

Electrowiring of artificial enzymes – New hybrid metallo protein catalysts for selective oxydation by dioxygen

Postdoctoral fellowship – 12 months (ANR CATHYMETOXY),

Employment: in the course of 2013.

Laboratory: Laboratoire d'Electrochimie Moléculaire, UMR 7591 CNRS - Université Paris Diderot, Paris

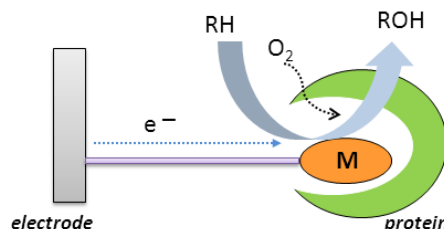
Website: <http://www.lemp7.cnrs.fr/>

Scientific expertise: analytical electrochemistry, surface modification, organic synthesis, coordination chemistry

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Context

The question of how selective alkane oxidation can be addressed has recently been reviewed, the “biological/biomimetic approach” being now considered as an alternative “hot approach” by researchers coming from heterogeneous chemistry.^[1] Due to the advent of large-scale gas to liquid (GTL) processing,^[2] higher alkanes will become available in ever increasing amounts, and the future efficient use of these carbon resources will depend on the development of highly active, selective and stable oxidation catalysts. Considering fine chemistry and oxidation of molecules of pharmaceutical interest, selective oxidation of drugs, and better understanding of metabolic profile is still an important challenge.^[3] Enzymes such as Cytochromes P450 are prototypical examples of biological oxidation catalysts capable of carrying out catalytic selective oxidative transformations of organic molecules using dioxygen under mild conditions. In this context we have chosen the development of “artificial enzymes”^[4,5] composed of synthetic metal complexes in tight association with a protein immobilized on an electrode surface. The protein matrix is expected to stabilize the active center and to induce the desired regio- or stereo-selectivity whereas a covalent connection of the catalytic site with the electrode is supposed to provide the necessary electrons for the reductive dioxygen activation



Project

Iron oligo-pyridyl complexes and metallo porphyrins which have been prepared in the laboratory, will be covalently connected to the electrode surface (via SAM formation or electro-grafting). The electrochemical and electrocatalytical properties of the formed mono layers are to be studied and we will focus in particular on their reactivity towards molecular dioxygen in order to elucidate mechanistic aspects of the reductive O₂ activation. The optimization of the catalysts might involve the variation of length and nature of the molecular bridge (wire) connecting the metal complex and the electrode surface. The metal complex/protein adduct (artificial enzyme) will be studied in the second part of the project.

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4. J. Steinreiber, T.R. Ward, *Coord. Chem. Rev.* **2008**, *252*, 751.
5. F. Rosati, G. Roelfes, *ChemCatChem* **2010**, *2*, 916.