

# PhD position in Synthetic Bio-Inorganic Chemistry And Electrocatalysis

## *Heterometallic sulfide clusters for CO<sub>2</sub> activation and conversion*

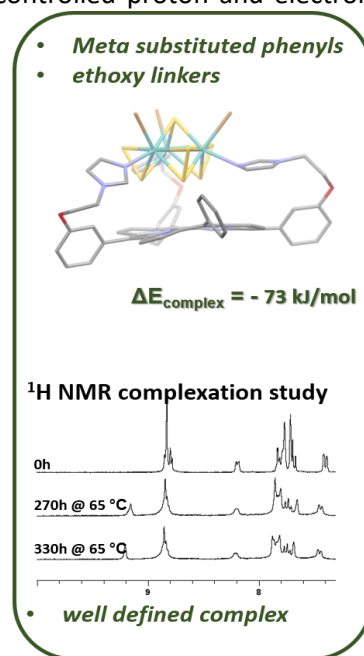
**Topics :** Synthetic bioinorganic chemistry, electrocatalysis, CO<sub>2</sub> activation and conversion

A CEA/USTH-funded PhD position is available between the **Laboratoire de Chimie et Biologie des Métaux** (LCBM, UMR 5249 Univ. Grenoble Alpes-CNRS-CEA; Grenoble, France) and the **University of Science and Technology of Hanoi** (USTH; Hanoi, Vietnam). The position will open between the SolHyCat group, ([www.solhycat.fr](http://www.solhycat.fr)) and the *Department of Applied and Fundamental Sciences* (<https://usth.edu.vn/en/department-of-fundamental-and-applied-sciences/>) for a 3-year international PhD research-project dedicated to the synthesis and study of bio-inspired metal-sulfides clusters for the activation of diluted CO<sub>2</sub> and its derivatives. **The position will offer a unique opportunity to enroll in an international research program between two leading Vietnamese and French universities.** The successful candidate will spare his time between the two host institutions, and will prepare a dual USTH/UGA PhD.

### **Project summary:**

The development of new routes for the activation and conversion of small molecules (H<sub>2</sub>O, CO<sub>2</sub>) into basic chemicals feedstock (H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>) is a fundamental challenge for the transition towards a more sustainable economy. In stark contrast with the demanding thermochemical processes currently used in the industry, such as the Water Gas Shift reaction or Fisher-Tropsch process for the conversion of CO<sub>x</sub> into syngas (H<sub>2</sub>/CO mixtures) and the synthesis of alkanes, some living organisms offer examples of fascinating pathways supporting related transformations by the use of specialized biocatalysts.[1] One family of enzymes, the Nitrogenases, has recently demonstrated a particularly intriguing activity towards CO/CO<sub>2</sub>. Historically known for driving the reduction of N<sub>2</sub> into NH<sub>3</sub> *in vivo*, via controlled proton and electron transfers, it has been shown to support the unexpected reduction of carbon oxides into low-mass alkane/alkene derivatives (CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>...) when activated *in vitro* by strong chemical reductants.[2] This remarkable activity is promoted by unusual (hetero)metallic sulfides cofactors of the general formula [MFe<sub>7</sub>S<sub>9</sub>C] (M = Mo, V, Fe) and has driven the preparation of a variety of bio-inspired metal-sulfide clusters.[3] Interestingly, synthetically accessible [Fe<sub>4</sub>S<sub>4</sub>(SR)<sub>4</sub>], [Mo<sub>2</sub>F<sub>6</sub>S<sub>8</sub>(SR)<sub>9</sub>], and [Mo<sub>3</sub>FeS<sub>4</sub>(Cp)<sup>\*3</sup>]<sub>3</sub> cores appear to support related activities, under reductive conditions.[4]

In this project, we aim to investigate the ability of advanced synthetic ligand frameworks to stabilize and control the reactivity of [MMo<sub>3</sub>S<sub>4</sub>] (M = none, Mo, Ni, Fe) clusters towards nitrogenase substrates, including CO<sub>2</sub> and related derivatives. The LCBM partner has recently developed porphyrin-based ligands able to coordinate trinuclear molybdenum sulfide clusters in solution. Following this work we now aim to design ligands with improved coordination ability and investigate in details the reactivity of the assemblies towards CO<sub>2</sub> under electrochemical conditions.



## Project organization:

**A) Synthesis and characterization of new polypyrrole-based ligands (synthetic organic chemistry) -1<sup>st</sup> year- LCBM.** Extending our initial designs, we will integrate bidentate anchoring groups around the macrocyclic scaffold as well as investigate alternative macrocyclic platforms to prepare new families of ligands for the complexation of polynuclear metal-sulfide clusters.

**B) Ligand-cluster assembly (coordination chemistry/physical organic chemistry-spectroscopy) -1<sup>st</sup> and 2<sup>nd</sup> year- LCBM.** Using classical optical and NMR spectroscopies, we will investigate the complexation between archetypal tri/tetranuclear molybdenum sulfide clusters with the new ligands obtained and select the most promising (stable, well defined) family of ligands-cluster assemblies. The assembly of heterometallic clusters within the ligands will also be investigated.

**C) Reactivity studies (electrochemistry/analytical chemistry-spectroscopy) -2<sup>nd</sup>-3<sup>rd</sup> year- USTH.** The reactivity of the hybrid systems obtained will be investigated against CO<sub>2</sub> and selected CO<sub>2</sub>-derivatives under electrochemical conditions.

**Expected candidate background:** We are looking for a self-motivated candidate with a strong interest in molecular chemistry, electrochemistry, and spectroscopies. He/She should have a solid experience in coordination chemistry and or synthetic organic chemistry as well as demonstrate a good knowledge of the usual spectroscopic and electrochemical analytical methods applied to molecular systems. The successful candidate will spend half of his/her time in each institution.

**Affiliation :** Ecole Doctorale de Chimie et Sciences du Vivant (EDCSV), Université Grenoble Alpes, France / University of Science and Technology of Hanoi (co-tutelle)

**Starting date expected by April 2025**

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## REFERENCES

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- [2] A. J. Jasniewski, C. C. Lee, M. W. Ribbe and Y. Hu, *Chem Rev*, 2020, **120**, 5107.
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