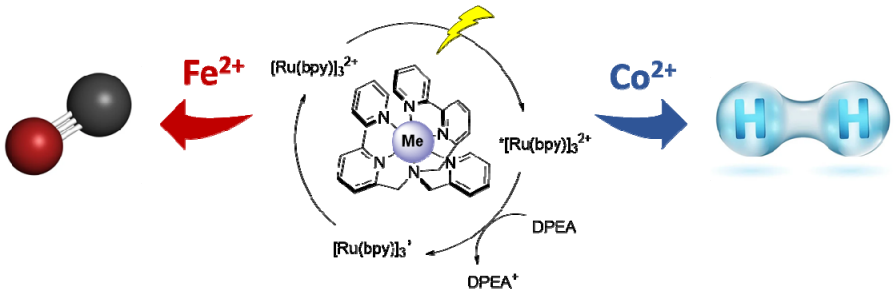
A TALE OF TWO METALS: SWITCHING SELECTIVITY TOWARDS CO_2 REDUCTION IN HEPTACOORDINATE COMPLEXES

Albert Ruggi[a], Federico Droghetti[b], Mirco Natali[b]

[a] Département de Chimie, Université de Fribourg, Fribourg, Switzerland
[b] Dipartimento di Scienze Chimiche, Farmaceutiche ed Agrarie, Università di Ferrara, Ferrara, Italy

Solar fuels, i.e. fuels generated by using sunlight as a source of energy, are the most promising alternatives to fossil fuels, both because of their availability and of their reduced environmental impact. CO_2 reduction, in particular, is one of the most popular strategies to obtain solar fuels[1]. However, protons and efficient catalysts are necessary to respectively decrease the thermodynamic and kinetic barrier. These conditions often also trigger the reduction of protons to hydrogen, which represents a competitive process[2]. We have recently found that a heptacoordinate Co complex (known to efficiently produce hydrogen)[3] can also catalyze CO_2 reduction in acetonitrile/water solutions, although with low selectivity, the hydrogen generation being the predominant process. Remarkably, replacement of the Co(II) center with Fe(II) induces a switch in selectivity towards CO_2 reduction. The resulting heptacoordinate Fe(II) catalyst is extremely active and it reaches selectivities > 90% in carbon-based products (CO + formate) in the presence of 1-10% H_2O as proton source. In this talk we will present our results concerning the electrochemical, photochemical and computational investigations of these two catalysts.



[1] Segev, G.; Kibsgaard, J.; Hahn, C.; Xu, Z. J.; Cheng, W.-H.; Deutsch, T. G.; Xiang, C.; Zhang, J. Z.; Hammarström, L.; Nocera, D. G.; Weber, A. Z.; Agbo, P.; Hisatomi, T.; Osterloh, F. E.; Domen, K.; Abdi, F. F.; Haussener, S.; Miller, D. J.; Ardo, S.; McIntyre, P. C.; Hannappel, T.; Hu, S.; Atwater, H.; Gregoire, J. M.; Ertem, M. Z.; Sharp, I. D.; Choi, K.-S.; Lee, J. S.; Ishitani, O.; Ager, J. W.; Prabhakar, R. R.; Bell, A. T.; Boettcher, S. W.; Vincent, K.; Takanabe, K.; Artero, V.; Napier, R.; Cuenya, B. R.; Koper, M. T. M.; Van De Krol, R.; Houle, F., The 2022 solar fuels roadmap. *J. Phys. D: Appl. Phys.* **2022,** *55* (32), 323003.

[2] Boutin, E.; Merakeb, L.; Ma, B.; Boudy, B.; Wang, M.; Bonin, J.; Anxolabéhère-Mallart, E.; Robert, M., Molecular catalysis of CO2 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* (16), 5772-5809.

[3] Lucarini, F.; Pastore, M.; Vasylevskyi, S.; Varisco, M.; Solari, E.; Crochet, A.; Fromm, K. M.; Zobi, F.; Ruggi, A., Heptacoordinate CoII Complex: A New Architecture for Photochemical Hydrogen Production. *Chem. Eur. J.* **2017,** *23* (28), 6768-6771.