M2 internship / PhD position available in organic synthesis and photocatalysis

M2 internship: expected starting date January/February 2024
PhD: expected starting date by fall 2024
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Harvesting singlet fission to improve molecular photo-catalysis: design and synthesis of advanced photosensitizers for multielectron oxidation reactions

The **use solar light for driving catalytic reactions in aqueous media,** remains very challenging due to several issues: i) detrimental charge recombination between the catalyst and the photosensitizers, ii) low excitation rates of photosensitizers under ambient light conditions, and iii) scarcity of molecular (photocatalytic) systems compatible with aqueous conditions. A promising approach to tackle the first two issues **is to develop photosensitizers capable of generating more than one exciton upon the absorption of a single photon.** Singlet fission (SF) allows for such conversion, where two excited triplet states (T_1+T_1) can be generated after the absorption of a single photon in an ensemble of chromophores. Under specific conditions, when two or more chromophores are in close contact, an excited singlet state (S_1) can share half of its energy with the ground singlet state of a neighbor to generate ultimately two dissociated triplets living in µs time-scale that are relevant for driving a catalytic reaction. SF, thus, raises the bar of the theoretical efficiency of photon-to-charge conversion to 200%. **The overarching goal of this project is to design the first molecular system capable to perform singlet fission-mediated multi-electronic photocatalytic oxidations in water.**

Recently Wasielewski *et al.*[1] demonstrated efficient SF in bis-terrylene derivatives built around triptycene scaffolds. **We propose to take advantage of the versatility of the triptycene core to prepare similar architectures and couple them to archetypal Ru polypyridyl complexes (Figure1) to harness the potential of such assemblies to drive photocatalytic 2-electrons alcohol oxidation reactions.** In close collaboration with teams from Paris Saclay and Sorbonne Universities, in charge of investigating the detailed photophysical properties of the systems and developing advanced theoretical models to understand the key parameters governing the efficiency of SF and electron transfer in these assemblies, respectively, the most promising systems will be redesigned to improve the reactivity towards increasingly challenging substrates and reactions conditions. **The final goal being the design of functional molecular assemblies working under fully aqueous conditions and ambient solar irradiation.** This project is part of a multi-partner ANR program and student exchanges between the 3 groups involved will be considered during the course of the project (PhD). In addition to the development of strong skills in synthetic organic chemistry and (photo)catalysis this program will allow the successful candidate(s) to gain valuable knowledge in advanced spectroscopy techniques and theoretical modelling applied to (photo)catalysis.

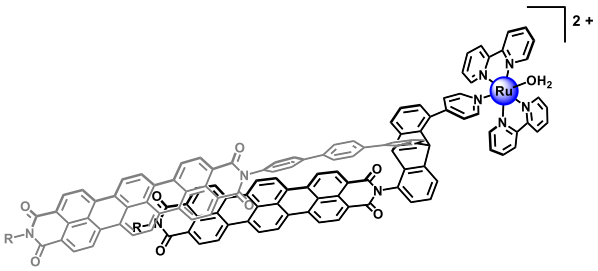

Figure 1: photosensitizer-catalysts assemblies for singlet fission mediated multielectron oxidation reactions.

[1] E. A. Margulies, C. E. Miller, Y. Wu, L. Ma, G. C. Schatz, R. M. Young, M. R. Wasielewski *Nat. Chem.* **2016**, *8*, 1120–1125.

Candidate background:

Candidates are expected to demonstrate a strong motivation for synthetic organic chemistry with a practical experience in molecular synthesis, as well as knowledge of the classical analytical techniques applied to molecular chemistry (NMR, UV-Vis, IR, MS….). Training in coordination chemistry and electrochemistry will be valuable assets. Notions of photocatalysis will be appreciated.

The SolHyCat team:

Part of the *Laboratoire de Chimie et Biologie des Métaux,* in Grenoble, France, the SolHyCat team offers perfectly fitted lab-space to support the synthesis and characterization of novel organic and organometallic compounds (NMR, IR, UV-Vis, MS) as well as all the tools required for investigating photocatalytic reactions (solar simulator, GC, GC-MS, LC-MS, IC, electrochemical/optical probes for O_2). The teams offers a stimulating international working environment. Please visit our website for further information:

https://www.solhycat.com/

https://www.cbm-lab.fr/

Applications must be sent to matthieu.koepf@cea.fr and will be considered until the positions will be filled. Anticipate a minimum 2 months delay prior to the start of the contract in order to complete the CEA administrative tasks.