PhD project 2023-2026

Clusters-polyoxometallates eco-compatible tandems for the production of hydrogen: from molecular assemblies to the device.

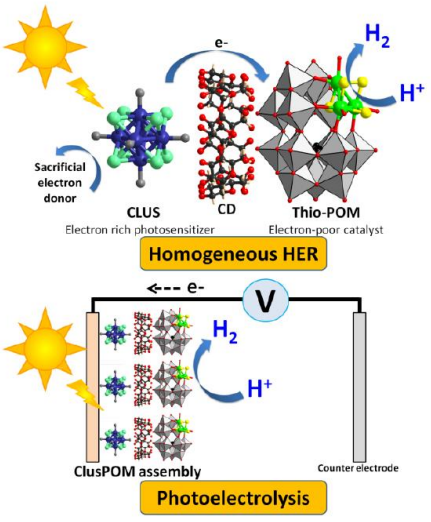
Institut des Sciences Chimiques de Rennes (UMR CNRS 6226) – Univ. Rennes
Institut des Sciences Moléculaires d'Orsay (UMR 8214) – CNRS/Université Paris-Saclay

Required skills:
- Master 2 course
- Motivation for experimental chemistry and chemical-physics
- Mastering English
- Ability to work in a team, good organization
- Documents requested: CV, M1 results, M1 (or L3) internship report, for an interview

Description:

Scientific context:

The topic of the PhD work is a part of the ANR CLUSPOM-H2 project which aims to develop photosystems that can be integrated into devices for converting solar energy into chemical energy *via* the production of hydrogen. The project focuses i) on the development of eco-compatible photocatalytic systems free of strategic elements and ii) on their integration into photoelectrodes. The targeted photosystems are based on the association of molybdenum-based molecular building blocks whose physical properties are complementary: metallic clusters and polyoxometallates (POM). The cluster will act as a robust photosensitizer for light absorption and generation of electron/hole pairs and the POM will act as a reaction catalyst for the proton reduction reaction and the formation of H_2.



Topic:
The work at ISCR will focus on studies of the optical and photoelectrochemical properties of molecular bricks containing metal clusters of types $[\{Mo_6I^i_8\}Cl^a_6]^{2-}$ and $[\{W_6I^i_8\}Cl^a_6]^{2-}$. After deposition on conductive or semi-conductive surfaces (i.e. NiO, TiO_2, ITO), the energy diagrams of the photoelectrodes thus designed will be established from electrochemical measurements, X-ray photoemission spectroscopy (XPS) and complex impedance spectroscopy. The localization of the energy levels of the cluster-based layers will then make it possible to choose the complementary molecular building block: the POM favoring an efficient charge transfer. The cluster-POM tandem (CLUSPOM) will then be assembled *via* an organic connector, a 'linker' of the type γ-cyclodextrine, and the interactions between the molecular building blocks will be studied. The entire CLUSPOM tandem will finally be covered with a protective polymer in order to avoid cluster and/or POM release phenomena.

The PhD work at ISMO will focus on the study of charge and electron transfers in these tandems. Through measurements combining stationary and time-resolved absorption and emission spectroscopies, competing processes will be analyzed and conditions favoring high charge transfer quantum efficiency will be identified. These measurements will exploit femtosecond and nanosecond transient absorption devices for wide time range (*fs-ms*) measurements, as well as picosecond to microsecond luminescence measurements. The challenge will focus on the comparisons of the dynamics in the excited electronic states of the clusters in the presence of POM and the charge separation states, between the experiments carried out in homogeneous solution with those carried out directly on the photoelectrodes prepared at the ISCR.

The thesis project implies that the doctoral student, mainly located at the ISCR, will carry out regular and long-term missions at the ISMO in order to make effective progress on the development of photosystems.

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ISCR contacts

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ISMO contacts

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