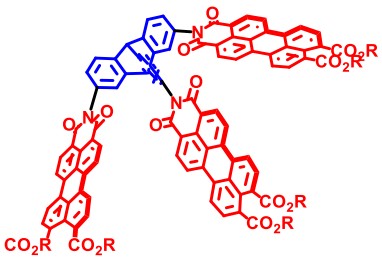
PhD position @ CEA Grenoble in artificial photosynthesis

Topic: Design of advanced photosensitizers for multielectron oxidation reactions

Supervisor : Matthieu Koepf (matthieu.koepf@cea.fr)

We are seeking a highly motivated PhD candidate to join the SolHyCat group at the LCBM, CEA Grenoble, to work on the design and synthesis of advanced photosensitizers capable of singlet fission to enhance the efficiency of multi-electron photooxidation reactions. Expected starting date: 1 october 2024.

Project context & overview: Solar-driven chemical synthesis involving multi-electronic processes still faces major challenges for finding wide range applications. A fundamental bottleneck faced by molecular systems lies in the inability of most photosensitizers to deliver more than one charge after photoexcitation. This leads to a high probability of charge recombination or detrimental side reactions to occur before closing the targeted catalytic cycle. With this project we propose to design and investigate polyrylene-based antennae capable to perform singlet fission, and couple them to polypyridyl ruthenium catalysts, to tackle these challenges in archetypal 2-electron oxidation reactions. Singlet fission is a photophysical phenomenon occurring in chromophores assemblies, where one excited singlet state evolves into two spin-triplet states. Rylene antenna leading to the generation of two excited states bearing enough driving force for charge injection into an appropriate catalyst, could help drastically reduce the detrimental back electron transfer processes in multi-electronic catalysis. Following our initial work on perylene-based antennae (figure) we will 1) implement terrylene units around a triptycene scaffold as the latter chromophores are known to promote singlet fission more efficiently and 2) transpose the successful design to fully water-soluble systems. The antennae will next be grafted onto ruthenium oxidation catalysts and evaluated as advanced photosensitizers to drive alcohol oxidation reactions.



Perylene-triptycene antenna for photocatalytic applications.

This project is part of a collaborative ANR funded program between the SolHyCat group in charge of the synthesis of the antenna and the antenna-catalyst assemblies, as well as the characterization of the photocatalytic activity of the latter; the LBMS team (SB2SM, University Paris Sacaly) in charge of the advanced photophysical characterization of the antenna and antenna-catalaysts assemblies; the CI team (LCT, Sorbonne University) in charge of the computational analysis of the system.

Candidate requirements: The candidates are expected to demonstrate strong background in multistep synthetic organic chemistry, and classical characterization techniques applied to molecular systems (NMR, MS, UV-Vis, IR). Knowledge in coordination chemistry and electrochemistry will be a plus.

Key Responsibilities:

- Design, synthesize and characterize the antenna / antenna-catalysts assemblies
- Evaluate the photocatalytic activity of the antenna-catalysts assemblies
- Participate in the analysis and writing of scientific publications
- Disseminate the results in meetings, congresses, and talks

Inquiries and applications can be sent to Matthieu Koepf (matthieu.koepf@cea.fr) **until the 5th of June 2024.**