoon, A. Szorcsik, L. Fülöp, Z. I. Papp, N. V. Mayc, T. Gajda *Dalton Trans.*, **2022**,51, 17241.
4. R. J. Gómez-Piñeiro, D. A. Pantazis, M. Orio *Chem. Phys. Chem.*, 2020, 21, 2667.
5. R. J. Gómez-Piñeiro, M. Drosou, C. Decroos, A. J. Simaan, D.A. Pantazis, M. Orio *Inorg. Chem.*, **2022**, 61, 8022.

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Molecular electrochemical COx (CO_2, CO) catalytic reduction using a Co corrole complex

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Keywords: Metallocorrole, Cobalt, electrochemical catalysis, nanotubes, carbon dioxide, carbon monoxide, methanol, formaldehyde.

Metallocorrole represents a promising molecule for a wide range of applications, including organic reactions, water splitting, small molecule (H_2,O_2, CO_2) activation, sensors, solar cells, and medical industries.[1] Here, we report on cobalt based triphenylcorrole ($CorCo^{III}$(DMSO), referred to as **Cat 1**) for its potential in electrochemical CO_x (carbon dioxide or CO_2 and carbon monoxide or CO) reduction. In a homogeneous CH_3CN-H_2O mixture, **Cat 1** reduces CO_2 to CO with excellent efficiency. When immobilized on multi-walled carbon nanotubes (MWCNTs) and coated onto a carbon paper electrode (referred to as **Cat 1@E**), the catalyst achieved a Faradaic efficiency (FE_{CO}) of 92.9 ± 3.9% for CO_2-to-CO conversion at -0.6 V_{RHE}, including methanol ($FE_{CH3OH} \approx 0.34\%$) and formate ($FE_{HCOO-} \approx$ 0.28%) as side products, at a near-neutral pH of 8.64. Replacing CO_2 with CO (a key intermediate in CO_2RR) as feed gas further enhances the liquid product yield, reaching a maximum FE_{CH_3OH} of 5.0 ± 0.5% at -0.75 V_{RHE} at pH 8.64 and a FE_{HCHO} of 3.8 ± 1.6% at -0.65 V_{RHE} at pH 9.64.[2]

We will present and discuss these results and the underlying catalytic mechanisms, which highlight the remarkable properties of this class of coordination complexes to reduce CO_2 with 2, 4 and 6 electrons.

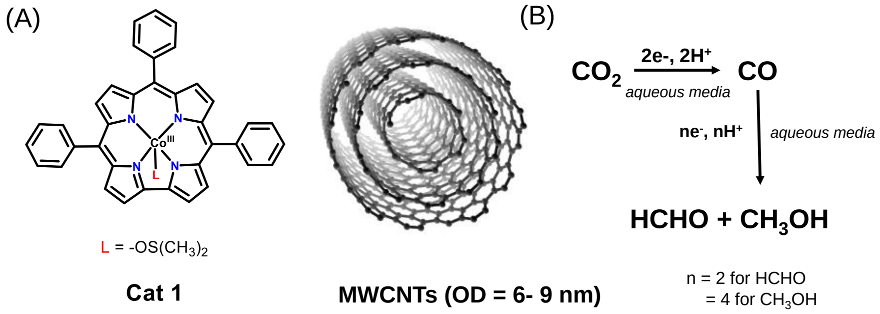

Figure 1 (A) Chemical structure of (triphenylcorrole)Co^{III}(DMSO) or **Cat 1** and MWCNTs (OD = 6-9 nm) ; (B) schematic representation of the electrochemical CO_xRR activity shown by **Cat 1@E**.

