Project 1: Artificial Photosynthesis: transformation of water and carbon dioxide into fuels

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Permanent staff involved in the project:
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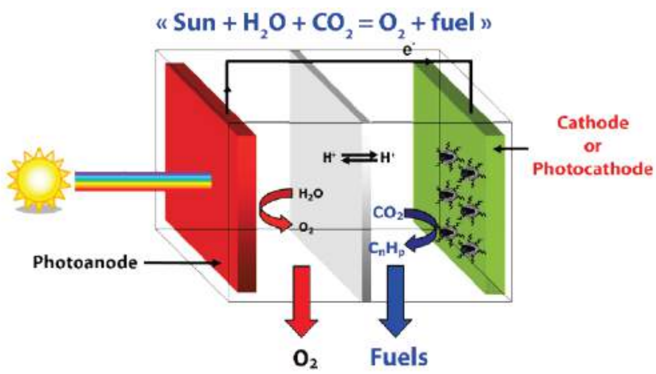
One of the challenges of the 21st century is energy. The limitation of fossil fuels (oil, gas and coal) and the need to limit emissions of CO_2, a greenhouse gas, require the development of technologies aimed at valorizing CO_2 as a C1 feed-stock in particular by converting it into energy-dense organic molecules such as hydrocarbons. One of the most fascinating strategies is that used by nature. The complex process of photosynthesis uses solar energy to realize a thermodynamically unfavorable reaction: the reduction of CO_2 by H_2O. Photosynthesis thus can store solar energy in the form of biomass with high energy content, and also in the form of hydrogen by water splitting. These reactions require photosensitizers for photon absorption and charge separation, as well as catalysts to accelerate multi-electronic processes required in, CO_2 and proton reduction (at the cathode or photocathose) and water oxidation (at the anode or photoanode).

An artificial photosynthetic system must first include an efficient photon collector absorbing a broad spectrum of visible sunlight. These can be molecular photosensitizers or semiconductor materials. They allow charge conduction and separation, stabilization of excited states, and have to be interfaced with catalysts. The latter are the other important elements of the device. They allow using the holes for the oxidation of water and the excited electrons to reduce protons (H_2 production) and/or transform the CO_2 molecules (production of CO, formate, methanol, hydrocarbons). Another strategy is to couple a solar panel, which converts solar energy into electricity, with an electrolyser, in which electrical energy is transformed and stored in the form of chemical energy. In the case of electrolysis, it is possible to use solid metal electrodes which provide both electron conducting and catalysis functions or use soluble molecular catalysts, which are then grafted onto electrodes or incorporated into porous materials. deposited on the electrode.

Towards Artificial Photosynthesis



A large range of catalysts are developed in the laboratory: heterogeneous catalysts, molecular catalysts (organometallic) and metalloenzymes (natural or artificial). This is a bioinspired approach, still little implemented, which is followed in the laboratory to develop in particular these new catalysts, solid or molecular, preferably based on non-noble and abundant metals (Fe, Cu, Co, Ni). In the case of molecular and enzymatic systems, various heterogenization strategies of these catalysts are used to build new photosystems or solid materials of electrodes and photoelectrodes. Finally, we are developing various electrochemical (flow cells, gas diffusion electrodes) and photochemical devices.

This project is developed along several directions:

Synthesis and characterization of molecular complexes as catalysts for the reduction of CO_2 or water (homogeneous catalysis)

- New molecular mononuclear catalysts based on Cobalt (Co), Nickel (Ni), Rhodium (Rh) and Rhenium (Re) (**Figure 1a-c**)
- Dithiolene complexes of Molybdenum (Mo) or Tungsten (W), whose structures are inspired by the active sites of formate dehydrogenase having a Mo (W)-molybdopterin center (**Figure 1d**)
- Polynuclear complexes of Mo and Copper (Cu) inspired by active sites of class II of CO dehydrogenases

