

Synthesis of *meso*, β -fused Thiazinamine-Porphyrins via Oxidative C-N Fusion of Pyrimidinyl-substituted Porphyrins

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π -Extension of aromatic molecules via intramolecular C-C or C-N coupling(s) interests numerous research teams for several decades. The C-C or C-N fused compounds demonstrate important change in their electronic properties such as bathochromic shift of their absorption/emission spectrum, two-photon cross-section increase, HOMO-LUMO gap decrease. They found applications in photovoltaic cells [1], molecular electronics [2], photodynamic therapy [3], non-linear optical materials [4], near-IR electroluminescence displays [5].

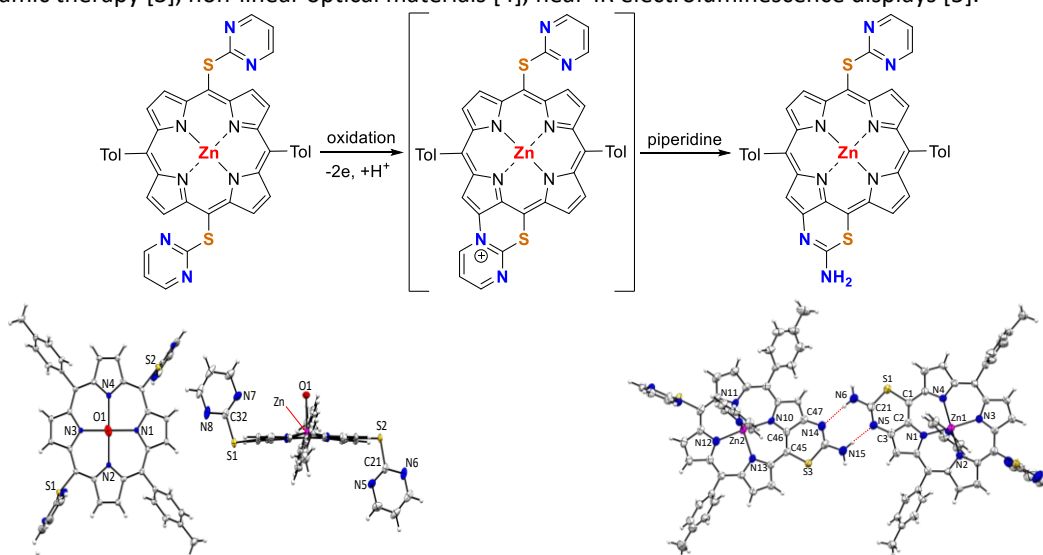


Figure: Chemical preparation of porphyrinthiazin-2-amine.

In this work, 5,15-bis(pyrimidin-2-ylthio)porphyrins have been synthesized. Their electrochemical oxidation leads to the formation of the mono- and bis-C-N-fused thiopyrimidinium intermediates depending on the applied charge and potential. These latter undergo a nucleophilic attack with water during work-up that drives the ring opening of the pyrimidinium moiety. When piperidine is added before or after work-up, the neutral fused porphyrinthiazin-2-amines are generated and they exhibit a significant bathochromic shift of their Soret and Q bands.

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Study of a new hydrosoluble cytochrome c oxidase model

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Cytochrome c oxidase is a bimetallic enzyme that catalyzes the reduction of dioxygen via a 4-electron pathway. This finely tuned reactivity is only possible because of the high degree of sophistication of the peptide structure that surrounds the “active” metallo-porphyrin unit. In these molecular scaffolds, the polypeptide envelope controls the solubility, the access of exogenous ligands, and the reactivity of the central heme. Due to the extreme sophistication of these natural systems, the design of functional and structural hemoprotein models has always been a synthetic challenge.

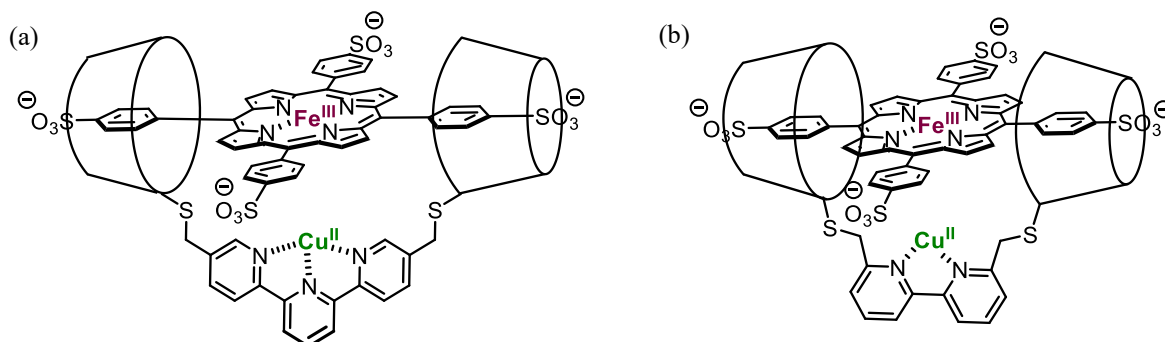


Figure 1: Molecular structure (a) *FeTPPS/CuTerpy-CD₂* (b) *FeTPPS/CuBipy-CD₂*.

In collaboration with the group of Prof. Kitagishi, specialized in the synthesis and studies of hemoproteins models, a previous model of cytochrome c oxidase *FeTPPS/CuTerpy-CD₂* was prepared for O₂ reduction (Figure 1a) [1]. This model combines a tetraphenylporphyrin *FeTPPS*, and a cyclodextrin dimer with a copper-binding terpyridine linker *CuTerpy-CD₂*. The latter provides water solubility and mimics a globular environment. In electrochemical studies, *FeTPPS/CuTerpy-CD₂* showed an efficient reactivity versus O₂ but was not totally selective for the 4-electron pathway [1]. This non-selectivity was attributed to difficulties in reducing copper due to a rigidity of the terpyridine ligand.

