2023-24 – doing a Master internship at UBO

Synthesis and reactivity studies of diiron organometallic complexes related to the active site of [FeFe]-hydrogenase for small molecule activation

LAB & PEOPLE

- Name of the hosting lab: **Laboratory of Chemistry, Molecular Electrochemistry and Analytical Chemistry** (CEMCA UMR CNRS 6521)
  General activities of the lab: Chemistry (organic, coordination, analytical)
  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**

Activation of strong and often inert chemical bonds like H-H, C-F, C=O, N≡N found in small molecules as H_2, N_2, CO_2 or persistent organic pollutants (C_xF_y, C_xCl_y…) allows the isolation of valuable compounds restraining, for some of them, their damaging environmental impact. Chemists are designing novel catalysts based on earth-abundant first row transition metals (Mn, Fe or Co) to achieve this goal. In the nature, various metalloenzymes are able to catalyze the activation of 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, organometallic diiron complexes, an eco-friendly metal, are synthesized and studied.[2,3] While the oxidation of H_2 remains challenging,[4,5] novel strategies to complete the H-H bond activation have been recently developed in our group from the formation of intermolecular Frustrated Lewis Pair (FLP).[6] Parallel studies in literature revealed the ability of such diiron compounds to perform 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 site 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. Spectroscopic characterizations will be used to understand structural properties at each step of synthesis and reactivity studies (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.
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(5) Ahmed, M. E.; Nayek, A.; Križan, A.; Coutard, N.; Morozan, A.; Ghosh Dey, S.; Lomoth, R.; Hammarström, L.; Artero, V.; Dey, A. A Bidirectional Bioinspired [FeFe]-Hydrogenase Model. *J. Am. Chem. Soc.* **2022**, *144* (8), 3614–3625.
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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.

- **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.

PROFILE OF THE DESIRED STUDENT

- Minimum level of study required: Master degree
- Field(s) of study: Chemistry
- Scientific skills: syntheses, knowledge on analytical methods
- 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: flexible starting date from October 2023 to May 2024
Indicative weekly schedule: 35h / week
Remuneration: 600€/month, paid on national SEA-EU funds for a maximum of 5 months

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 before the 01/10/ 2024.