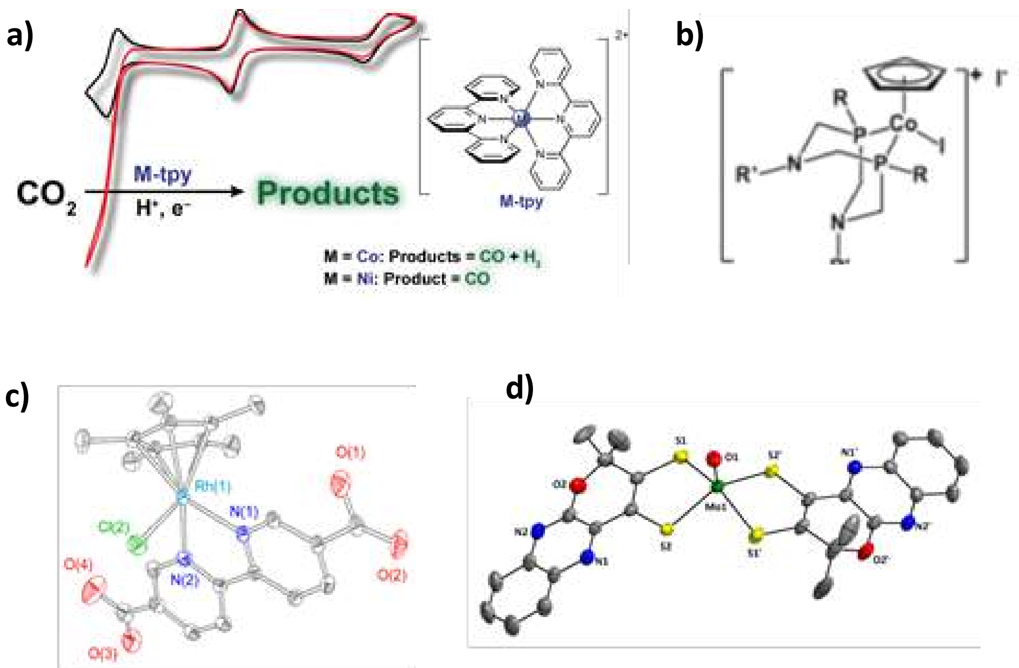


Figure 1: a) Terpyridine complexes of cobalt and nickel are electrocatalysts for the reduction of CO_2 to CO, as shown in the cyclic voltammogram in the presence of CO_2 (*Chem Soc. Rev.* **2017**, 46, 761-796); b) A cobalt complex catalyzing reduction of CO_2 to formic acid (*J. Am. Chem. Soc.* **2017**, 139, 3685-3696); c) A rhodium-based catalyst for reduction of CO_2 into formic acid (*Inorg. Chem.* **2019**, 58, 6893-6903); d) A Molybdenum-dithiolene complex that mimics the active site of formate dehydrogenase (*Angew. Chem. Int. Ed. Engl.* **2018**, 57, 17033-17037).

Towards heterogeneous catalysts for water oxidation, proton reduction and CO_2 reduction

- By covalent grafting of molecular complexes on the electrode surfaces and by electrodeposition of metals from molecular or salt precursors (figure 2).
- By incorporating, covalently or not, catalytic or photosensitive complexes in coordination polymers or in MOFs (Metal Organic Frameworks) and shaping them into thin films. Examples are

polyoxometallates encapsulated in MOFs (POM@MOFs) for the oxidation of water (**Figure 3**) or encapsulated photosystems into MIL-101 for the reduction of CO_2.

- By electrodeposition of metals and metallic oxides from metallic salts, leading to dendritic porous catalysts (**Figure 4a**). By doping carbon graphite-like (nano)materials with nitrogen and metals (Fe, Cu) (**Figure 4b**).