In this work, to facilitate the copper reduction during the catalysis and to improve selectivity for the 4-electron pathway, a new cytochrome c oxidase model *FeTPPS/CuBipy-CD₂*, with a more flexible bipyridine ligand, instead of the terpyridine, was prepared (Figure 1b). As expected, UV-visible titration and mass spectroscopy confirmed the formation of a 1:1 inclusion complex between *FeTPPS* and *CuBipy-CD₂* in water. The electrochemical properties versus O₂ reduction of *FeTPPS/CuBipy-CD₂* (CV, RRDE) were studied in solution and compared with *FeTPPS/CuTerpy-CD₂*.

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Stepwise Oxidative C-C Coupling and/or C-N Fusion of Zn(II) *meso*-Pyridin-2-ylthio-Porphyrins

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Extending the π -conjugation of aromatic molecules, in particular porphyrinoids, *via* C-C or C-N coupling(s) with peripheral aromatic fragment(s) has been the focus of numerous researches over the last two decades [1]. Indeed, C-C/C-N fusion of one or several hydrocarbon(s) or aromatic heterocycle(s) onto the porphyrin periphery forces the porphyrin core and the substituent to be coplanar, that enhances the electronic communication between both fragments. π -extended porphyrins display important changes in their optical and electrochemical properties such as decrease of the HOMO/LUMO gap, bathochromic shift in their absorption/emission spectra, large absorption and fluorescence in the NIR range [2]. Nowadays, π -extended C-C/C-N linked porphyrins are commonly obtained using toxic and/or expensive chemicals, often under harsh conditions. Due to the extension of the conjugation path, the oxidation potential decreases which may lead to over-oxidation during the fusion process.

In this work, the (electro)chemical oxidation of original zinc(II) *meso*-(pyridin-2-ylthio)porphyrins will be presented affording the C-N fused (bis)pyridinium derivatives in a stepwise manner [3]. When one *meso* position remains free, the first oxidative reaction consists in the *meso,meso* C-C dimerization. The resulting pyridinium derivatives exhibit important changes in their physico-chemical properties (NMR, UV-vis., CV) as compared to their initial unfused precursors.

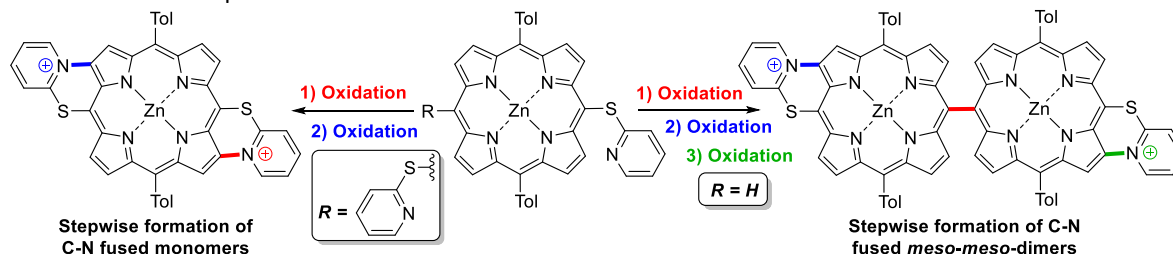


Figure: Oxidative C-C or C-N fusion of Zn(II) *meso*-Pyridin-2-ylthio-Porphyrins.

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Phospholipid-Porphyrin vs Phospholipid-Phthalocyanine conjugates: Study of their interfacial behavior, their supramolecular assemblies and photophysical properties

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The design of supramolecular assemblies based on modified organic chromophores has gained significant importance in various applications such as solar cells, biomedical imaging, and phototherapy. Porphyrin derivatives, which are abundant in nature and possess versatile structures, have emerged as promising scaffolds for supramolecular assemblies. These assemblies can be achieved by conjugating porphyrin derivatives to different types of scaffolds, including peptides [1], dendrimers [2], carbohydrates [3], or lipids [4], depending on the desired application. The unique properties of these chromophores and their ability to be modified allow for efficient tuning of their assembling and photophysical properties, making them highly attractive for multifunctional supramolecular assemblies.

In this work, the interfacial behavior, the supramolecular assemblies, and the photophysical properties of phospholipid-porphyrin and phospholipid-phthalocyanine conjugates were compared. Langmuir balance coupled to X-ray reflectivity experiments were used to study their interfacial behavior and the finite structure of the monolayers at the air-water interface, revealing differences in chromophore orientation. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) were employed to characterize the nanostructures and morphologies of the supramolecular assemblies. UV-Vis absorption and fluorescence spectroscopy were used to investigate their optical properties, showing significant differences between the assemblies compared to their non assembled counterparts. These findings provide insights into the structure-property relationships of these chromophore-based assemblies and their potential applications in nanotechnology, biomedical imaging, and phototherapy.

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AN ALLOSTERICALLY CONTROLLED SYNTHESIS OF A [2]ROTAXANE

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Rotaxanes are molecular assemblies belonging to the family of mechanically interlocked molecules (MIMs).^[1] In the case of [2]rotaxanes, they are composed of a macrocycle threaded by a linear axle with two bulky end groups to prevent the dissociation of the subcomponents.^[2]

The goal of this project is to synthesize a [2]rotaxane (Fig.1c) in which the traditional macrocycle is replaced by a molecular cage described in the laboratory.^[3,4] This cage is composed with two zinc porphyrins as recognition sites for guest molecules, and triazoles as allosteric sites to control the opening/closing of the molecular cage.^[5] This allows the transition from a so-called flattened conformation to an open conformation by the addition of four equivalents of silver(I) ions that are coordinated to the triazoles (Fig.1a).

The assembly of the pseudo-rotaxane will take advantage of this allosteric control by threading a monostoppered axle into the cage only once the cage is in its open conformation (Fig.1b). This step is followed by the addition of the second stopper to form the [2]rotaxane.

