Postdoctoral Fellowship in molecular inorganic chemistry

Location: Sorbonne Université - Institut Parisien de Chimie Moléculaire (IPCM) - E-POM team
UMR CNRS 8232, 4 place Jussieu 75 005 Paris website
Start: May- June 2025 for a period of 18 months
Monthly gross salary: €2,900 to €4,000 depending on experience

Physico-chemical parameters of the photo-assisted electron storage/electron release in/from polyoxometalates

Context: this 18-month post-doctoral position is funded by the ANR project PH_2O_2TOREACT which aims at producing H_2O_2 by activation of molecular oxygen by photo-reduced polyoxometalates. As molecular oxides, polyoxometalates (POMs) are endowed with remarkable redox properties, combining the reducibility of solid-state metal oxides and the high tunability of molecular species. The rationalization of the formation of their reduced forms through photo-irradiation and the subsequent electron release are at the core of the project.

Research objectives: The development of clean processes that reduce waste, minimize environmental impact and improve the overall efficiency has become a critical challenge for a sustainable chemical industry. In this context, POMs have very promising potentialities in photo-redox chemistry, that yet require to be rationalized. The efficiency of both the photo-reduction of the POM (electron storage) in the presence of an organic substrate and the subsequent electron release from the reduced POM (possibly coupled to protons in proton coupled electron transfer PCET), to O_2 or other organic substrates will be analyzed from the perspective of the thermodynamic parameters, redox potentials and acidity constants, defining the X-H bond dissociation free energy (BDFE) of the partners (O-H bonds of reduced/protonated POM and C-H bond of organic substrates or O-H bond in the reduced species of O_2).[1] Under irradiation, the oxidizing power of POM is greatly enhanced and we propose to seek the possible correlations between the efficiency of the photo-induced electron transfer to the POM, the dynamics of its excited states, and the molecular and electronic structures of the POM.
Photo-assisted catalytic activity of POMs is dominated by the use of decatungstate $[W_{10}O_{32}]^{4-}$ (DT), which has been successfully applied to the oxidation of a broad range of organic substrates.[2,3] The key features of the excited and transient reactive states of DT have been identified by ultra-fast spectroscopy.[4] By comparison much less is known for other POMs, which is puzzling given the high molecular diversity encountered in this family. In this project we will thus investigate other POMs.

Research activities: the post-doctoral researcher will:

- study the efficiency of POM photo-reduction under steady-state irradiation under anaerobic conditions, in the presence of sacrificial electron donors. The progress of the reduction will be monitored by UV-Vis-NIR absorption spectroscopy;
- investigate the dynamics of the relaxation of the excited state, in anaerobic conditions, formation and decay of reactive transient species, using fs-transient absorption spectroscopy TAS, in the presence of organic substrates of various BDFE as electron source. We indeed have

some experience in TAS, in the characterization of the photo-excited and charge separation states of hybrid POM-photosensitizers, on which we will rely.[5,6]

- push the understanding of the electron release from the reduced POMs to molecular oxygen and selected model organic substrates, to complete previous studies carried out in the E-POM team on hydrogen evolution from reduced POMs.[7] The photo-assisted reduction under aerobic conditions will be carried out in parallel by a PhD student.

Candidate profile

We are looking for a motivated researcher with a solid training in molecular photochemistry, in the characterization of excited states, more generally with a sound physico-chemical background to be able to handle thermodynamic and kinetic data and to propose reaction mechanisms. A background in the thermodynamics and kinetics of proton-coupled electron transfers would be appreciated. Knowledge in experiments under air-sensitive conditions will be welcome.

Communication skills in English with a proven track record of publications and conference presentations is required.

Applications, to be sent to guillaume.izzet@sorbonne-universite.fr, geoffroy.guillemot@sorbonne-universite and anna.proust@sorbonne-universite.fr will include

- a CV including a publication list and a concise description of previous research experience
- a cover letter outlining research interests, motivation and adequacy to the project,
- the contact details for at least two academic references.

References

(1) Warren, J. J.; Tronic, T. A.; Mayer, J. M. Thermochemistry of Proton-Coupled Electron Transfer Reagents and Its Implications. *Chem. Rev.* **2010**, *110* (12), 6961–7001. https://doi.org/10.1021/cr100085k.

(2) Ravelli, D.; Fagnoni, M.; Fukuyama, T.; Nishikawa, T.; Ryu, I. Site-Selective C–H Functionalization by Decatungstate Anion Photocatalysis: Synergistic Control by Polar and Steric Effects Expands the Reaction Scope. *ACS Catal.* **2018**, *8* (1), 701–713. https://doi.org/10.1021/acscatal.7b03354.

(3) West, J. G.; Huang, D.; Sorensen, E. J. Acceptorless Dehydrogenation of Small Molecules through Cooperative Base Metal Catalysis. *Nat Commun* **2015**, *6* (1), 10093. https://doi.org/10.1038/ncomms10093.

(4) Waele, V. D.; Poizat, O.; Fagnoni, M.; Bagno, A.; Ravelli, D. Unraveling the Key Features of the Reactive State of Decatungstate Anion in Hydrogen Atom Transfer (HAT) Photocatalysis. *ACS Catal.* **2016**, *6* (10), 7174–7182. https://doi.org/10.1021/acscatal.6b01984.

(5) Black, F. A.; Jacquart, A.; Toupalas, G.; Alves, S.; Proust, A.; Clark, I. P.; Gibson, E. A.; Izzet, G. Rapid Photoinduced Charge Injection into Covalent Polyoxometalate–Bodipy Conjugates. *Chem. Sci.* **2018**, *9* (25), 5578–5584. https://doi.org/10.1039/C8SC00862K.

(6) Toupalas, G.; Karlsson, J.; Black, F. A.; Masip-Sánchez, A.; López, X.; Ben M'Barek, Y.; Blanchard, S.; Proust, A.; Alves, S.; Chabera, P.; Clark, I. P.; Pullerits, T.; Poblet, J. M.; Gibson, E. A.; Izzet, G. Tuning Photoinduced Electron Transfer in POM-Bodipy Hybrids by Controlling the Environment: Experiment and Theory. *Angew. Chem. Int. Ed.* **2021**, *60* (12), 6518–6525. https://doi.org/10.1002/anie.202014677.

(7) K/Bidi, L.; Desjonquères, A.; Izzet, G.; Guillemot, G. H_2 Evolution at a Reduced Hybrid Polyoxometalate and Its Vanadium-Oxo Derivative Used as Molecular Models for Reducible Metal Oxides. *Inorg. Chem.* **2022**, acs.inorgchem.2c01741. https://doi.org/10.1021/acs.inorgchem.2c01741.