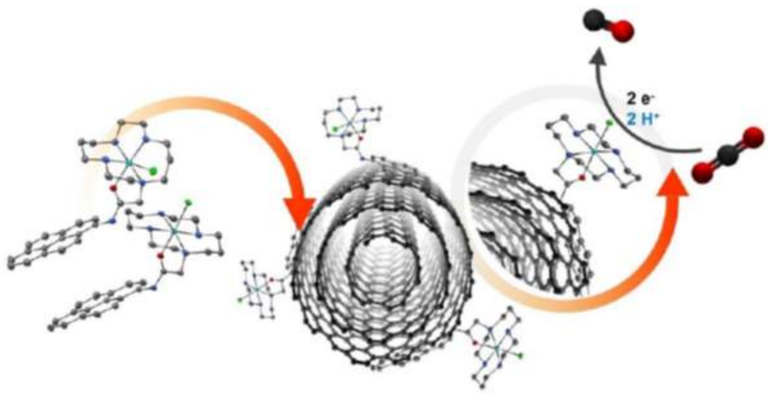


Figure 2 : Heterogeneous molecular catalyst, for the electroreduction of C_{O2}, obtained by immobilization of an Ni (cyclam) complex, carrying a pyrene group, on carbon nanotubes (*ChemSusChem.* **2020**, 13, 6449-6456).

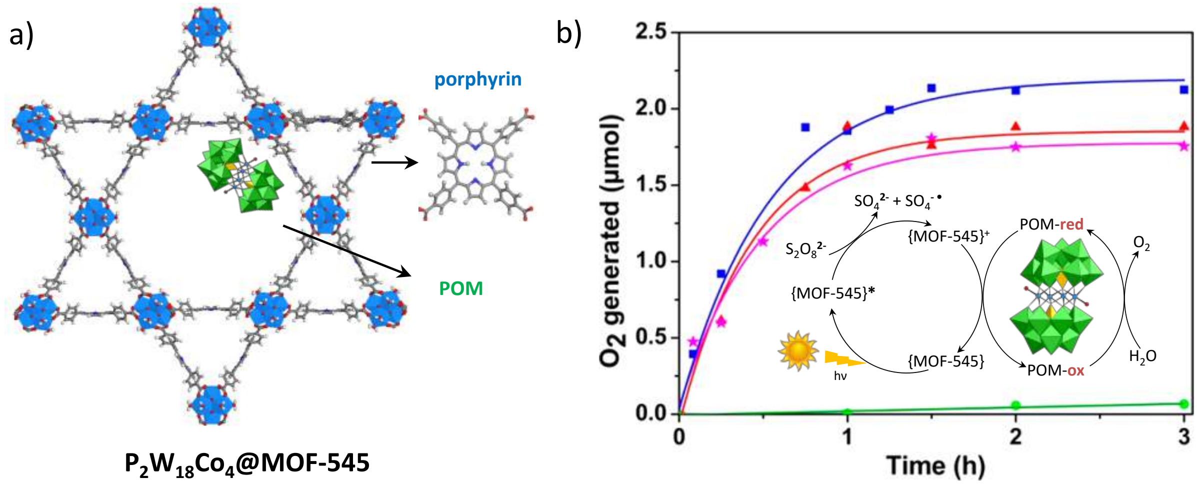


Figure 3: a) Components of $P_2W_{18}Co_4$@MOF-545. The position of the POM is obtained from computations (see Figure 6). Colour code: WO_6, green polyhedra; ZrO_8, blue polyhedral or spheres; Co, cyan spheres; O, red spheres; C, H, grey; N, dark blue. b) Kinetics of visible-light-driven O_2 production measured by GC analysis over 0.5 mg of $P_2W_{18}Co_4$@MOF-545 (blue square), $P_2W_{18}Co_4$@MOF-545 recycled once (red triangle), twice (pink stars), 131 µM TCPP-H_2 and 13 µM $P_2W_{18}Co_4$ in solution (green circle). Reaction conditions: 5 mM $Na_2S_2O_8$ in 2 mL of 80 mM borate buffer solution, pH 8, visible light (λ > 420 nm, 280 W). Inset: Schematic representation of the proposed mechanism for the light-driven OER by $P_2W_{18}Co_4$@MOF-545 (*J. Amer. Chem. Soc.* **2018**, 140, 10, 3613-3618).

a) b)