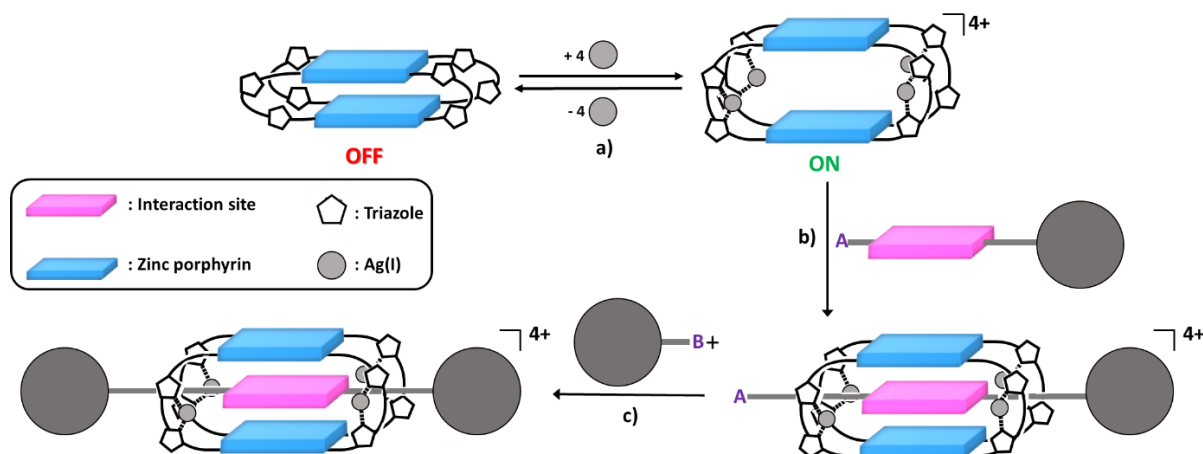


Figure 1. Scheme of the targeted [2]rotaxane

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Investigation of the roles of porphyrin and Zr₆ clusters in the photocatalytic activity of Metal-Organic-Frameworks for CO₂ reduction

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These last few years have seen growing interest in the use of porphyrins^{1,2} as linkers in porous solids for photocatalytic purposes as such immobilization may bring increased chemical stability and tunable selectivity while allowing easier recyclability. In particular, the Zr- and porphyrin-based MOF-545, built by connecting Zr₆ clusters and tetra(4-carboxyphenyl)porphyrin linkers, exhibits high activity for the photocatalytic reduction of CO₂ into formate with triethanolamine as sacrificial electron donor.³ In this material the porphyrin must play the role of a photosensitizer while DFT calculations suggested that the Zr₆ cluster acts as a Lewis acid and the catalytic center.^{3b} In order to confirm these hypotheses, we aim to study the activity of isolated Zr₆ clusters (Figure 1, right) in presence of porphyrins in homogeneous conditions. We therefore report here the first results obtained from the study of the photocatalytic activity of such Zr₆/porphyrin photosystems considering zinc and iron metalated A₃B type porphyrins having three phenyl groups and one p-carboxy phenyl group on meso-position (Figure 1, left) where the presence of the carboxylate may allow the *in situ* attachment of the porphyrin on the 4d cluster while the incorporated 3d metal may exalt its photocatalytic or photosensitizer properties.

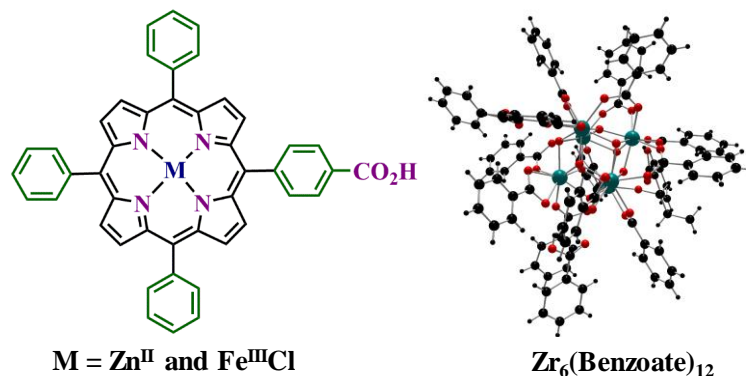


Figure 1: Molecular structures of zinc and iron metalated A₃B type porphyrins and [Zr₆(Benzoate)₁₂] cluster

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Hexaphyrin-cyclodextrin hybrids: the story so far

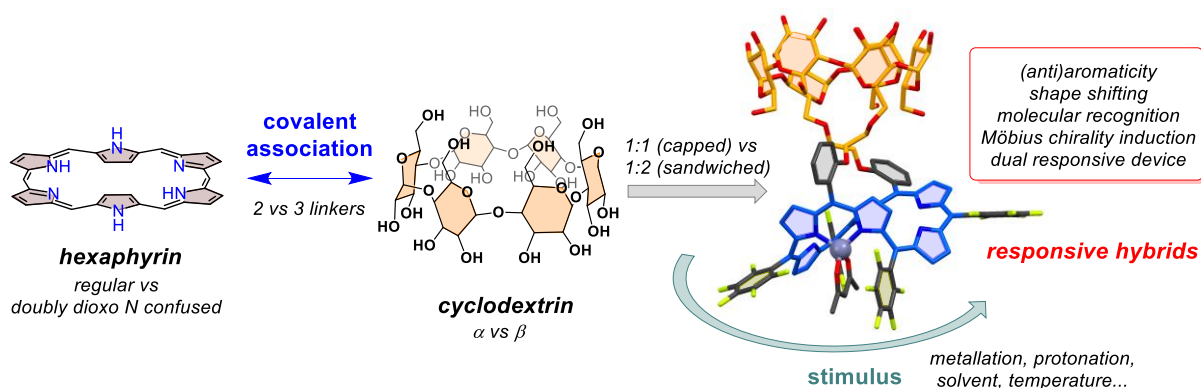
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In the last two decades, the flourishing chemistry of azaannulenic systems larger than porphyrins has witnessed an ever-growing diversity of scaffolds. Beyond β - and *meso*-functionalization, isomeric, core-modified, fused, π -extended, twisted, among other types of congeners, afford a huge set of possibilities for the emergence of novel π -functional systems. Besides, conformational flexibility, coordination/organometallic chemistry, aromaticity, inherent chirality, are key interlinked features of expanded porphyrins. Orchestrating these features with appropriate external stimuli opens the way to ever-complex adaptive systems.

