PhD Fellowship in molecular inorganic chemistry

Location: Sorbonne Université - Institut Parisien de Chimie Moléculaire (IPCM) - E-POM group
UMR CNRS 8232, 4 place Jussieu 75 005 Paris E-POM group molecular nanosciences

Supervisor: Pr Anna Proust **Co-Supervisors**: Dr Florence Volatron, Dr Guillaume Izzet

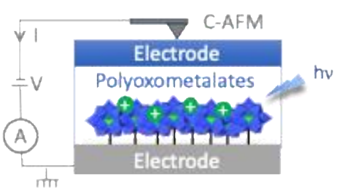
Context: **Multi-responsive molecular materials for brain-inspired nanoelectronics**

Artificial intelligence is transforming our societies. Its development is supported by *deep learning* within artificial neural networks (ANNs). Most of them are virtual, but some so-called physical ones integrate nanomaterials or even molecules. Furthermore, an approach inspired by the functioning of the brain, called neuromorphic, is being developed. It consumes less energy than traditional Von Neumann architectures because logic operations and memory sites are co-located (in-memory computing). The rise of neuromorphic computing therefore relies on non-volatile memories, among which RRAM (Resistive Random Access Memory) or memristors—artificial analogs of synapses—are key. Crossbar arrays of memristors have demonstrated their efficiency in complex recognition, classification or forecasting tasks and, more generally, the relevance of their integration into ANNs.[1] Vertical memristors are simply made of a layer of active material deposited between two electrodes. Bulk oxides such as HfO_2, Ta_2O_5 and, to a lesser extent, WO_3, are particularly studied in this context.

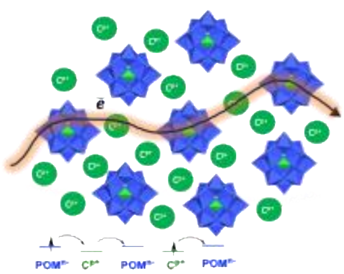
Molecular oxides combining the robustness and redox properties of oxides with the diversity of molecules at the nanometric scale, **polyoxometalates** (POMs) are natural candidates for the development of multi-sensitive molecular materials for neuromorphic nanoelectronics. They follow the general formula $[X_xM_mO_p]^{n-}$, for example $[PMo_{12}O_{40}]^{3-}$ or $[P_5W_{30}O_{110}]^{15-}$. In recent years, the E-POM group at IPCM has studied the electron transport properties of POMs in vertical molecular junctions[2–4] and has also explored their integration into *Reservoir Computing* (RC, a particular form of ANN where only the outer layer is trained).[5] However, their performance in lateral conduction devices is limited by the low conductivity of their films—a limitation shared with most molecular materials. To tackle this bottleneck and improve the performances of POM-based devices, we plan to exploit a unique feature of POMs: their polyanionic character and therefore the presence of counter-cations, by using counter-ions that are also redox-active as electron relays.

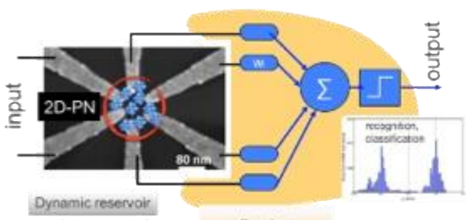
Research Objectives: because they are polyanions, associated to modular counter cations, POMs offer a unique opportunity:

- to figure out the effect of the cations (re)organization and mobility on the intimate mechanism of charge transport and resistive switching, particularly in vertical molecular junctions/memristors;
- to introduce new functionalities for multi-responsive materials;[3]
- to enhance the conductivity of POM-based molecular materials by using redox-active cations as electron relays. This will enlarge the scope of their applications from vertical to planar device configurations with multi-electrodes, such as that encountered in RCs.[6]



Electric measurements in a Vertica molecular junction





Scheme of a reservoir computing

Research activities

- Synthesis of functional cations;
- Design and electronic properties characterization of original POMs/cation combinations (molecular engineering) by various spectroscopic tools and electrochemistry;
- Fabrication of thin films;
- Thermal activation under electric field or photochemical conditions, electrical measurements of charge carrier mobility.

The ability to respond to multiple stimuli (redox, optical, pH change, etc.) is one of the great advantages of molecular materials for executing complex algorithms. They are also flexible, facilitating their integration into devices for the IoT (Internet of Things) and human–machine interaction, for example in the field of personal healthcare.

Candidate profile: we are looking for a highly motivated student, with a background in molecular chemistry, with skills in organic and inorganic synthesis, ready to be trained in the classical characterization methods of coordination chemistry and with an appetence to participate in the charge transport experiments, to be carried out in collaboration with physicists.

Applications, to be sent to anna.proust@sorbonne-universite.fr, copy to florence.volatron@sorbonne-universite.fr and guillaume.izzet@sorbonne-universite.fr, will include
- a CV with a cover letter outlining the candidate's research interests and the motivation for the project
- a transcript of M1 and M2 records together with a recommendation from the M2-intership supervisor

References

(1) Lanza, M.; Sebastian, A.; Lu, W. D.; Le Gallo, M.; Chang, M.-F.; Akinwande, D.; Puglisi, F. M.; Alshareef, H. N.; Liu, M.; Roldan, J. B. Memristive Technologies for Data Storage, Computation, Encryption, and Radio-Frequency Communication. *Science* **2022**, *376* (6597), eabj9979. https://doi.org/10.1126/science.abj9979.

(2) Volatron, F.; Izzet, G.; Vuillaume, D.; Proust, A. Unveiling Polyoxometalate Redox Properties at the Nanoscale. *Comptes Rendus. Chimie* **2024**, *27* (G1), 255–268. https://doi.org/10.5802/crchim.344.

(3) Huez, C.; Guérin, D.; Lenfant, S.; Volatron, F.; Calame, M.; Perrin, M. L.; Proust, A.; Vuillaume, D. Redox-Controlled Conductance of Polyoxometalate Molecular Junctions. *Nanoscale* **2022**, *14* (37), 13790–13800. https://doi.org/10.1039/D2NR03457C.

(4) Huez, C.; Renaudineau, S.; Volatron, F.; Proust, A.; Vuillaume, D. Experimental Observation of the Role of Countercations in Modulating the Electrical Conductance of Preyssler-Type Polyoxometalate Nanodevices. *Nanoscale* **2023**, *15* (25), 10634–10641. https://doi.org/10.1039/D3NR02035E.

(5) Huez, C.; Guérin, D.; Volatron, F.; Proust, A.; Vuillaume, D. Low-Frequency Noise in Nanoparticle–Molecule Networks and Implications for *in Materio* Reservoir Computing. *Nanoscale* **2024**, *16* (46), 21571–21581. https://doi.org/10.1039/D4NR02428A.

(6) Liang, X.; Tang, J.; Zhong, Y.; Gao, B.; Qian, H.; Wu, H. Physical Reservoir Computing with Emerging Electronics. *Nat Electron* **2024**, *7* (3), 193–206. https://doi.org/10.1038/s41928-024-01133-z.