

From Switchable Molecules to Multi-Level Memory Devices

A collaborative project between Rodrigue Lescouëzec, Sorbonne Université (Partner1)
& Pooi See Lee, Nanyang Technological University (Partner 2)

Switchable Molecules showing reversible changes in their physical properties through external stimuli are claimed as promising candidates for the design of molecule-based memories. In this context, Partner 1 has recently developed an attractive family of cubic molecules showing multiple (reversibly accessible) electronic states under external stimuli (pressure, temperature, light irradiation, electric field). This feature can be associated to drastic changes in the magnetic, dielectric or optical properties.¹⁻³ It can also be highly valuable for the design of multi-level memory devices, since transport properties through molecular junction are affected by the molecule electronic states. Progresses are now required for integrating these systems into prototype of devices in order to make decisive step toward an actual molecule-based nano-technology.

To this end, we propose to explore a strategy developed by Partner 1 and based on the electropolymerization of switchable cubic complexes (showing both controllable charge transfer and multiple accessible redox states) to obtain (ultra)thin switchable films deposited on conductive/transparent substrates (ca. 1 cm²). The thin films will be then inserted into two-electrode device configuration using the expertise of Partner 2.⁴⁻⁶ Different approaches mastered by partner 2 will be explored to deposit top electrodes onto the thin films: soft evaporation techniques, ink jet printing, etc. The electronic/transport characteristics of the devices will be investigated into standard conditions and under external stimuli (light, magnetic field) in close collaboration between P1 and P2 using facilities already accessible in both Universities.

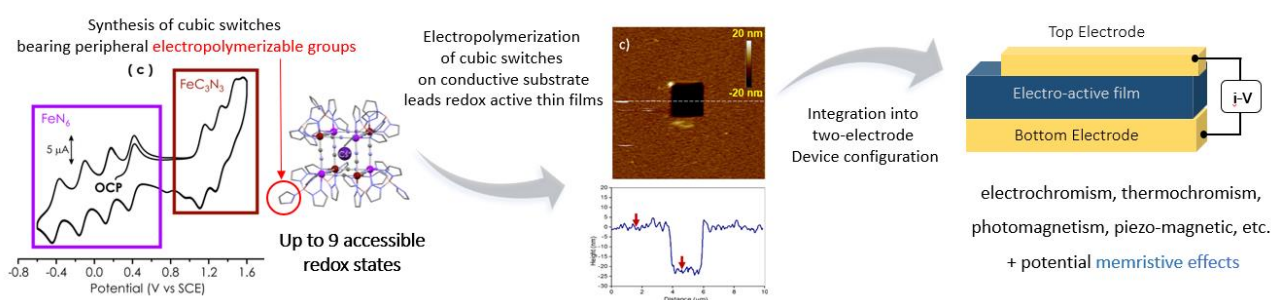


Figure 1. Firstly, cubic switches functionalized with peripheral electropolymerizable groups (thiophene, EDOT, etc.) are synthesized and characterized. They are then deposited onto conductive substrate (Pt, Au, ITO) by electropolymerization route using basic electrochemical cell set-up. The resulting thin-films are then integrated into two-electrodes devices by the methodologies already developed by P2 for various nanomaterials. Finally, their transport properties are investigated by P1 and P2. Different conductive regimes can be expected depending on the electronic states of the inserted cubic units of the thin films.

The simple soft chemistry approach based on the electropolymerization of cubic switchable molecules bearing peripheral electropolymerizable groups (EDOT) to lead responsive thin films contrasts with the vacuum evaporation methods that have been broadly applied on few switchable monometallic (spin-crossover) complexes and which lead to strongly isolating and fragile films that

make their integration into conductive devices challenging. Here, the resulting films that are reminiscent of those already used in actual electronic devices (polyEDOT like) will have conductive properties that will be adjustable by copolymerization techniques that have already been used by P2 . In a proof of concept, Partner 1 recently demonstrated that homogeneous ultra-thin films of controlled thickness (5-30 nm, a 10 μ m \times 10 μ m AFM image of a 20 nm thin film is shown in the center of Figure 1) can be obtained, maintaining both the redox flexibility and photo-switchable properties of the cubic switches.⁷ An iterative approach will be used in order to improve the materials responsiveness and its conductive properties.