Until recently, a particular domain of engineering consisting in the coupling of an expanded porphyrin with an hydrophobic cavity has remained under-explored. Considering the previous work achieved with porphyrin-cyclodextrin conjugates bringing selectivity in molecular recognition and catalysis, the emergence of novel properties was expected to arise from the controlled association of larger porphyrin congeners with such cavities. With this idea in mind, the covalent assembly of hexaphyrin and cyclodextrin subunits was recently developed by our groups leading to the so-called family of hexaphyrin-cyclodextrin hybrids.[1,2,3,4,5] This presentation will give an overview of the story so far.



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Synthesis of Metalated Corroles grafted on Porous Materials for Gas Detection

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Detection of carbon monoxide (CO) at very low concentrations is of great concern for the control of air quality as CO is responsible, every year, for serious intoxications that can lead to death. To prevent this, it is imperative to devise functional materials which readily detect this deadly gas before it reaches harmful levels.^[1] In this regard, cobalt corroles (a tetrapyrrole macrocycle of the porphyrinoid family) present a special interest for CO detection as they have been shown to coordinate CO even in the presence of interferents such as nitrogen and dioxygen.^[2] Moreover, Metal-Organic Frameworks (MOFs), a class of porous materials renowned for their high porosity and superior tunability, can host metallocorroles to synergistically combine the high sorption capacity of MOFs with the corrole selectivity. Following suit, our work aims to develop highly sensitive and selective materials for CO detection by combining cobalt corroles with stable MOFs. In particular, porphyrin-based MOFs such as the PCN-222 (Fig. 1a) can present natural vacancies on their metal cluster which can then be used to graft cobalt corroles. This way, the active molecule for detection is strongly anchored by coordination to the zirconium oxide cluster and hangs inside the MOF pores, allowing free access to the cobalt metal center. In this study, the synthesis of judiciously designed cobalt corroles grafted on porphyrin-based MOFs have been analyzed and compared with respect to their crystallinity, morphology, and specific surface area thanks to XRD, SEM images, ¹H NMR, and BET analysis.

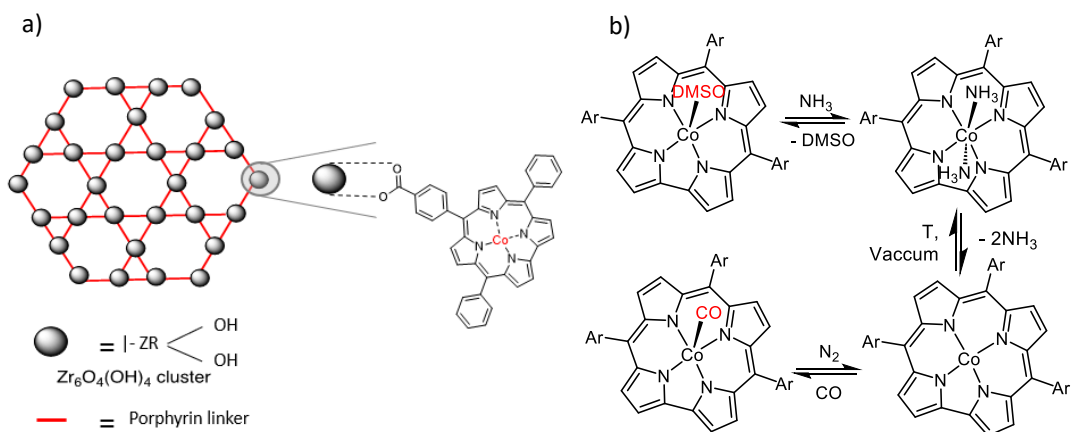


Fig. 1 a) Structure of a cobalt corrole grafted on PCN-222, b) Cobalt corrole activation for CO binding

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Non-covalent functionalization of cellulose with phthalocyanine: Synthesis, characterization and PDT activity

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Antimicrobial resistance is a major global public health problem. One of the main reasons why microorganisms can easily overcome antimicrobials is antibiotics' specific mode of action. Small changes in bacterial targets increase resistance to antimicrobials and therefore bacteria become more difficult to eradicate with antimicrobial therapies with non-specific targets. Self-disinfecting materials (SDMs) such as fabrics, films, and coatings can play a vital role in preventing the transmission of pathogens from, e.g., hospital surfaces to patients, and from patient to patient. Ideally, self-sterilizing surfaces should be nonspecific to pathogens, easy-to-make, scalable and robust. To this end, materials utilizing principles of photodynamic therapy represent a promising approach to combat pathogenic species, including antibiotic-resistant ones [1,2]. Porphyrinoids can be a distinguished alternative for abrogating pathogenic microorganisms via a PDT mechanism [3,4]. Especially, cationic metallated phthalocyanines (Pc) show remarkable phototoxicity due to their high yield of ROS generation [5]. Broad absorption bands combined with high molar absorption coefficients and long triplet state lifetimes allow phthalocyanines to generate high concentrations of ROS even at low light intensities.

