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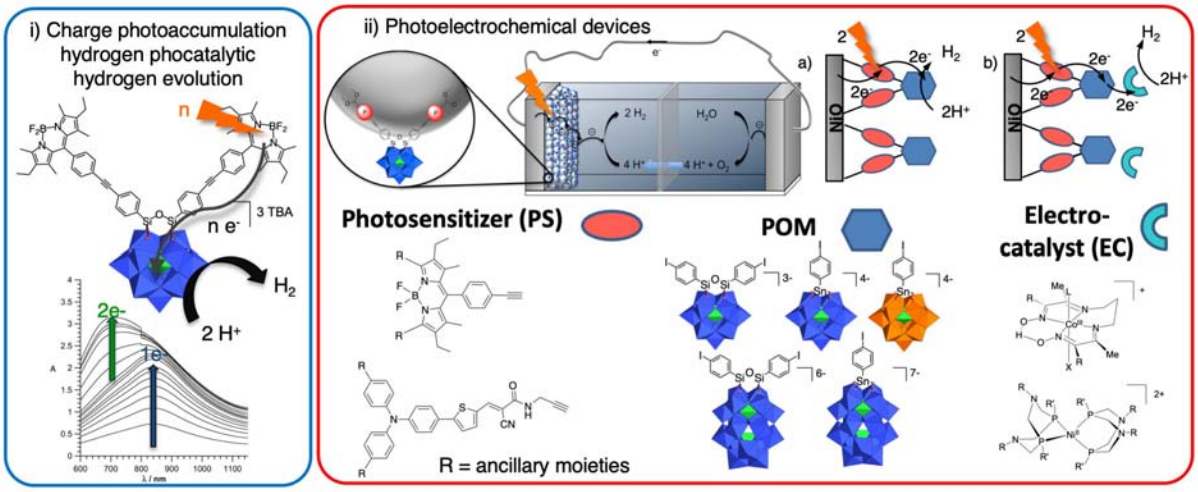
# Photosensitized polyoxometalate-based hybrids for solar energy conversion.

The design of artificial photosynthetic devices is emerging as a major challenge because of the continuously increasing global energy demand and the human contribution to atmospheric and climatic changes. Owing to their electron reservoir properties and the activity of their reduced form for the hydrogen evolution reaction, polyoxometalates POMs are attractive candidates for the development of artificial photosynthetic devices.[1][2] POMs form a remarkable class of well-defined molecular nano-scale oxoclusters of the early transition metals with an unmatched diversity of structures, properties and functionalization pathways. This project relies on the covalent association of functionalized polyoxometalates with bodipy[3] and push-pull organic dyes.[4] The first photosensitized POM-Ir(III) hybrids developed in the e-POM team allowed the photoaccumulation of electrons and the photoproduction of hydrogen.[5][6] More recently, POM-bodipy hybrids also displayed remarkable photophysical properties. In such compounds, photoinduced electron transfer from the chromophore to the POM occurred with kinetics down to dozens of picoseconds, making this system appropriate for applications in NiO-based photocathodes.[7] Furthermore these compounds allowed to study in-depth the parameters governing photoinduced electron transfers, notably the effects of the solvent, the acidity or the counter-ions.[8][9] The objective is now to study the charge photo-accumulation and photo-catalytic hydrogen evolution of these compounds. In addition, the development of molecular photocathodes by their covalent grafting to an oxide surface will constitute a second research axis of this project. The work carried out during this thesis will focus on the following points:

- *Synthesis of the target compounds.* This will involve the modification of the polyanion, the organic dye and its functionalization with ancillary moieties for further grafting on an oxide surface (NiO). The synthesis of bodipy-based chromophores will be done at the IPCM while push-pull compounds will be synthesized thanks to an external collaboration (M. Chavarot-Kerlidou, LCBM Grenoble).[10]
- *Electronic and photophysical investigations of the synthesized compounds*. This work will be done either at IPCM or in collaboration with the team of Dr. Elizabeth Gibson (University of Newcastle, UK).
- *Charge photo-accumulation and photo-catalytic hydrogen evolution reaction.* These experiments will be monitored by in-situ UV-vis spectroscopy. Hydrogen photoproduction will be evaluated in the presence of proton electroreduction catalysts.
- *Development of molecular photocathodes.* Molecular photocathodes will by obtained by grafting the photosensitized hybrids on oxide surfaces (NiO, ITO). Their photoelectrocatalytic properties will be investigated in the presence of electrocatalysts that showed the highest hydrogen photoproduction performances in homogeneous conditions. The modified photocathodes should also be tested for photovoltaic applications.



Left: Charge photo-accumulation on a POM-bodipy. Right: Photoelectrochemical cell using a photosensitized POM-based photocathode. Top: different systems considered a) PS-POM, b) PS-POM / EC. Bottom: Molecular representation of the chromophores, POMs platforms and electrocatalysts considered.

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## Application

This is a multidisciplinary project with an important emphasis in synthetic chemistry. We are thus looking for a chemist with a strong background in molecular synthesis that have interests in working at the interface between molecular chemistry, photophysics and the development of photoelectrochemical devices. Applications must be sent before May 2nd 2022 to guillaume.izzet@sorbone-universite.fr. More information on the E-POM group and its research focus can be found on our website (http://www.ipcm.fr).

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