PhD offer

Project title: Non-noble metal catalysts with tetra-aza-derived macrocyclic ligands for electrocatalytic reduction of protons and CO_2 (Tetra-azaCat)

Starting – Duration : October 2024 – 36 months
Location: Département de Chimie Moléculaire (DCM) UMR 5250 UGA-CNRS
301 rue de la Chimie, 38000 Grenoble, France

Contact : Marie-Noëlle Collomb (PhD Director) marie-noelle.collomb@univ-grenoble-alpes.fr
Benjamin Darses benjamin.darses@univ-grenoble-alpes.fr

Project description: The development of artificial photosynthesis systems for water-splitting and CO_2 reduction for hydrogen and valuable chemicals production (CO, HCOOH...) requires the development of efficient, selective and stable catalysts capable of operating at low overpotential and based on earth abundant transition metals. Cobalt complexes with tetra- and penta-aza macrocyclic ligands including the pyridyldiimine motif constitute a very promising family of catalysts recently exploited for the electro- and photo-induced reduction of protons to hydrogen (HER) and the reduction of CO_2 (CO_2RR). In particular, the cobalt tetra-aza complex has received an increase interest since it is now considered as one of the most efficient and stable H_2-evolving catalyst (HEC) in fully aqueous solution. In addition, it has been recently shown that a simple substitution of the pyridine moiety of the macrocycle ligand by a pyridine or pyridinium allows selectivity for CO_2RR to be directed toward CO formation over H_2.
The aim of this thesis project is the development of this family of catalysts, still under-exploited by introducing various substituents on the macrocycle ligand.These substituents could induce a modification of the electronic properties of the metal center, act as axial ligands and/or proton relays and thus modify/enhance the reactivity, by promoting electron transfer coupled to proton transfer (PCET) reactions and/or directing the selectivity for HER or CO_2RR. As the complexes are synthesized by template effect, i.e. by reaction of the metal cation with bis-acetyl pyridine and a polyamine, precursors bearing different substituents will first be synthesized. The structures of all new complexes will be ascertained by X-ray diffraction. Electrochemical and spectroscopic properties (NIR/Vis. and EPR) of the initial complexes and their electrogenerated reduced forms as well as their performance as electrocatalysts for HER and CO_2RR in terms of efficiency, selectivity (for CO_2RR) and robustness will be assessed by cyclic voltammetry and electrolysis under homogeneous conditions. This project aims also to establish correlations between the catalytic performance, and the selectivity of the new complexes with tetra-aza derived macrocyclic ligands with their structural, electronic/spectroscopic properties.
This PhD thesis will be carried out in collaboration between two teams of the DCM, the Electrochimie Moléculaire et Photochimie Redox (EMPRe) team and the Synthèse et réactivité en Chimie Organique (SeRCO) team.

Keywords : cobalt catalyst, macrocyclic ligand, coordination chemistry, molecular electrochemistry, electrocatalysis, small molecule activation, artificial photosynthesis.

Applicant profile: The candidate should hold a master's degree in chemistry with interest for synthesis, coordination chemistry and molecular electrochemistry. Experience in electrocatalysis would be an asset.
Funding: Labex ARCANE, CBH Graduate School

Application: Apply before April 8th, 2024 (CV and motivation letter)

Selected references

- Boutin, E.; Merakeb, L.; Ma, B.; Boudy, B.; Wang, M.; Bonin, J.; Anxolabéhère-Mallart, E.; Robert, M. Molecular catalysis of CO_2 reduction: recent advances and perspectives in electrochemical and light-driven processes with selected Fe, Ni and Co aza macrocyclic and polypyridine complexes. *Chem. Soc. Rev.* **2020**, *49*, 5772.
- Leung, C. F.; Chen, Y. Z.; Yu, H. Q.; Yiu, S. M.; Ko, C. C.; Lau, T. C. Electro- and photocatalytic hydrogen generation in acetonitrile and aqueous solutions by a cobalt macrocyclic Schiff-base complex. *Int. J. Hydrogen Energy* **2011**, *36*, 11640-11645.
- McCrory, C. C. L.; Uyeda, C.; Peters, J. C. Electrocatalytic Hydrogen Evolution in Acidic Water with Molecular Cobalt Tetraazamacrocycles. *J. Am. Chem. Soc.* **2012**, *134*, 3164-3170.
- Varma, S.; Castillo, C. E.; Stoll, T.; Fortage, J.; Blackman, A. G.; Molton, F.; Deronzier, A.; Collomb, M.-N. Efficient Photocatalytic Hydrogen Production in Water Using a Cobalt(III) Tetraaza-Macrocyclic Catalyst: Electrochemical Generation of the Low-Valent Co(I) Species and its Reactivity Toward Proton Reduction. *PCCP,* **2013**, *15*, 17544-17552.
- Gueret, R.; Castillo, C. E.; Rebarz, M.; Thomas, F.; Hargrove, A.-A.; Pécaut, J.; Sliwa, M.; Fortage, J.; Collomb, M.-N. Cobalt(III) Tetraaza-Macrocyclic Complexes as Efficient Catalyst for Photoinduced Hydrogen Production in Water: Theoretical Investigation of the Electronic Structure of the Reduced Species and Mechanistic Insight. *J. Photochem. Photobiol. B: Biol.* **2015**, *152*, 82-94
- Roy, S.; Bacchi, M.; Berggren, G.; Artero, V. A Systematic Comparative Study of Hydrogen-Evolving Molecular Catalysts in Aqueous Solutions. *Chemsuschem* **2015**, *8*, 3632-3638
- R. Gueret, L. Poulard, M. Oshinowo, J. Chauvin, M. Dahmane, G. Dupeyre, P. P. Lainé, J. Fortage, and M.-N. Collomb, Challenging the $[Ru(bpy)_3]^{2+}$ photosensitizer with a triazatriangulenium robust organic dye for visible light-driven hydrogen production in water, ACS Catalysis, **2018**, 8 (5), 3792–3802.
- Sandroni, R. Gueret, K. D. Wegner, P. Reiss, J. Fortage, D. Aldakov and M.-N. Collomb, Cadmium-Free $CuInS_2$/ZnS Quantum Dots as Efficient and Robust Photosensitizers in combination with a Molecular Catalyst for Visible Light-Driven H_2 Production in Water. Energy Environ. Sci. **2018,** 11 (7)**,** 1752-1761.
- R. Gueret, C. E. Castillo, M. Rebarz, F. Thomas, M. Sliwa, J. Chauvin, B. Dautreppe, J. Pécaut, J. Fortage, and M.-N. Collomb, Cobalt(II) Pentaaza-Macrocyclic Schiff Base Complex as Catalyst for Light-Driven Hydrogen Evolution in Water: Electrochemical Generation and Theoretical Investigation of the One-Electron Reduced Species, Inorg. Chem. **2019**, 58 (14), 9043-9056.
- Nie, W.; Tarnopol, D. E.; McCrory, C. C. L. Enhancing a Molecular Electrocatalyst's Activity for CO_2 Reduction by Simultaneously Modulating Three Substituent Effects. *J. Am. Chem. Soc.* **2021**, *143*, 3764-3778.