Proposition de sujet de thèse

Coordination-Driven Construction of Chromophore Nano-ribbons

Supervisor : **Sylvie Choua**, MC, UdS, Laboratoire des Propriétés Optiques et Magnétiques des Architectures Moléculaires, UMR 7177 Unistra-CNRS. E-mail : sylvie.choua@unistra.fr

Co-supervisor : **Jean Weiss**, DR, UdS, Laboratoire de Chimie des Ligands à Architecture Contrôlée, UMR 7177, Unistra-CNRS. e-mail : jweiss@unistra.fr

In the field of self-organized nanomaterials, the ability to control the linear morphology of self-assembled nanomaterials from the nano- to the micro-meter scale with porphyrins would be a major conceptual breakthrough. Two different approaches were developed by the J. Weiss team to build porphyrin wires: a) Linkages by coordination bonds were used to generate long porphyrin wires[1] starting from the monomeric porphyrins (Figure 1a). The second approach takes advantage of external coordination sites integrated in the porphyrinic core (Figure 1b). For both coordination modes, molecular wires were generated by self-assembly in solution and at a liquid/HOPG interface (Highly Oriented Pyrolytic Graphite, Figure 2). Starting from these observations, this project will aim at tailoring the optic, magnetic and electronic properties of these self-assemblies.

- The strategy (iterative coordination) used with porphyrins will be applied to new and simplified building blocks accessible in larger quantities and bearing functionalities (magnetic, optical, electronic). An experimental approach based on Electron Paramagnetic Resonance (EPR) spectroscopy in the P. Turek team, including pulsed hyperfine spectroscopy (ESEEM, ENDOR, HYSCORE) will be used to characterize the magnetic and electronic properties of the building blocks and the oligomers. For surface studies, scanning probe microscopy (AFM, c-AFM and STM) will be the techniques used to visualize the molecular wires at the interface.

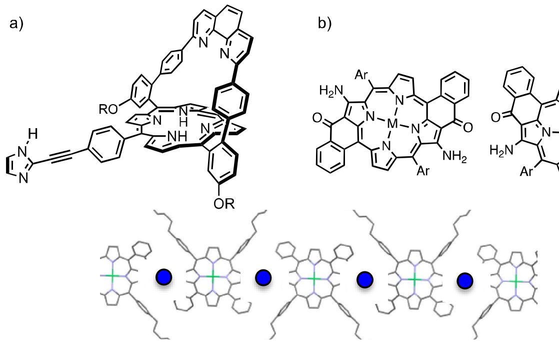

Figure 1. *Building blocks for porphyrin wires*.

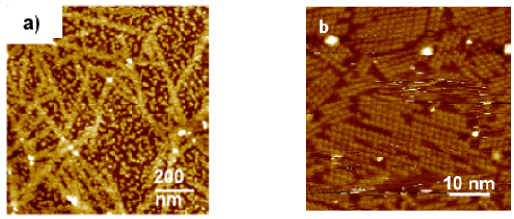

Figure 2. *a) AFM images of wires from building-blocks of Fig. 1a; b) STM images of wires from builfing blocks of Fig. 1b.*

- The preparation of oligomeric porphyrins (by using approach a) and b)) and the study of the conductivity (or the photoconductivity) of the molecules as a function of their lengths, taking advantage of a stepwise construction of the wires, is planned in collaboration with the University of Delft (with Pr H. van der Zant).

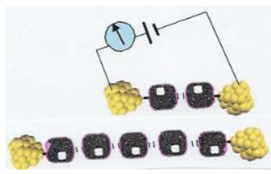

Figure 3. *Stepwise construction of porphyrin wires in break junctions*

Candidate profile:

The applicant must have a Master of Science in Chemistry and good knowledge in Physical-Chemistry. Highly motivated, independent and dynamic, he/she should be able to work in a multidisciplinary team. Applications including (1) a detailed CV (2) an application and motivation letter, and (3) a recommendation letter of the Master's internship supervisor should be sent by e-mail at sylvie.choua@unistra.fr

Selected references:

1) "Metal-mediated linear self-assembly of porphyrins" J. A. Wytko, R. Ruppert, C. Jeandon and J. Weiss, Chem. Commun., **2018**, *54*, 1550-1558.

2 "Nickel(II) *meso*-Hydroxyporphyrin Complexes Revisited: Palladium-Catalysed Synthesis, Electronic Structures of Derived Oxy Radicals, and Oxidative Coupling to a Dioxoporphodimethene Dyad" 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.