

## Photo(redox)active and photo(electro)switchable materials based on polyoxometalates and/or (iso)porphyrins

Laurent Ruhlmann<sup>a</sup>, Yanzi Lin<sup>a</sup>, Yimin Liang<sup>a</sup>, Jingjing Wang<sup>a</sup>, Ning Jiang<sup>a</sup>

<sup>a</sup> Université de Strasbourg, Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, Institut de Chimie de Strasbourg, UMR 7177, 4 rue Blaise Pascal, 67000, Strasbourg.  
Email / Courriel de l'auteur présentant : [lruhlmann@unistra.fr](mailto:lruhlmann@unistra.fr)

The conference will be divided into two parts. The first part will be on the development of hybrid systems incorporating polyoxometalates (POMs) which is a promising approach to elaborate new redox active materials. To expand the practical applications, their association to a visible-light photosensitizer is needed and has been explored (Fig. 1). In this context, we have also developed a method of electropolymerization of POMs based on nucleophilic attack onto the electrogenerated porphyrin radical cation or dications. The

formation of hybrid POM-porphyrin copolymeric films (Fig. 1b) can be obtained by the electro-oxidation of porphyrin in the presence of the hybrid POM bearing two pyridyl groups (Py-POM-Py).<sup>[1-2]</sup> Using the same methodology, the synthesis of a diarylethene-(iso)porphyrin photoswitchable copolymer has been developed (Fig. 1c). The incorporated diarylethene maintains its reversible photochromism upon the UV-Vis radiation with multiple cycles of ring-opening and closing.<sup>[3]</sup> A photo-switchable molecular capsule based on Keggin-type POM and diarylethene has been also formed and studied (Fig. 1a).<sup>[4]</sup> In the second part, the photoredox-switchable molecular grippers based on resorcin[4]arene cavitand platforms equipped with alternating quinone (Q) and quinoxaline walls carrying hydrogen bond donating groups will be presented. The semiquinones (SQ) state can be generated electrochemically and photochemically.<sup>[5]</sup> It was

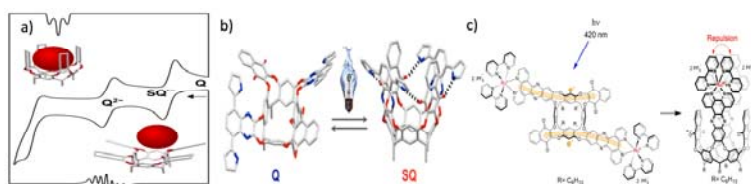


Fig. 2 Photoredox-switchable molecular grippers based on resorcin[4]arene cavitand platforms.

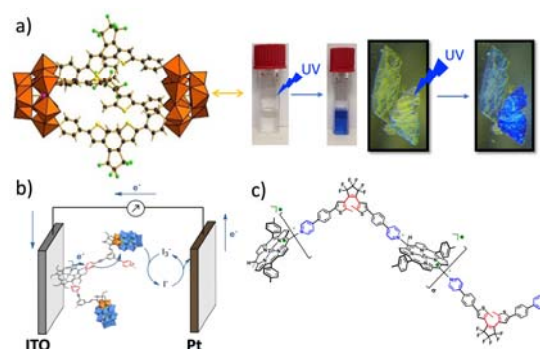


Fig. 1 Various type of photo(redox)-active or photo(electro)switchable systems studied.

shown that these systems adopt an open conformation in the oxidized Q state until redox interconversion to the paramagnetic SQ radical anion provides the stabilization of the closed form through hydrogen bonding.

### References

- (1) Z. Huo, S. Yang, D. Zang, R. Farha, M. Goldmann, H. Xu, B. Antoine, G. Izzet, A. Proust, L. Ruhlmann *Electrochimica Acta*, **2021**, 368, 137635. (2) Y. Liang, M. N. Sokolov, M. A. Mikhaylov, H. Ibrahim, M. Goldmann, S. Choua, N. Le Breton, C. Boudon, V. Badets, A. Bonnefont, L. Ruhlmann, 2021, *Electrochimica Acta*, **2021**, 388, 138493. (3) Z. Huo, V. Badets, H. Ibrahim, M. Goldmann, H. Xu, T. Yi, C. Boudon, L. Ruhlmann, *Eur. J. Org. Chem.* **2021**, 6636. (4) M. Choudhari, J. Xu, A. I. McKay, C. Guerrin, C. Forsyth, H. Z. Ma, L. Goerigk, R. A. J. O'Hair, A. Bonnefont, L. Ruhlmann, S. Aloise, C. Ritchie, *Chemical Science*, **2022**, 13, 13732-13740. (5) J. V. Milić T. Schneeberger, M. Zalibera, F. Diederich C. Boudon, L. Ruhlmann, *Electrochimica Acta*, **2019**, 313, 544-560.