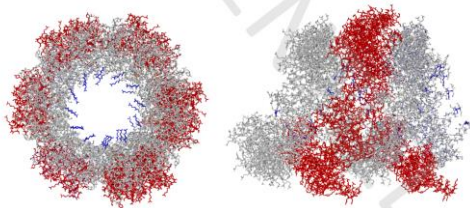


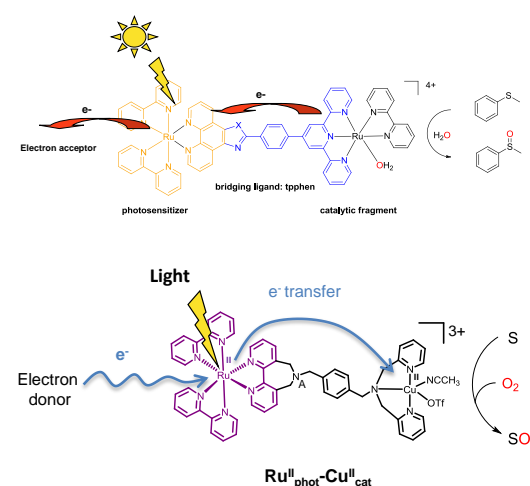
Two-years Post doctoral position: new functional hybrid materials for asymmetric photocatalytic oxygenation (Beginning September-October 2016)

The LEAFY protein (LFY) plays an essential role in the beauty of the plant kingdom: it governs the development of flower buds and their different organs (sepals, petals, stamens and pistils). This protein is a transcription factor that is necessary to decipher the genetic code and is endowed with two important domains: the C-terminal domain that binds to DNA to activate floral genes, and the N-terminal domain, an "oligomerization" domain that allows the LEAFY proteins to assemble in small chains. The crystallographic structure of the LFY-Nter has been reported and shows an auto-organisation of the monomers into a helical structure. It has been observed that two helices can interlock into each other yielding to polypeptide tube with accessible residues localized inside the helix (R. Dumas et col. *Nature Comm.* **2016**, DOI: 10.1038/ncomms1122). These amino-acids could be used to



anchor molecules of interest.

Moreover, for the last decades the development of sustainable chemistry becomes a priority for our society. Exploiting our



expertise in the development of bio-inspired catalysts for oxidation we are interested in the development of "eco-aware" catalysts using water as an abundant and safe oxygen atom source and light to activate such a stable molecule. Thanks to a close collaboration with photochemists, we reported the synthesis of two photocatalytic systems, constituted by the covalent association of a photosensitizer and a ruthenium-based catalyst ($Ru_{\text{phot}}-Ru_{\text{cat}}$; see scheme) for oxidation of organic substrates using water as the unique oxygen atom source (Hamelin et col, *inorg. Chem.* **2011**, *50*, 7954 and **2012**, *51*, 2222). More recently, we were able to develop a $Ru_{\text{phot}}-Cu_{\text{cat}}$ photocatalyst able to activate O_2 for oxygenation reaction.¹ In presence of sacrificial electron donor and light, this dyad proved to be efficient for sulfide, phosphine and alkene catalytic oxygenation (Hamelin et col. *Angew. Chem. Int. Ed.* **2015**, *54*, 8415). Mechanistic investigations gave evidences about a predominant 3O_2 activation by the Cu(I) moiety. In all systems, a proton-coupled electron-transfer (PCET) process from the photosensitizer in its excited state to the catalytic partner was highlighted.

In the field of sustainable chemistry it is envisaged to gather these two projects with the objective to generate **new functional hybrid materials for asymmetric photocatalytic oxygenation** of organic substrates using O_2 or H_2O as oxygen atom source.

This is a collaborative project between two laboratories of the Biosciences and Biotechnology Institute of Grenoble localized at the Commissariat à l'Énergie Atomique in Grenoble. The Laboratoire de Physiologie Cellulaire Végétale has the expertise in the LFY protein, while the Laboratoire de Chimie et Biologie des Métaux is developing for several years bio-inspired catalytic and photocatalytic systems. Web site: <http://big.cea.fr/drif/big/Pages/Presentation.aspx>

Due to its pluridisciplinarity, this project involves the synthesis of dyads, their full characterization using various methods (electrochemistry, UV-visible spectroscopy, NMR, EPR,...), the production of the protein, the anchoring of the complex, the characterization of the bio-material and the evaluation of the catalytic activity. The host laboratory has long history on bioinorganic chemistry and develops projects in the interface of chemistry and biology. This environment is suitable for the development of bioinspired catalysis.

Candidate's profile: Candidates should have solid skills in both organic and inorganic syntheses, as well as in spectroscopic methods. The successful candidate should have a good mix of synthetic and spectroscopic competence, physical/chemical intuition and independent thinking.

Keywords: photocatalysis, functional bio-material, oxidation.

Grenoble location and activity:

<http://en.wikipedia.org/wiki/Grenoble>



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