

Molecular Switches based on Inorganic Cubic systems (MOSAIC)

The emerging field of molecular electronics opens the possibility to code information on more than one byte thanks to the ability of molecules to store several electrons. In this context, the ERMMES (Equipe de Recherche en Magnétisme Moléculaire et Spectroscopie) team at IPCM (Institut Parisien de Chimie Moléculaire) is able to propose molecules that are organized as cubes (cf. figure 1). Each corner is occupied by a metallic center, the redox state of which can be changed, so that up to one octet could be stored on a single molecule.

MOSAIC aims at gathering the competences of the ERMMES team in inorganic synthesis and physical and molecular electrochemistry to those of our Indian partner on single molecule experiments (IISc Bangalore) to understand and evaluate the potential of molecular cubes for molecular electronic devices.

This project participates to the integration of Emmanuel Maisonhaute in the ERMMES team and at IPCM, and will boost our emerging collaboration with IISc (Indian Institute of Science, Bangalore).

General context and state of the art

Evaluation of electron transport properties of molecular structures is under increasing focus, the aim being to provide not only guidance for building efficient signal transduction for future bottom-up devices but also deep insights into chemical/electrochemical processes. Several experimental approaches are relevant in this field. Among them, transient spectroscopy has proven to be useful to initiate electron transfer between an acceptor A and a donor D separated by a bridge in a molecule. Replacing A or D by an electrode allows registering a current towards or from a redox center incorporated into the bridge by electrochemical techniques. Both of these two types of techniques afford rate constants, thus kinetic parameters of thermalized electron transfer. Furthermore, though in voltammetry the method is statistical, being performed onto a large number of molecular systems, only a single electron per molecule is transferred creating a permanent change in the molecule. Conversely, when both A and D are replaced by electrodes, a steady state current flows, hence a conductivity through the bridge can be estimated. Development of the mechanically controllable break junction technique (MCBJ) or those derived from scanning tunneling microscopy (STMBJ) have presently reached the single molecule limit of molecular conductance determination in the junction. In the case where a redox system is incorporated in the bridge itself, charge transport could become more complicated. Current modulation or rectification may depend on the redox state of the redox moiety.

Both teams provide very complementary skills that will be an excellent opportunity to impact the field of molecular electronics thanks to our new system and investigation tools.

On the one hand, the ERMMES team recruited Emmanuel Maisonhaute this year (official transfer in September 2024 but already present in the laboratory). His interests focus on developing novel instrumental approaches in physical chemistry and more specifically in electrochemistry.¹ Particularly, he is able to measure very rapid electron transfer kinetics of grafted molecules with home-made ultrafast potentiostats. Additionally, he already performed single molecule measurements onto electroactive systems, though playing only with one redox center.² On the other hand, the Kaliginedi team is internationally recognized for implementing single molecule measurements by the MCBJ and -EC-STMBJ technique.³ Of major interest, those may be performed under illumination.

Objectives and methodology

In this three years project, we wish to synthesize a family of cubes with different redox levels that could be triggered either electrically and/or photochemically. Electron transfer and photomagnetic properties will be studied by ultrafast cyclic voltammetry and SQUID in Paris, and conductance through single molecules will be realized in IISc Bangalore.

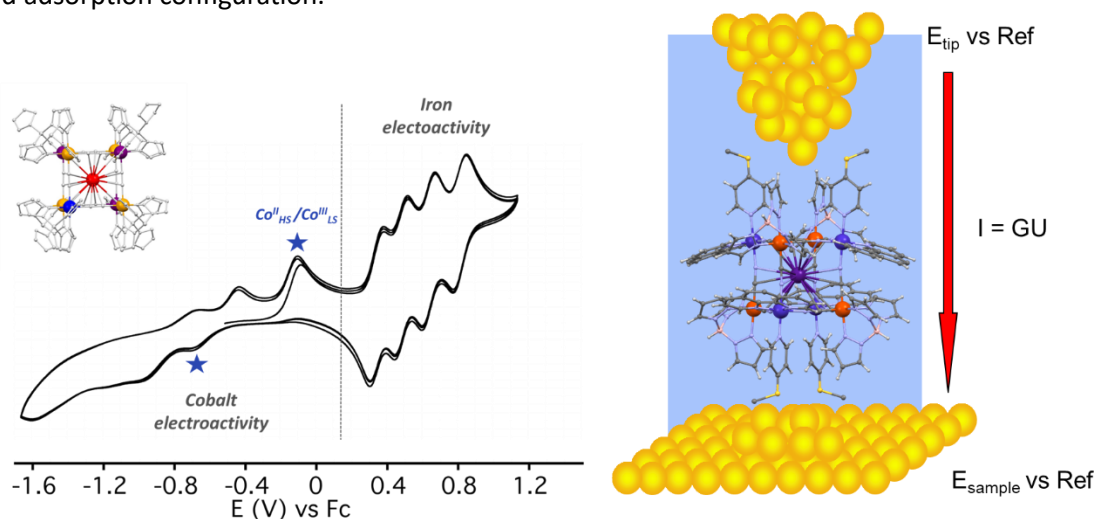
1) Tailored cubes through organic/inorganic synthesis