References

1. Di Natale, C., Gros, C.P., and Paolesse, R. *Chem. Soc. Rev.*, **2022,** 51 (4), 1277–1335.
2. Zamader, A., Gros, C.O., Robert, M. *submitted*

Exploring the reactivity of iron complexes by manipulating their fluorescence

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Keywords: Iron complexes, fluorescence, photoinduced electron transfer

Text: Unraveling the reactivity and changes in the coordination sphere of metal complexes by fluorescence imaging is attractive for several applications, and particularly in the development of bioactive complexes.[1] Granting to metal-based drug candidates the ability of switching their fluorescence signal as a consequence to modification of their coordination sphere is an ideal feature to unravel their reactivity in complex environments like living systems.[2-3] However, controlling the photoactivity of iron complexes is challenging, due to their ultrafast non-radiative relaxation.[4] We developed bioactive iron(II) complexes stabilized with several families of tridentate ligands and functionalized them with fluorescent probes so as to modulate their photoactivity. Both homoleptic and heteroleptic complexes are presented with a special emphasis on chemical strategies used to selectively synthesize the heteroleptic complexes. We discuss the effects of ligand design on controlling the photoactivity of the complexes via a photoinduced energy transfer (PET). This approach aims at establishing a structure-activity relationship for ultimately rationalizing the design of iron(II)-based drugs and guide future drug design.

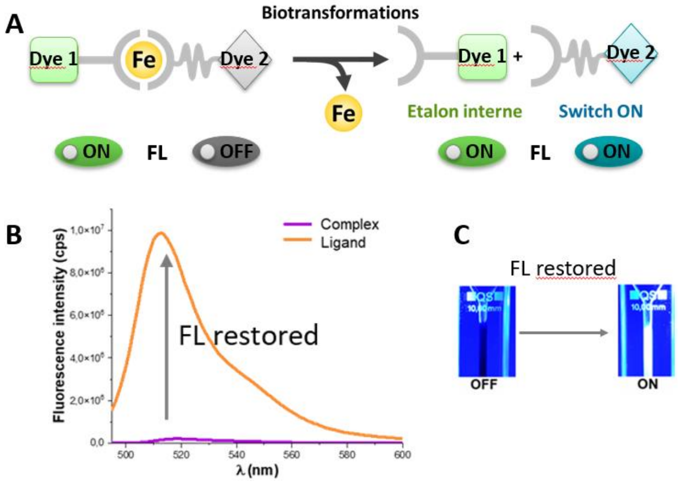

Figure 1 Manipulating fluorescence in heteroleptic iron(II) complexes

1. X. Xiong, L.-Y. Liu, Z.-W. Mao, T. Zou, *Coord. Chem. Rev.* **2022**, *453*, 214311.
2. N. Yamamoto, S. Danos, P.D. Bonnitcha, T.W. Failes, E.J. New, T.W. Hambley, *J. Biol. Inorg. Chem.* **2008**, *13*, 861.
3. M. Ali, L. Dondaine, A. Adolle, C. Sampaio, F. Chotard, P. Richard, F. Denat, A. Bettaieb, P. Le Gendre, V. Laurens, et al. *J. Med. Chem.* **2015**, *58*, 4521.
4. O. S. Wenger, *J. Am. Chem. Soc.* **2018**, *140*, 13522.

Harnessing the Pyclen Macrocycle for Advanced Two-Photon Bioimaging

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Keywords: Lanthanide Luminescent Bioprobes; pyclen, two-photon bioimaging.

Polyazacycloalkanes are well-known for their ability to form highly stable metal complexes. Among these, pyclen, with its rigid pyridine unit, has emerged as a promising platform for developing Ln^{3+} complexes with promising photophysical properties under one-photon excitation.[1] However, UV excitation, due to its limited tissue penetration, restricts the potential of these bioprobes.

Two-photon (2P) microscopy using lanthanide(III) complexes has gained significant attention in optical imaging. It offers the benefits of sharp emission and long excited-state lifetimes characteristic of lanthanides, and the advantages of 2P excitation (near-infrared excitation in the biological transparency window, deeper tissue penetration, reduced background fluorescence, and 3D resolution).[2] However, developing 2P-Luminescent Lanthanide Bioprobes (2P-LLBs) with desirable photophysical properties and the ability to enter living cells remains a challenge.