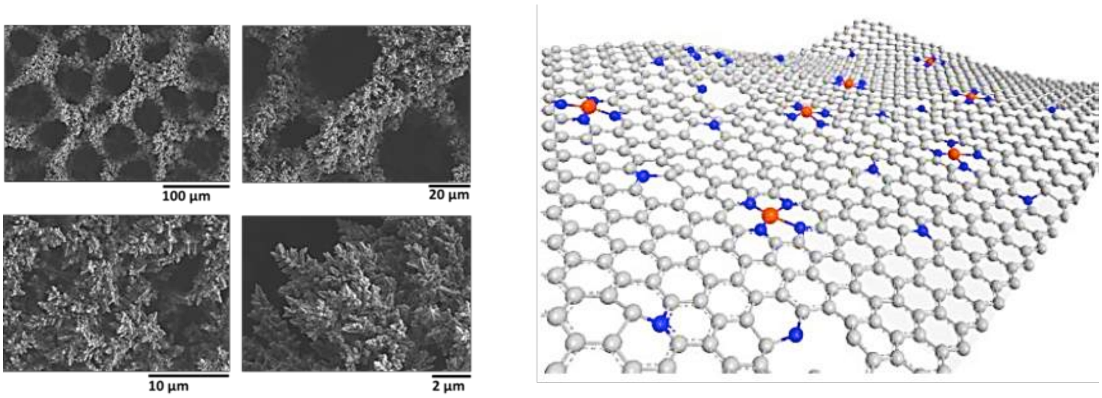
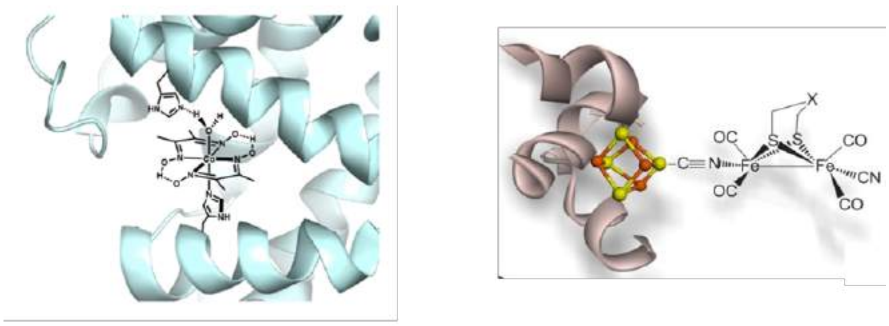


Figure 4 : a) Porous dendritic copper-based materials for the reduction of CO_2 into ethylene (*Proc. Natl. Acad. Sci.* **2019**, 116, 9735-9740; *Nature Materials* **2019**, 18, 1222-1227) and the oxidation of water (*Angew. Chem. Int. Ed.*, **2017**, 56, 4792–4796); b) N- and Cu-doped carbon materials, containing Cu single sites, as catalysts for CO_2 reduction to ethanol (*Angew. Chem.* **2019**, 58, 15098-15103).

The preparation and study of artificial hydrogenases

The combination of well-selected receptor proteins and catalysts can lead to new "enzymes" called “artificial enzymes”. They have the advantage of being optimized both by chemical modification of the catalyst and by protein engineering (site-directed mutagenesis). This original approach is not only used for the construction of artificial hydrogenases (**Figure 6**) but also for CO_2 reductases, which catalyse the reduction of CO_2 into CO.



a) b)

Figure 6. a) The active site of an artificial hydrogenase resulting from the combination of myoglobin in its *apo* form and a synthetic complex, cobaloxime (*Inorg. Chem.* **2014**, 53, 8071; *Curr. Op. Chem. Biol.* **2015**, 25, 36–47; *ChemPlusChem* **2016**, 81, 1083-1089). b) An artificial hydrogenase with an active site mimicking that of [FeFe]-hydrogenases (*ACS Catal.* **2019**, 9, 4495-4501).

The evaluation of these chemical and enzymatic systems

- For their electro-catalytic properties for the reduction of protons and carbon dioxide and for water oxidation (electrochemical analysis such as cyclic voltammetry and electrolysis)
- For their photochemical catalytic properties in combination with organic or inorganic photosensitizers, and a sacrificial electron donor/acceptor.
- From a structural point of view, by the implementation of PDF diffraction techniques (Pair Distribution Function) and profile analysis **(Figure 7**).

- From a theoretical point of view to elucidate the atomic structure (by DFT quantum calculations) and the electronic properties of functionalized porous hybrid solids and the elucidation of reaction mechanisms of molecular catalysts (**Figure 8**).