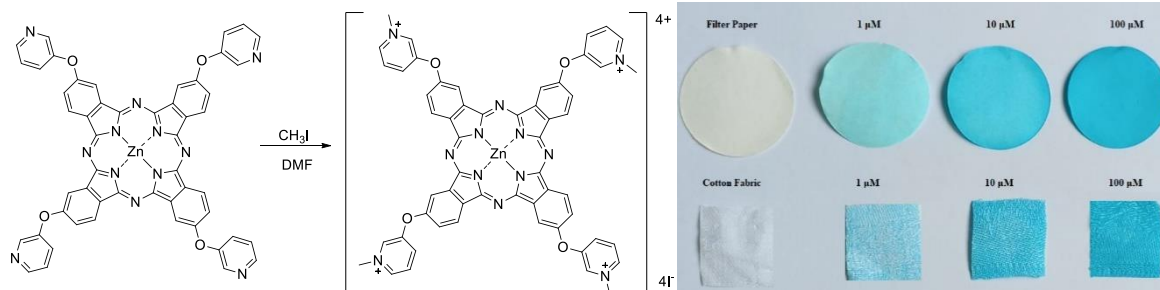


Figure: Left: Synthesis of cationic Zinc phthalocyanine. Right: application to materials (filter paper and cotton fabric)

In present study, we synthesized a photosensitizing cationic symmetrically substituted zinc phthalocyanine and impregnated it on paper and cotton fabric with different concentrations (1 μM , 10 μM and 100 μM). The molecular structure of the phthalocyanines were confirmed by FT-IR, NMR and MALDI-TOF/MS. The spectroscopic properties of phthalocyanines and functionalized materials will be presented.

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Synthesis and characterization of new nanoparticles bearing photosensitizers of natural origin for anticancer applications.

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In 2020, colorectal cancer is the second leading cause of cancer death with 9.4% mortality [1]; it remains a major public health problem. As part of our project, we are therefore interested in the development and vectorization of photosensitizers for photodynamic cancer therapy applications. In this approach, a new stable photosensitizer, with an absorption band in the near infrared was designed from chlorophyll according to a method described in the literature. [2,3]. However, these photosensitizers are not soluble in aqueous medium and they are not selective towards tumors. To resolve these two issues, we have developed nanoparticles which are known for their ability to accumulate preferentially in tumors by EPR effect and which allow drug transport thus increasing the bioavailability of these molecules.

For that purpose, cellulose nanocrystals bearing cyclodextrins were prepared [4]. Then the photosensitizers were functionalized with an adamantyl group to allow their encapsulation by hydrophobic interaction in cyclodextrins. Tests are currently underway to evaluate the in vitro PDT activity of this complex on colorectal cancer cells.

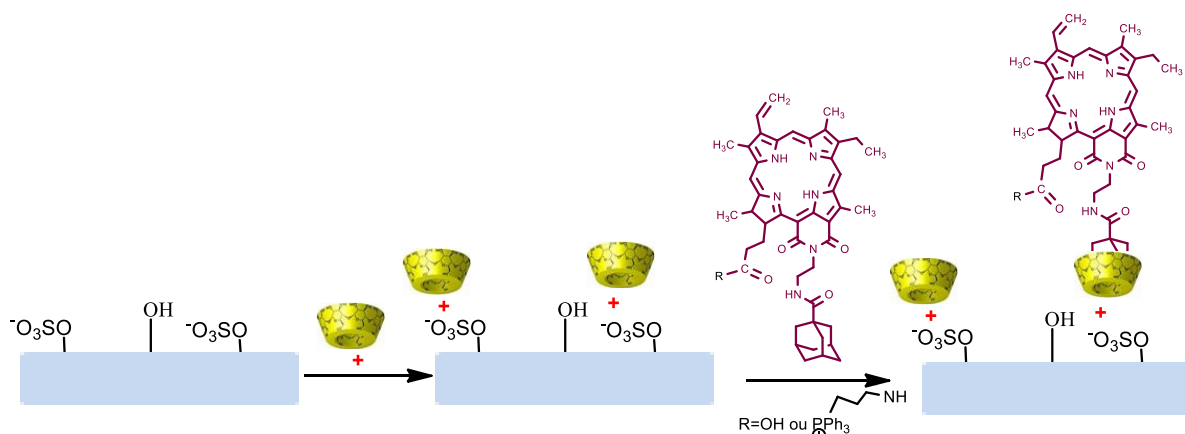


Figure: Encapsuled photosensitizers in cyclodextrins carried by cellulose nanocrystals.

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Catalytic Properties of Porphyrins Bearing Peripheral N-Heterocyclic Carbene Rhodium Complexes

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N-heterocyclic carbenes (NHCs) are both relevant ligands in the fields of coordination and organometallic chemistry. ^[1-2] During the last decade, several molecular systems combining porphyrins and NHC ligands were reported in the literature. ^[3] Merging metalloporphyrins and NHC-metal complexes within unimolecular systems may lead to multimetallic species with new catalytic properties such as cooperative effects between inner and outer metal cations. Here, we present the synthesis and characterization of some molecular systems combining porphyrins and NHC-rhodium(I) complexes (see below). The catalytic properties of these complexes were investigated for the conjugated addition of phenylboronic acid to cyclohexen-2-one. ^[4-6] We notably show the effect of the inner metal cations on the catalytic properties of the outer rhodium(I) complexes according to the structure of the ligand and the distance between the two metal centres. The results of this structure-function relationship study show a modulation of the catalytic properties of NHC-Rh(I) complexes by the porphyrin.

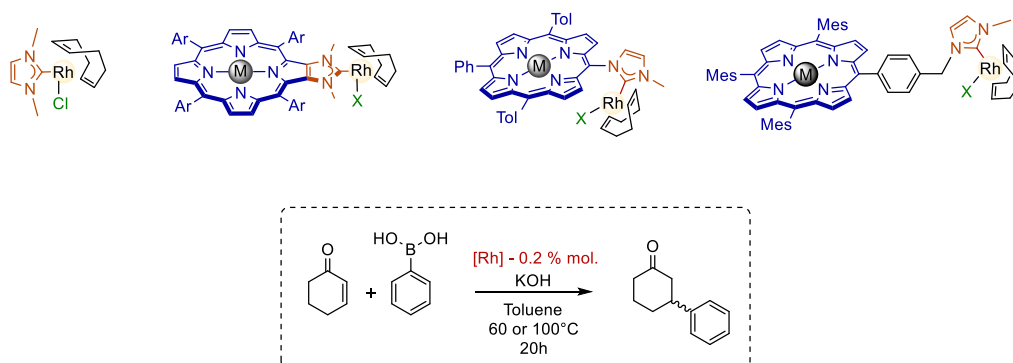


Figure: Structures of the porphyrins linked to NHC-rhodium(I) complexes (top), Rhodium catalysed 1,4-addition of phenylboronic acid to cyclohex-2-en-1-one reaction conditions (bottom).