We have developed new generations of LLBs (Figure 1) that utilize two-photon excitation in the biological transparency window for enhanced tissue penetration and resolution. Indeed, by functionalizing the pyclen macrocycle with π-conjugated antennas, we have created LLBs with remarkable brightness.[3] These highly luminescent bioprobes have enabled successful cancer cells imaging, even with both excitation and detection in the near-infrared (NIR) channel. Additionally, *in vivo* imaging studies on zebrafish have demonstrated the potential of these LLBs for biological applications. We have further confirmed that bioconjugation of the LLBs with different peptides maintains the good photophysical properties of these bioprobes. Thanks to our well-mastered chemical toolbox (Figure 1), we have developed a range of customizable 2P-LLBs[4] that can be coupled to various targeting vectors for specific cancer cell recognition.

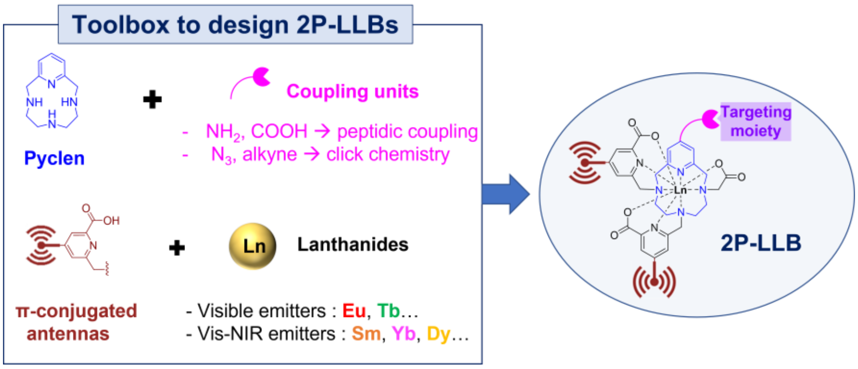

Figure 1: General structure of the pyclen complexes developed.

1. M. Le Fur, E. Molnar, M. Beyler, O. Fougere, D. Esteban-Gomez, O. Rousseaux, R. Tripier, G. Tircso, C. Platas-Iglesias, *Inorg. Chem.* **2018**, *57*, 6932-6945.
2. J.-C. G. Bünzli, *Chem. Rev.* **2010**, *110*, 2729-2755.
3. (a) N. Hamon, M. Galland, M. Le Fur, A. Roux, A. Duperray, A. Grichine, C. Andraud, B. Le Guennic, M. Beyler, O. Maury, R. Tripier, *Chem. Comm.* **2018**, *54* (48), 6173-6176. (b) N. Hamon, A. Roux, M. Beyler, J.-C. Mulatier, C. Andraud, C. Nguyen, M. Maynadier, N. Bettache, A. Duperray, A. Grichine, S. Brasselet, M. Gary-Bobo, O. Maury, R. Tripier, *J. Am. Chem. Soc*. **2020**, *142*, 10184-10197.
4. N. Hamon, L. Bridou, M. Roux, O. Maury, R. Tripier, M. Beyler, *J.Org. Chem.* **2023***, 88*, 8286-8299.

Surface Coordination Chemistry of Graphitic Carbon Nitride from Ag Molecular Probes

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Keywords: Graphitic carbon nitride (g-C_3N_4); Surface OrganoMetallic Chemistry (SOMC); Solid-state NMR