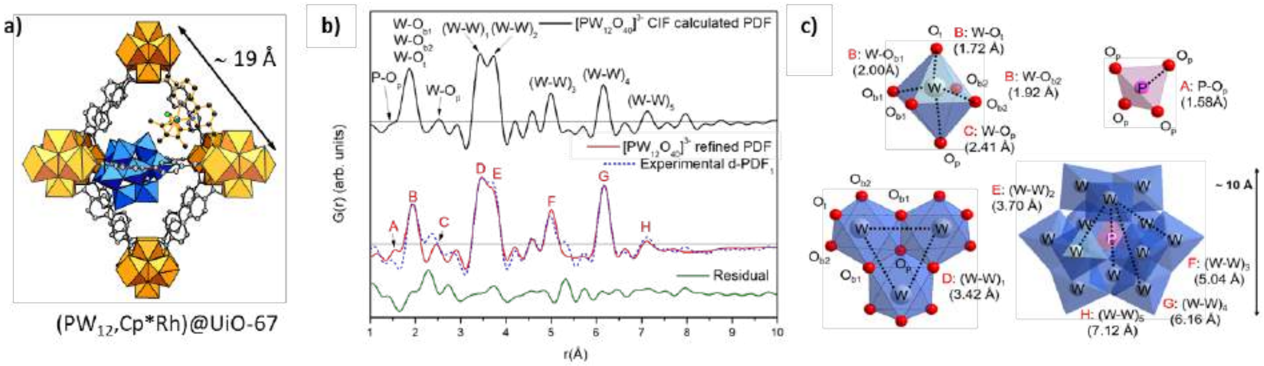


Figure 7. (a) Positioning of the POM in the composite (PW_{12},Cp*Rh)@UiO-67 obtained thanks to Monte Carlo simulations and DFT-D3 calculations. (b) Comparison of the calculated PDF of an isolated PW_{12} (black) and the experimental differential PDF (d-PDF) of the PW_{12} in UiO-67 (blue dashed line), superimposed on the adjusted refined d-PDF (red) using the structural model of $[PW_{12}O_{40}]^{3-}$ from the CIF file, and the residual profile (green). The AH labels of the peaks correspond to the refined distances indicated in the POM shown in (c) for the tetrahedron PO_4, the octahedron WO_6, the trimer of octahedra WO_6 and in the structure of the complete polyoxometalate PW_{12} (Mellot-Draznieks et al. J . Am. Chem. Soc. **2020**, 142, 9428–9438).

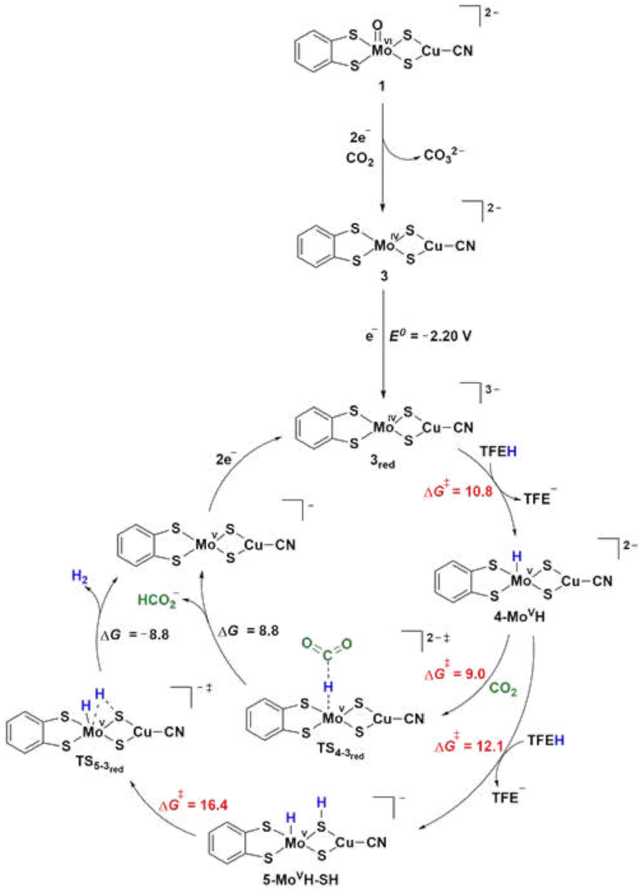


Figure 8: Mechanism proposed for the reduction of CO_2 to formic acid by a dinuclear Mo-Cu complex, mimicking the active site of CO-dehydrogenases (*Chem. Sci.* **2020**, 11, 5503–5510).

