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PhD POSITION

**Hybrid polyoxometalates for the photocatalytic reduction of CO₂:
from homogeneous to heterogeneous catalysis**

October 2024 – October 2027

Application deadline 4th April 2024

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Title: Hybrid polyoxometalates for the photocatalytic reduction of CO₂: from homogeneous to heterogeneous catalysis

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Context: Photocatalytic reduction is an attractive option for converting CO₂ into high value-added chemicals and moving towards a low-carbon chemical industry. This reaction requires the use of catalysts. Polyoxometalates (POMs) are described as soluble molecular oxides based on metal centres with a high degree of oxidation (W(VI), Mo(VI), V(IV,V)...). These inorganic species can incorporate a wide range of transition metal ions (Fe, Co, Ni, etc.) in their structure, and can be functionalised by organic ligands. POMs are attracting growing interest in catalytic reactions because of their redox behaviour and in particular their ability to store electrons reversibly. While POMs have been widely studied as catalysts for photocatalytic proton reduction, there are far fewer examples of their use for CO₂ photoreduction. Recently, we have shown that several Ni(II)-substituted POMs based on vacant polyoxotungstates can reduce CO₂ under visible irradiation under homogeneous conditions (K. Talbi et al. *Applied Catal. B Environ.* 2024, 345, 123681).

We now plan to extend this study to compounds based on polyoxomolybdate anions. These POMs have remarkable electronic properties, can be easily functionalized and are stable in solution. On the other hand, hybrid crystalline porous solids or MOFs (Metal-Organic Frameworks) are ideal platforms for developing new heterogeneous catalysts. They can themselves be catalytic, selective and recyclable, but they also have the possibility of incorporating active species into their network, enabling their properties to be finely modulated (A. Dolbecq et al., *Chem. Soc. Rev.* 2021, 50, 6152). It therefore seems particularly interesting to combine these two lines of research to obtain highly active materials for CO₂ reduction.

Objectives : The first stage of the project will involve exploring the synthesis of a family of hybrid POMs based on polyoxomolybdates, transition metal ions and photosensitive ligands, and studying their photocatalytic properties under homogeneous conditions. The second step will consist in synthesizing POM-based materials, either by immobilizing the POMs in the cavities of preformed MOFs or by using the POMs as building units of new coordination polymers. The molecules and materials will be characterized (IR and UV-vis spectroscopies, NMR, single crystal and powder X-ray diffraction, EDX analysis, nitrogen adsorption isotherms, ICP analysis) at the ILV laboratory. Photocatalytic experiments in homogeneous and heterogeneous conditions will be carried out at Collège de France. Finally, DFT calculations will be performed by our collaborators in Collège de France in order to apprehend the mechanism of the photocatalytic reduction.

Knowledge and skills: A good knowledge of coordination chemistry and material chemistry as well as a high level of motivation is required. An experience in photocatalysis would be appreciated. Candidates should also be autonomous and able to organize themselves quickly to manage the various aspects of their project (synthesis, characterization, photocatalytic properties), which will be carried out in two laboratories (ILV (Versailles) and Collège de France (Paris)).

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