Text: Graphitic carbon nitride (g-C_3N_4) has gained significant attention for its catalytic properties, especially in the development of Single Atom Catalysts (SACs).[1-2] However, the surface chemistry underlying the formation of these isolated metal sites remains poorly understood. In this study we employ Surface OrganoMetallic Chemistry (SOMC) together with advanced microscopic and spectroscopic techniques for an in-depth analysis of functionalized g-C_3N_4 materials, where tailored organosilver probe molecules are used to monitor surface processes and characterize resulting surface species. A multi-technique approach – including high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), X-ray absorption spectroscopy (XAS), and multinuclear solid-state Nuclear Magnetic Resonance spectroscopy (ssNMR), coupled with density functional theory (DFT) calculations – identifies three primary surface species in Ag-functionalized g-C_3N_4: *bis*-NHC-Ag^+, dispersed Ag^+ sites, and physisorbed molecular precursor. These findings highlight a dynamic grafting process and provide insights into the surface coordination chemistry of functionalized g-C_3N_4 materials.[3]

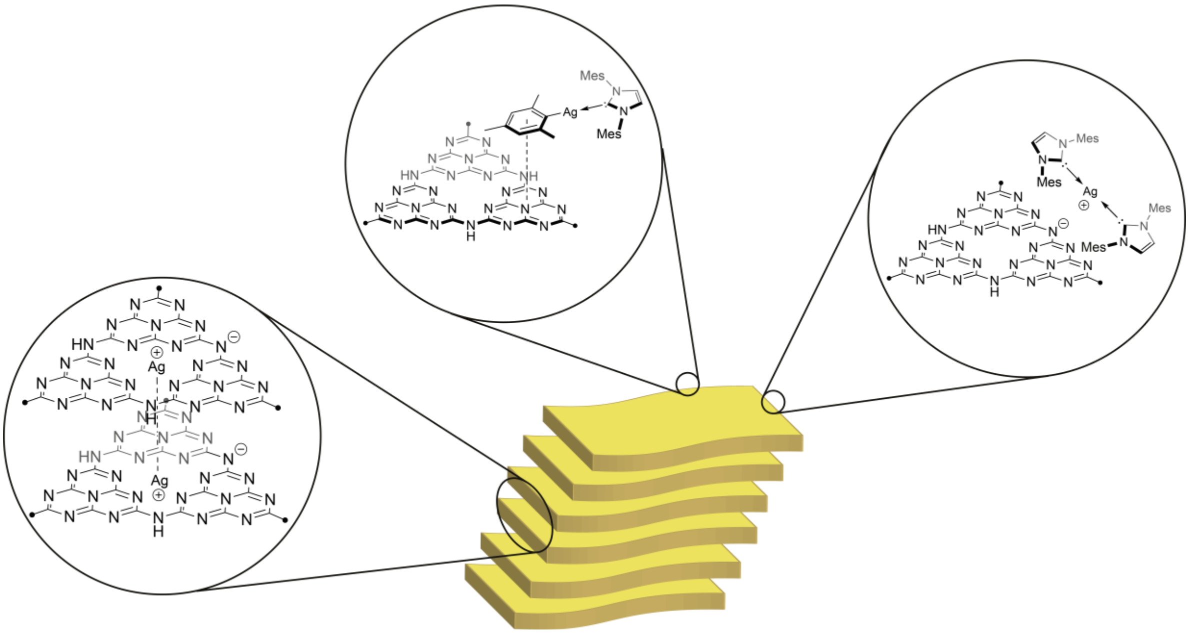

Figure 1 Schematic representation of the surface sites on g-C_3N_4

1. W.-J. Ong, L.-L. Tan, Y. H. Ng, S.-T. Yong, S.-P. Chai, *Chem. Rev.* **2016**, *116*, 7159–7329.
2. F. K. Kessler, Y. Zheng, D. Schwarz, C. Merschjann, W. Schnick, X. Wang, M. J. Bojdys, *Nat. Rev. Mater.* **2017**, *2*, 17030.
3. S. Amanullah, W. Cao, E. Brack, M. Plodinec, C. Copéret, *Angew. Chem. Int. Ed.* **2024**, e202417428. Pre-print available in ChemRxiv, DOI. 10.26434/chemrxiv-2024-kmvvw