The implementation of these systems within technological devices

The most efficient molecules (photosensitizers and catalysts) and materials (semiconductors and catalysts) are exploited to develop an electrochemical or a photoelectrochemical cell to couple water oxidation (anode) to the reduction of CO_2 or protons (cathode), the source of electrons being preferentially an external photovoltaic system (see *Proc. Natl. Acad. Sci.* **2019**, 116, 9735-9740). Different types of electrodes/electrolyzers (H cells, flow cells and gas diffusion electrodes) are developed (**Figure 9**).

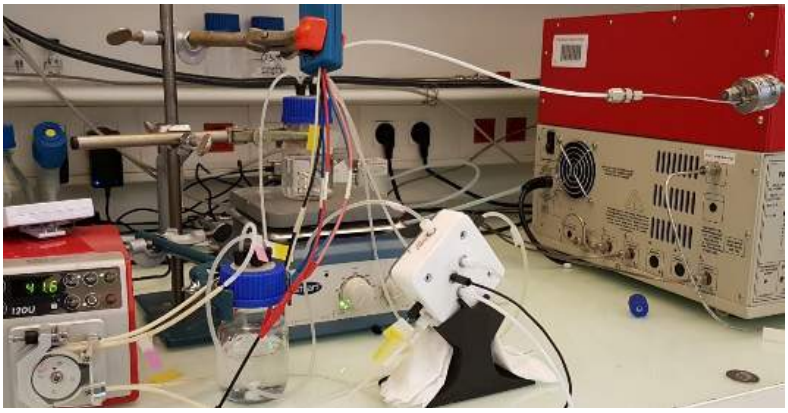


Figure 9: a flow electrochemical cell (in the center) with online product analysis for reaction products (see *Proc. Natl. Acad. Sci.* **2019**, 116, 9735-9740).

Methods and competences

- Organic and organometallic synthesis
- Materials synthesis and characterization
- Coordination chemistry
- Electrochemistry
- Photochemistry
- Hydrogenation reactors-
- Computational chemistry (VASP, Gaussian ...)
- Analytical Platform (gas chromatography, ion exchange, HPLC ...)
- Platform for protein crystallography (glove box, robots ...)
- Optical Spectroscopy
- Protein cloning, expression and purification
- Molecular biology: directed mutagenesis...

Academic collaborations

- Vincent Artero, CEA Grenoble (electrodeposition, hydrogenases, Cobalt complexes)
- Carlos Sanchez-Sanchez, Sorbonne Université (molecular electrochemistry)
- Thibault Cantat, CEA Saclay (tandem reactions)
- Thomas Jaramillo, Université de Stanford (heterogenous catalysts)
- Mohamed Atta, CEA Grenoble (hydrogenases)
- Capucine Sassoye, UPMC (PDF for MOFs)
- Jérôme Canivet, IRCE Lyon (MOFs)
- Florian Wisser, Regensburg University , Allemagne (porous polymers)
- Anna Proust, UPMC Paris (POMs)
- Anne Dolbecq, Pierre Mialane UVSQ, Versailles (POM@MOF)
- Céline Pagis, Audrey Bonduelle, IFPEN, Lyon (Photocatalysis with MOFs)
- Christophe Léger, CNRS Marseille (hydrogenases)
- Andrea Zitolo, Synchrotron Soleil (XAS spectroscopy)
- Dario Taverna, Sorbonne Université (microscopy)

Industrial partnership

A tight collaboration between the laboratory and the company TOTAL aims at developing catalysts for electrolysis of carbon dioxide into hydrocarbons (ethylene) and alcohols (ethanol).

Another industrial partnership with the company VEOLIA aims to develop hybrid devices (electrochemistry-thermochemistry) for the recovery of formic acid.

A collaboration with the startup company SPHERE aims at developing electrochemical cells.

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