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Light-induced CO₂ reduction catalysis with urea-modified iron porphyrin

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Finding ways to valorize and transform CO₂ into fuel using renewable energies as an alternative to fossil fuels is crucial in the current scientific research. A possible approach is electro or light induced molecular catalysis. Iron porphyrins had been reported to be active catalysts for CO₂ electroreduction since the 80s¹. Our group has previously developed a highly active iron porphyrin catalyst bearing urea groups in the second coordination sphere (UrFe)². The use of the urea scaffold to stabilize the CO₂ adduct enabled the catalyst to display low overpotentials and high turnover frequency. These results lead us to investigate its catalytic activity in a light induced catalytic system. When using ruthenium tris-bipyridine as a photosensitizer, our study shows that the second coordination sphere effect can also be transposed to homogeneous photocatalysis for CO₂ reduction. Careful tuning of the photocatalytic reaction parameters and modification of second coordination sphere led to a great enhancement of catalyst durability, with one of the highest turnover numbers (TON>7000) reported in the literature, and excellent selectivity for CO (>99%)³.

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CORROLE-BASED POROUS MATERIALS FOR THE DETECTION OF SMALL VOLATILE COMPOUNDS (CO, NH₃...)

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Keywords: Metal-Organic Frameworks; Covalent Organic Frameworks; Corroles; Volatile Organic Compounds; Toxic gases

Volatile Organic Compounds (VOCs) and other toxic gases are ever-present in the atmosphere and can have a detrimental effect on human health. Thus, it is imperative to devise new methods in order to detect and monitor low concentrations of these small molecules (namely CO, CO₂, acetone, or ammonia) and maintain a healthy environment. In this regard, materials with high sensitivity and selectivity towards these gases are required to optimize detection devices. Cobalt corroles, belonging to the porphyrin family, have been shown to selectively bind CO *via* the cobalt center (Fig. 1a) ^[1,2]. However, the π -stacking of corrole macrocycles limits their CO sorption capacity when deposited multilayers from a solution. For this reason, we have explored the incorporation of metallocorroles within organized porous structures such as Metal-Organic Frameworks (MOFs) and Covalent-Organic Frameworks (COFs) ^[3,4]. These highly porous materials have received considerable attention for their high surface area and tailorability, making them useful for many different fields of study, especially gas detection and capture. Herein, we investigate the synthesis of MOFs and COFs based on cobalt corroles. In particular, a new hybrid MOF was built from two different linkers (porphyrins and corroles, Fig. 1b) with the hope of obtaining stable, selective, and sensitive materials for CO and NH₃. The synthesis of the new materials has been analyzed and compared by XRD, SEM, ¹H NMR, and BET analysis.

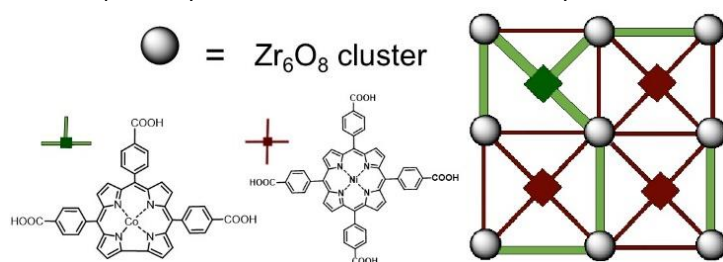


Fig. 1 – Design of a hybrid corrole-porphyrin MOF

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Electrocatalytic Reduction of Carbon Dioxide using Iron and Cobalt-based Covalent Organic Frameworks

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The electrocatalytic reduction of carbon dioxide (CO₂) using covalent organic frameworks (COFs) is an attractive approach for the sustainable production of value-added chemicals and fuels.[1] In recent years, significant efforts have been made to develop Fe- and Co-based COFs as efficient electrocatalysts for CO₂ reduction due to their unique electronic and structural properties.[2,3] Here, we report the synthesis and electrocatalytic performance of iron and cobalt-based COFs for CO₂ reduction using an electrocatalytic H-cell setup.

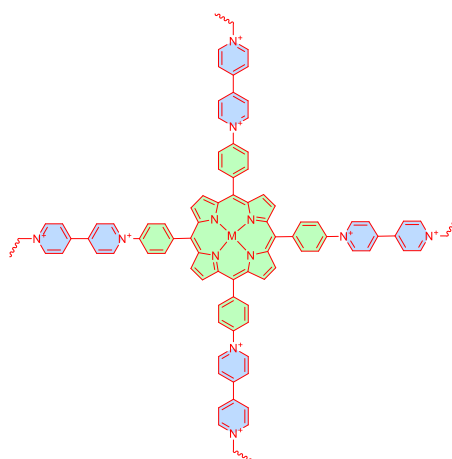


Figure: Chemical structure of repeating unit in covalent organic framework

The Fe and Co-based COFs were synthesized using solvothermal method and characterized using various techniques, including powder X-ray diffraction (PXRD) and Fourier-transform infrared (FTIR) spectroscopy. The electrocatalytic performance of the COFs was evaluated using cyclic voltammetry (CV) and chronoamperometry (CA). The results showed that both Fe and Co-based COFs exhibited excellent electrocatalytic activity towards CO₂ reduction.

