Proposition de sujet de thèse
Studies of new thin layers based on polyoxometalate and porphyrin.

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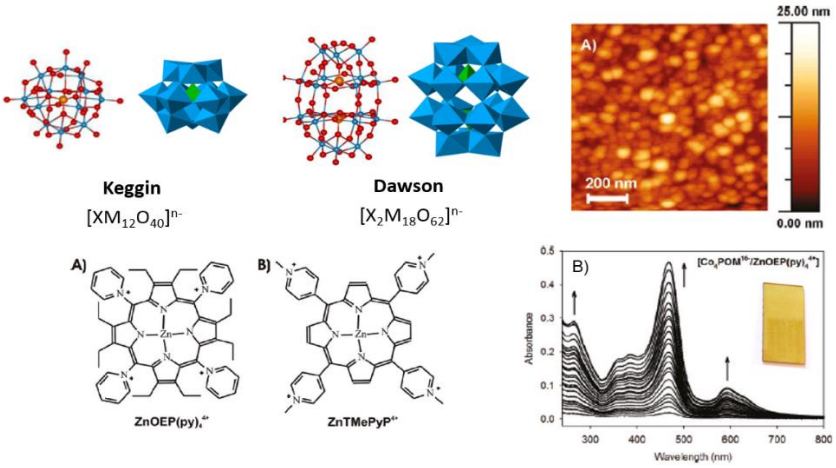
The elaboration, understanding and exploration of the physical properties of thin layers attract considerable attention in the field of the energy storage, energy conversion and photocatalysis. This area of research, already rich by the diversity of the objects that may be envisaged, has rapidly evolved to functional molecular architectures. Polyoxometalates (POMs) are well-known as component of functional materials because of their molecular and electronic tunability and they have found applications in photocatalysis and photoelectrocatalysis. Recently, films based on the electrostatic interactions between tetracationic porphyrin and Dawson type polyoxometalates showed promising properties for photovoltaic applications.

This project targets the formation of thin layers on the electrode surfaces based on hybrid POMs and/or porphyrins compounds. Different strategies have been developed to link these type of compounds on the surface.



Right: structures of POMs and of tetracationic porphyrins. Left: tapping mode AFM topography and UV-visible absorption spectra of $[POM/ZnOEP(py)_4^{4+}]_n$ films (onto quartz) with different numbers of deposition cycles (n).

Physical properties of the new hybrid compounds will be studied in solution at the molecular level, then onto various type of surface (ITO, quartz). Several techniques will be used to characterize electrocatalytic, electronic and magnetic properties (electrochemical, spectroelectrochemistry (UV-VIS-NIR) spectroscopy, Quartz Crystal Microbalance, AFM/STM, etc.). Especially, paramagnetic assemblies will be elaborated and advanced EPR (Electron Paramagnetic Resonance) spectroscopy will give additional informations. The molecular arrangement in the layers on the surface might be attained by line-shape analysis of the EPR signal and/or by the analysis of the *g*-factor anisotropy.

Selected references:

1- I. Ahmed, R. Farha, M. Goldmann, L. Ruhlmann, *Chem. Comm.*, 2013, *49*, 496-498.
2-D. Schaming,R. Farha, H. Xu, M. Goldmann, L. Ruhlmann. *Langmuir*, 2011, 27(1), 132–143.
3-L. J. Esdaile, L. Rintoul, M. See Goh, K. Merahi, N. Parizel, R. M. Wellard, S. Choua, D. P. Arnold. *Chem. Eur. J.* **2016**, *22*, 3430-3446.
4-Y. Liu, C. M. Ndiaye, C. Lagrost, K. Costuas, S. Choua, P. Turek, L. Norel, S. Rigaut., *Inorg. Chem.*, **2014**, *53*, 8172–8188.