Laboratoire de Chimie et Physique Quantiques
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DFT insights into light-driven charge accumulation based on Earth-abundant high potential photosensitizers

Funded 3-year Ph.D. project, starting October 1st, 2023

Keywords : theoretical photochemistry - photoinduced electron transfer - redox potential - potential energy surface

Context : Photoinduced electron transfer is an elementary reaction step of natural photosynthesis and, as such, plays a key role in the conversion of sunlight into biological matter. The transfer of single electrons is nowadays fairly well understood, but the **photoinduced transfer and accumulation of multiple electrons** has remained extremely challenging, although natural or artificial photosynthesis crucially relies on multi-electron transfer reactions. Against this background, we will develop new concepts for the light-driven accumulation of multiple redox equivalents to unravel its basic operating principles.

Objectives : We will develop new photosensitizers made from abundant transition metals featuring higher reducing power than well-known precious metal-based photosensitizers such as $Ru(bpy)_3^{2+}$. We will also develop new molecular electron storage units that help us exploit the concept of redox potential inversion to facilitate the light-driven accumulation of several electrons. The design of **high-potential photosensitizers (HiPoPS) based on molybdenum(0) complexes** will be guided by computational chemistry. Subsequently and in parallel to the experimental work in the partner labs, novel photosensitizer-acceptor (**PS-A**) dyads or triads **PS-A-PS** with acceptors capable of storing up to four electrons will be studied. In a third stage, selected donors (**D**) will be covalently connected via two Mo(0) HiPoPS to a central acceptor unit, to form molecular pentads **D-PS-A-PS-D**.

Figure 1 : Schematic dyads, triads and pentads composed of Mo(0) photosensitizers, electron donors D and acceptors A for the study of photoinduced multielectron transfer and charge accumulation

Framework : international collaboration with experimentalists (Katja Heinze, U. Mainz and Oliver Wenger, U. Basel), fully funded by the 2022 Solar-driven chemistry call (CA-HiPoPS project). Three PhD students will be starting simultaneously and will combine their synthetic, spectroscopic and computational efforts to reach the objectives.

Skills : Master 2 in theoretical chemistry or physics, with a particular taste for photochemistry and discussion with experimentalists. Programming skills are a plus (Fortran, python), as well as good written and oral skills in English to ensure efficient communication within the project consortium.

Procedure : applications proceed in three steps
1) applicants send a CV, motivation letter, Master results and recommendation letter to Isabelle Dixon isabelle.dixon@irsamc.ups-tlse.fr
2) meanwhile, applicants apply online to the doctoral school https://ed-sdm.univ-toulouse.fr/as/ed/proposition.pl?site=edsdm
3) applicants selected by the doctoral school will then apply to the corresponding offer through the CNRS job portal : https://emploi.cnrs.fr/

The Ph.D. student will be hosted at the LCPQ Toulouse (about 30 staff members + 30 doc/postdoc).