2023 Master internship at UBO

LAB & PEOPLE

- Name of the hosting lab: **CEMCA UMR CNRS 6521**
  General activities of the lab: Chemistry, Electrochemistry, Spectroscopy
  Website: https://www.umr6521.cnrs.fr/en/
- Number of staff / PhD: 27 professors, assistant-professors and CNRS-researchers, 8 engineers and technicians and about 20-30 non-permanent members (PhD and postgraduate students, postdoctoral researchers, Emeritus and invited visitors).
- Supervisor name and contact: **Dr Lucile Chatelain**, lucile.chatelain@univ-brest.fr

TOPIC OF THE INTERSHIP

- Scientific context of the internship

To develop sustainable chemical processes, the research in the field of chemistry intensifies on new catalysts able to convert small molecules as resources products such as: H_2 an energy vector in the sustainable energy field, CO_2 one important greenhouse gas or persistent organic pollutants in the environment, as carbonated building blocks for the synthesis of valuable organic molecules. In particular, to reach these objectives, the strong and often inert chemical bonds like H-H, C-F, C=O, N≡N need to be activated. More and more chemists design and build novel catalysts based on abundant first row transition metals such as Mn, Fe or Co, in order to limit the use of expensive and rare noble metals like Pt and Pd. In the nature, various metalloenzymes are able to activate inert chemical bonds, that is why biomimicry, inspiration from nature, is developed to propose novel sustainable chemical transformations.[1] Inspired from the [FeFe]-hydrogenases active site, a family of enzymes able to convert reversibly H_2 into protons,[2,3] organometallic diiron complexes, an eco-friendly metal, are synthesized and studied. Most of these reported diiron examples focused on the reactivity towards proton reduction while the oxidation of H_2 is much more challenging.[4,5] Novel strategies to complete the H-H bond activation have been recently developed in our group. An heterolytic cleavage of H_2 has been achieved using an external unsaturated borane molecules added to electron-rich diiron complexes, resulting in the formation of a Frustrated Lewis Pair (FLP).[6] In parallel, studies on related complexes revealed their ability towards electrocatalytic reduction of CO_2,[7,8] showing the strong potential of these organometallic complexes for the activation of small molecules.

At the crossing road between electrocatalysis and FLP chemistry, this Master's project proposes the synthesis of very reactive diiron complexes inspired from the enzymatic [FeFe]-hydrogenases active at low oxidation state, and to study their reactivity properties towards small molecules such as H_2, CO_2, CS_2, azide, and halogenated organic compounds in order to develop novel chemical transformations. The reactivity properties of the synthesized complexes as well as their products will be investigated. Notably, the stabilization of reactive species containing for example terminal hydride ligand, a relevant intermediate in the [FeFe]-hydrogenases catalytic cycle of H_2 oxidation, will be explored. Spectroscopic characterizations

will be used to understand structural properties at each step of synthesis and reactivity study (IR, NMR...).

Keywords: coordination chemistry, organometallic chemistry, small molecule activation, [FeFe]-hydrogenases

Bibliography

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(3) Elleouet, C.; Pétillon, F. Y.; Schollhammer, P. Chapter 17 - [FeFe]-Hydrogenases Models. In *Advances in Bioorganometallic Chemistry*; Hirao, T., Moriuchi, T., Eds.; Elsevier, 2019; pp 347–364. https://doi.org/10.1016/B978-0-12-814197-7.00017-0.
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- Tasks and duties entrusted to the student:

The intern will synthesize organic ligands and study their coordination properties to mononuclear and dinuclear organometallic iron-based complexes. The characterization of the resulting complexes will be performed using spectroscopic analysis (IR, NMR). The study of their reactivity towards small molecules such as H_2, CO_2, CS_2, azide, and halogenated organic compounds will be investigated. The group has all knowledge and technical facilities necessary to develop this organometallic chemistry and the reactivity studies.

- Skills to be acquired or developed:

Depending on the background of the student, skills into organic ligand synthesis, coordination studies on iron complexes and reactivity studies will be acquired or developed as this project is multidisciplinary. Based on the reactivity of these compounds towards air, strong

skills will be acquired during this internship in the manipulation of air-sensitive chemicals. Spectroscopic analysis will be carried out at each step. A report with the obtained results will be written at the end of the internship.

PROFILE OF THE DESIRED STUDENT

- Minimum level of study required: end of Bachelor or Master degree
- Field(s) of study: Chemistry
- Scientific skills: organic and organometallic syntheses, spectroscopic characterization (IR, NMR)
- Language skills required: English (spoken, written)

THE INTERNSHIP ASSIGNMENT:

Desired duration of the internship (in months): from 3 to 5 months
Desired Starting date of the mission: from February 2023 to May 2023
Indicative weekly schedule: 35h / week
Remuneration: 600€/month, paid on national SEA-EU funds for a maximum of 5 months; additional Erasmus grant could be asked to your own university.

Internship agreement: an internship agreement will be signed.

To SEA-EU students:
If you're interested please send your CV and letter of motivation to the scientist in charge: lucile.chatelain@univ-brest.fr asap and before the 1st February 2023.