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Toward a Fully Artificial Cytochrome P450-like System

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Cytochromes P450 (CYP) are hemoproteins involved in the oxidative metabolism of many drugs, whose structure is schematically shown in figure 1. They are composed of an iron(III)-protoporphyrin IX or heme as prosthetic group, which is bound to an apoprotein through an axial cysteinyl ligand. They are associated with a partner flavoprotein, cytochrome P450 reductase (Fig. 1). Thanks to its flavin cofactors FMN and FAD, this electron transporter shuttles the electrons from NADPH to a dioxygen molecule bound to the iron ion of the heme, where its reductive activation is performed. Even though the monooxygenase activity is very interesting for chemical synthesis, the complexity of these systems makes it difficult to use. In particular, there is a need to replace the reductase/NADPH system by a chemical electron transporter associated with a sacrificial electron donor or acceptor.^{1,2}

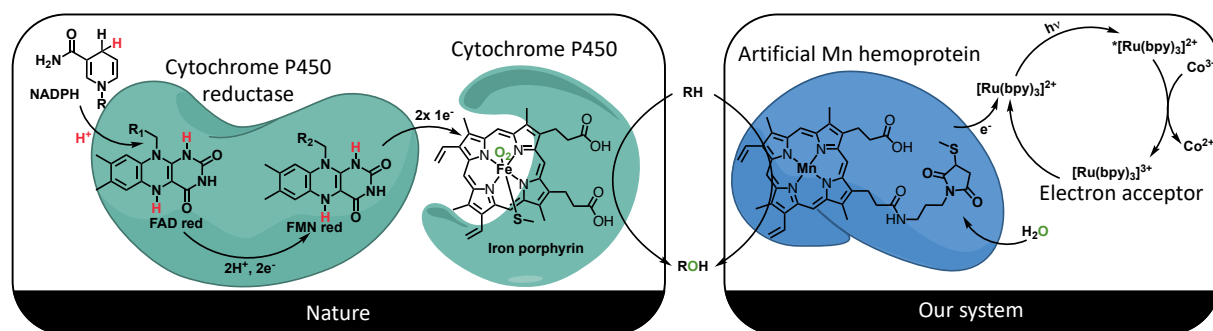


Figure 1: Comparison of our system and a natural P450 system

In this poster, we report the preparation of new artificial metalloenzyme with a P450 like activity that has been obtained by the covalent anchoring of a manganese heme into the cavity of an artificial repeat protein named alpha Rep (α Rep). This new artificial hemoprotein has been purified and characterized by Matrix Assisted Laser Desorption Ionization–Time of Flight Mass Spectrometry (MALDI-TOF MS), circular dichroism, and UV-Vis spectroscopy. The oxidant system reported in this work uses the oxygen atom of the $\text{Mn}^{\text{III}}\text{-OH}$ that naturally forms in water as an oxygen source by oxidizing it to $\text{Mn}^{\text{V}}\text{=O}$ which can then perform oxidation of organic substrates. The oxidation from $\text{Mn}^{\text{III}}\text{-OH}$ to $\text{Mn}^{\text{V}}\text{=O}$ is performed by a $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ photoredox complex regenerated by a sacrificial electron acceptor ($[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$).³

The synthetic P450 metalloenzyme has then been tested for the catalysis of oxidation reactions on different substrates including thioanisole using first as a green oxidant, hydrogen peroxide (H_2O_2), that produces water as a by-product. The results have then been compared with those obtained using the full system associating, in water, the artificial hemoprotein, $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ and $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$ as a sacrificial electron acceptor, which avoided the addition of an oxidant species, thus leading to a better atom economy.

Thus this work shows that oxidation catalysis can be carried out in an aqueous medium without any chemical oxidant and using visible light as the only energy input.

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Synthesis of bipyridine-strapped porphyrins using a remote template effect

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The use of metal templates to control allosteric properties or spatial orientation of remote substituents has been widely used for molecular architectures containing 2,2'-bipyridine moieties. [1,2] A remote metal template has now been used to synthesize two bipyridine-strapped porphyrins **1** and **2** (Figure 1) that could not be obtained by classical methods. [3] Binding of zinc(II) to a bipyridine incorporated within a strap bearing two aldehyde groups orients the aldehydes correctly for condensation with dipyrromethane or pyrrole. The presence of the metal template enhanced the yield 10-fold for the single-strapped porphyrin **1** and allowed the formation of a double-strapped porphyrin **2** that had been previously impossible to prepare. These strapped porphyrins provide binding sites for two or three distinct metal centers and the resulting homo- or heterometallic structures are of interest as study multispin scaffolds or as a scaffold for double-stranded rotaxanes. In addition, the flexibility of the bipyridine strap of porphyrin **1** may lead to interesting properties of an iron(II)-copper(I) derivative of this compound as a cytochrome c oxidase mimic.

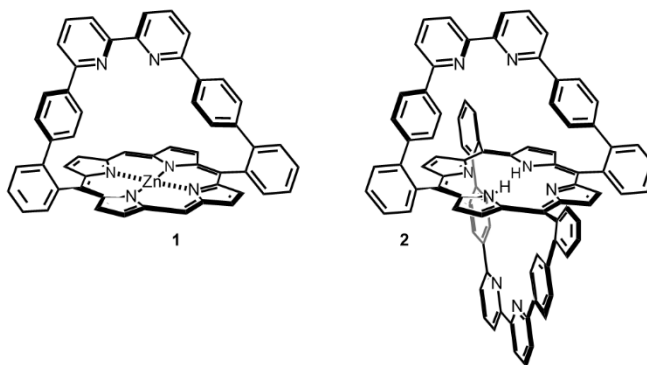


Figure 1: Bipyridine-strapped porphyrins prepared using a remote template effect.