We expect to observe (i) memristive effects similarly to those evidenced in seminal works on spin-crossover single-molecule junction, but in the present case, on prototype devices that are much closer to actual technological devices and thus more compatible with potential future application; (ii) multi-level memories (that are relevant for higher density data storage) due to the multiple accessible electronic states of the switchable cubic sub-units.

The consortium of this project gathers researchers with complementary skills. Rodrigue Lescouëzec is an expert in the design of molecular switches. In the recent years his group has developed a new family of switches which are robust, functionalizable and exhibit multiple accessible electronic states through external stimulation. His collaborative network at SU allows the design of ultra-thin films on different substrate. Pooi See Lee has a very strong expertise in the devices design. Her research interests include the design of pressure sensors, resistive switching memory devices, light emitting devices, energy devices, electrochromic devices, etc. She is using in her research a broad variety of inorganic (nano)materials and organic polymers, but more recently her interests has also turned toward the potentialities offered by molecular materials to reach original functionalities.

The Ph.D. candidate should have a background in chemistry or material science, and ideally a previous working experience in synthetic chemistry and some skills on the associated basic characterization tools. He/she should be curious and able to adapt to an interdisciplinary topic, which involves many interactions with colleagues/coworkers having different expertise fields.

- (1) Glatz, J.; Jiménez, J.-R.; Godeffroy, L.; von Bardeleben, H. J.; Fillaud, L.; Maisonhaute, E.; Li, Y.; Chamoreau, L.-M.; Lescouëzec, R. Enlightening the Alkali Ion Role in the Photomagnetic Effect of FeCo Prussian Blue Analogues. *J. Am. Chem. Soc.* **2022**, *144* (24), 10888–10901. <https://doi.org/10.1021/jacs.2c03421>.
- (2) Glatz, J.; Chamoreau, L.-M.; Flambard, A.; Meunier, J.-F.; Bousseksou, A.; Lescouëzec, R. Thermo- and Electro-Switchable Cs₂{Fe₄-Fe₄} Cubic Cage: Spin-Transition and Electrochromism. *Chem. Commun.* **2020**, *56* (74), 10950–10953. <https://doi.org/10.1039/D0CC04279J>.
- (3) Li, Y.; Benchohra, A.; Xu, B.; Baptiste, B.; Béneut, K.; Parisiades, P.; Delbes, L.; Soyer, A.; Boukheddaden, K.; Lescouëzec, R. Pressure-Induced Conversion of a Paramagnetic FeCo Complex into a Molecular Magnetic Switch with Tuneable Hysteresis. *Angew. Chem. Int. Ed.* **2020**, *59* (39), 17272–17276. <https://doi.org/10.1002/anie.202008051>.
- (4) Salles, R.; Poh, W. C.; Laurans, M.; Volatron, F.; Miche, A.; Alves, S.; Carino, C.; Tortech, L.; Izzet, G.; Lee, P. S.; Proust, A. Covalent Shaping of Polyoxometalate Molecular Films onto ITO Electrodes for Charge Trapping Induced Resistive Switching. *Inorg. Chem. Front.* **2024**, *11* (1), 255–268. <https://doi.org/10.1039/D3QI01761C>.
- (5) Shi, Q.; Wang, J.; Aziz, I.; Lee, P. S. Stretchable and Wearable Resistive Switching Random-Access Memory. *Advanced Intelligent Systems* **2020**, *2* (7), 2000007. <https://doi.org/10.1002/aisy.202000007>.
- (6) Lv, J.; Thangavel, G.; Lee, P. S. Reliability of Printed Stretchable Electronics Based on Nano/Micro Materials for Practical Applications. *Nanoscale* **2023**, *15* (2), 434–449. <https://doi.org/10.1039/D2NR04464A>.
- (7) Amina Benchohra. Magnetic Molecular Switches: From Their Synthesis to Their Integration into Hybrid (Nano)Materials, Sorbonne Université, Paris, 2019.