¹ Zhou, X.; Mao, B.; Amatore, C.; Compton, R.; Marignier, J.; Mostafavi, M.; Nierengarten, J.; **Maisonhaute, E.** Transient Electrochemistry: Beyond Simply Temporal Resolution. *Chem. Commun.* **2016**, 52 (2), 251–263. <https://doi.org/10.1039/c5cc07953e>

² Zhou, X.; Liu, L.; Fortgang, P.; Lefevre, A.; Serra-Muns, A.; Raouafi, N.; Amatore, C.; Mao, B.; Maisonhaute, E.; Schollhorn, B. Do Molecular Conductances Correlate with Electrochemical Rate Constants? Experimental Insights. *J. Am. Chem. Soc.* **2011**, 133 (19), 7509–7516

³ U. Rashid and V. Kaliginedi et al., Dithienylethene-Based Single Molecular Photothermal Linear Actuator *Angew. Chem* (2023), 135 (16), e202218767. U. Rashid and V. Kaliginedi et al., Chemistry of the Au–Thiol Interface through the Lens of Single-Molecule Flicker Noise Measurements *J. Am. Chem. Soc.* (2024), ASAP.

Synthesis of cubes is now well handled at ERMES, so that metals and ligands may be modulated according to specific purposes. Here, we will first synthesize a cube that bears 8 Fe^{II} centers. The ligands will bear pyridine, thiol or thiocetate groups for anchoring them on electrodes. Then a second cube bearing only 4 active Fe and 4 inactive Zn systems will be proposed as a comparison. Finally, we also expect interesting behaviour from a 4 Fe and 4 Co system. Indeed, electron transfer arising from the Fe centers are rather fast since they involve little structural reorganization, while those involving Co are rather slow because of the spin transition that induces important variations in metal/ligand distances. We underline that the advantage of our systems is that they will bear several rather rigid anchors, providing a single and thermodynamically favoured adsorption configuration.



Electrochemical response of a 4Fe-4Co cube and schematic of its insertion inside a STM Break Junction

2) Electrochemical and photomagnetic properties

Energy levels in molecules can easily be accessed through classical electrochemical measurements and are routinely performed in ERMES. More challenging, getting electron transfer rates necessitates to increase the scan rate in cyclic voltammetry, which can be achieved only through the use of ultramicroelectrodes. For adsorbed systems, a strategy that relies on gold balls electrodes allows to reach submicrosecond scales. By performing measurements at various temperatures, we will independently determine the reorganization energy and the electronic coupling for each of the 8 or 4 electron transfers. In a recent pioneer work, Lescouezec and Maisonhaute demonstrated that structural modifications are of prime importance for both electrochemical and magnetic properties.⁴ Therefore, we will also evaluate the photomagnetic response of our systems at low temperature as a way to probe intramolecular electron transfer properties.

3) Single molecule properties under illumination

At the single molecule level, the molecules will be trapped between two electrodes in MCBJ or STMBJs, and their conductance will be determined as a function of the voltage applied (under both electrochemical and non-electrochemical conditions). We expect to see important deviations from the Simmons model of electron transport each time the voltage reaches a new redox state of the molecule. Additionally, under illumination, electron transfer will be triggered within FeFe or FeCo pairs, thus modifying also the tunnel barrier between the two electrodes. We also plan to modulate the charge transport through these molecules by using combinations of external stimuli like light, electric field/electrochemical potential to achieve logic/memory operation at a single molecule level. Results under electrochemical conditions at the single molecule level will be compared to those resorting to transient electrochemistry performed on a large number of systems.

Therefore, we present a multidisciplinary project that mixes synthesis, advanced electrochemistry, magnetism and single molecule manipulation. Electrical and optical stimuli will be probe on an exceptional large range of energy levels, providing a strong potential for information storage. This project remains fundamental, but shows potential applied perspectives in the long term.

⁴ Enlightening the Alkali Ion Role in the Photomagnetic Effect of FeCo Prussian Blue Analogues. Glatz, J.; Jimenez, J.; Godeffroy, L.; von Bardeleben, H.; Fillaud, L.; Maisonhaute, E.; Li, Y.; Chamoreau, L.; Lescouezec, R. J. Am. Chem. Soc., 2022, 144, 10888.