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Two Metals Cooperativity in CO₂ Reduction by a Bio-Inspired Dinuclear Catalyst

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Since 1980s, iron tetraphenylporphyrin (**TPP-Fe**) has been reported as one of the good molecular catalysts for CO₂ reduction with excellent reaction rate to mitigate the climate change from atmospheric CO₂ accumulation.[1] Whereas, due to the high overpotential of CO₂/CO via **TPP-Fe**, it is still highly desirable to promote its catalytic performance. In nature, the bimetallic [NiFe] carbon monoxide dehydrogenase (**CODH**) enzyme could reversibly convert CO₂ to CO with excellent catalytic selectivity with minimum energy consumption.[2] The synergic effect of hydrogen bonds from amino acid residues could bind to CO₂ adduct and stabilize it. Importantly, the two metals, Ni and Fe, are working on CO₂ with “push-pull” cooperation. Inspiration by [NiFe]-centred **CODH** enzyme, the novel metalloporphyrin-based mimic (**P₂Ur-FeFe**) has been first time designed and synthesized combining the synergic effect of multipoint hydrogen bond relays and bimetallic activation for carbon dioxide adduct.

The urea group linked **P₂Ur-FeFe** was well employed for CO₂ reduction to CO in environment friendly solvent water. Compared with **TPP-Fe**, the study results suggested **P₂Ur-FeFe** showed more than 4 times higher current density with better CO selectivity and stability than that of **TPP-Fe**. Interestingly, quasi-identical catalytic performances are obtained when one of the two iron centers is replaced by a catalytically inactive competent Zn (**P₂Ur-FeZn**), supporting a cooperative action of the two metals.

In this study, we proved that we successfully mimic the [NiFe]-centred **CODH** enzyme by urea group linked **P₂Ur-FeFe** and **P₂Ur-FeZn** to first time combine the hydrogen bond and two metals cooperativity working mechanism in CO₂-electroreduction.

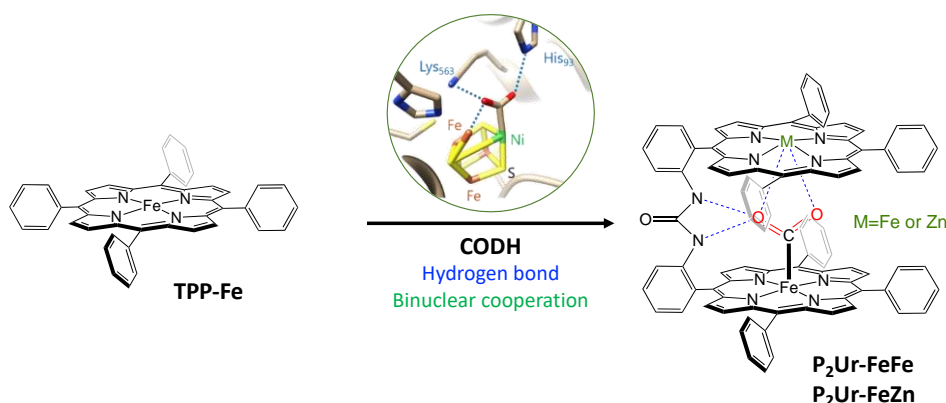


Figure 1 Schematic illustration of the combination of hydrogen bond and two metal operation for CO₂ reduction.

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Mabiq-based artificial metalloenzymes for small molecule activation

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CO₂ activation is integral to advances in both renewable energy and green chemistry. The development of efficient and selective catalysts for the various CO₂ activation routes is vital to efforts to harness and recycle this greenhouse molecule, but still presents significant hurdles.[1] The aim of the research is to generate artificial metalloenzymes (AMEs) for CO₂ activation named "CO₂zymes". The proposed strategy in this work involves the synthesis of macrocyclic bimetallic complex "Mabiq" and their attachment to the tHisF protein. On the one hand, Mabiq are good CO₂ activating complexes and tHisF is a thermostable protein that has been successfully transformed into AMEs but us and others.[2] The produced CO₂zymes will be used to catalyze the reduction of CO₂ as well as its direct incorporation into organic compounds (Figure 1). Mutation the AMEs active sites could yield to new more efficient catalysts for CO₂ activation, but also will inform our understanding of how the protein environment contributes to proton coupled electron transfer (PCET) processes and (regio)selectivity.

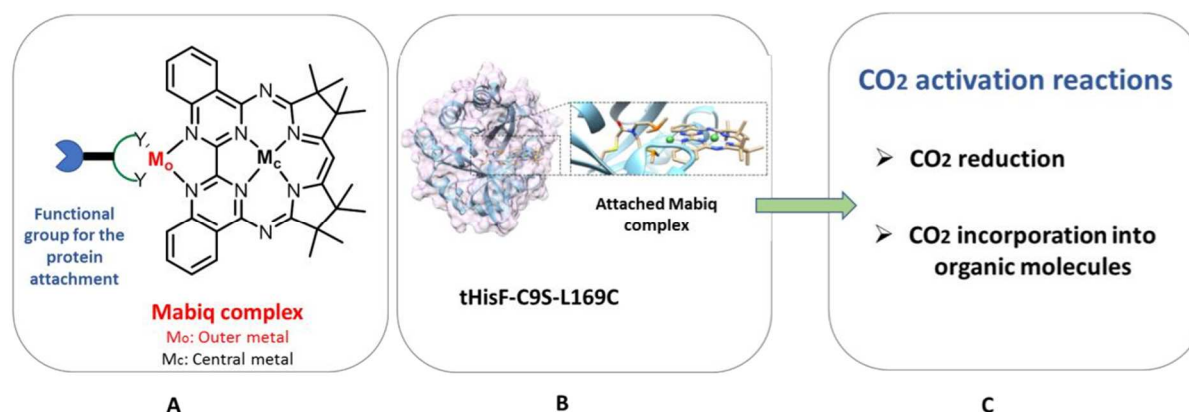


Figure 1 : A) Strategy of Mabiq attachment to proteins tHisF to form AME; B) Model of an AME formed through Mabiq binding to tHisF ; C) CO₂ activation reactions that will be assayed.

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