PhD research project 2023

Exploring the chemical reactivity of super-reduced polyoxometalates

Laboratory: Institut Lavoisier de Versailles (UMR 8180 CNRS-UVSQ) (link to the website).
The institute gathers all UVSQ chemists (more than 50 permanent staff) in a building and two annexes located on the site of UFR des sciences (45 avenue des Etats-Unis; Versailles, 78035).

PhD supervisor: Dr. Clément FALAISE

Starting date: between 01/11/2023 and 01/02/2024

Funding: The project involves a 36-month full-time contract (ANR program)

Candidate's profile

- Master or equivalent in Inorganic chemistry
- Strong experimental and lab/field work interest
- Enjoyment and motivations with respect to fundamental sciences
- Scientific rigor, dynamism, adaptability, teamwork, and writing abilities
- Good English level.

Context:

Polyoxometalates (POMs) are electro-active molecules studied for their potential applications in various fields, including energy, health, environment, or quantum technologies.[1] These inorganic polyanions produced upon acidification of metalate ions in water, exhibit an unmatched structural diversity in terms of compositions, shapes, and sizes. POMs can be simply described as discrete metal oxides built from corner- and edge-sharing pseudo-octahedral MO_6 units where M represents an early transition metal with d^0 electronic configuration (V^{5+}, Mo^{6+} and W^{6+}). Filling the non-bonding d_{xy}-orbitals of these metal centers offers the possibility to store several electrons in POM-based structures. Actually, this ability corresponds to their most striking property that makes them highly relevant for developing energy-storage devices (batteries & supercapacitors), catalytic processes (water splitting & C(sp_3)-H functionalization), or molecular electronics (qubits & flash memories).[2–4] In context, understanding how injected electrons influence the structures and properties of POMs correspond to a research area that links fundamental questions to practical interests. Although weakly reduced POMs have been largely studied, the fundamental investigations about the super-reduced POMs (POM reduced by at least 6e-) remain scarce.[5] Our group recently observed that such super-reduced POMs can contain one or more metal-metal bounded triads.[6] **This Ph.D. project aims to contribute to a better understanding of the chemistry of super-reduced POMs. More precisely, the Ph.D. candidate will focus his/her research on the preparation, the structural elucidation of super-reduced POMs, and the understanding of their physico-chemical properties.**

The thesis work as a whole will be supported by detailed characterizations obtained either in our laboratory (Single-crystal X-ray diffraction, multinuclear NMR, electrochemistry, UV-vis, RAMAN, TGA, IR, and ICP) or in synchrotrons (XANES/EXAFS, SAXS, or serial-crystallography). The Ph.D. student will be trained (e.g. participating in summer schools) for using and analyzing his/her data.

References:

1 D.-L. Long, R. Tsunashima and L. Cronin, *Angew. Chem. Int. Ed.*, 2010, **49**, 1736–1758.
2 J.-J. Chen, M. D. Symes and L. Cronin, *Nature Chem*, 2018, **10**, 1042–1047.

3 J. Lehmann, A. Gaita-Ariño, E. Coronado and D. Loss, *Nature Nanotech*, 2007, **2**, 312–317.
4 A. A. Fertig, W. W. Brennessel, J. R. McKone and E. M. Matson, *J. Am. Chem. Soc.*, 2021, **143**, 15756–15768.
5 J.-J. Chen, L. Vilà-Nadal, A. Solé-Daura, G. Chisholm, T. Minato, C. Busche, T. Zhao, B. Kandasamy, A. Y. Ganin, R. M. Smith, I. Colliard, J. J. Carbó, J. M. Poblet, M. Nyman and L. Cronin, *J. Am. Chem. Soc.*, 2022, **144**, 8951–8960.
6 C. Falaise, G. Mpacko Priso, N. Leclerc, M. Haouas and E. Cadot, *Inorg. Chem.*, 2023, **62**, 2494–2502.