

# PROGRAMME

2<sup>ème</sup> Journées Plénières du GDR NEMO

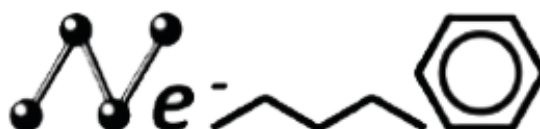
NEW MOLECULAR ELECTRONICS

16 – 18 Octobre 2023

IEMN, Université de Lille



GDR



New Molecular Electronics





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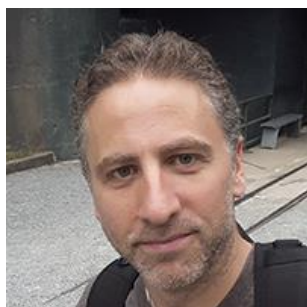
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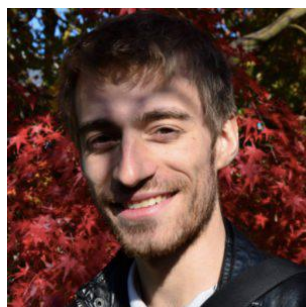
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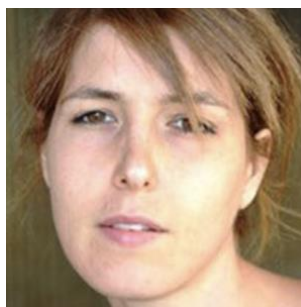
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**Axe 1 - Systèmes molécule unique, mémoires et switches**

**Dr. Rémy Pawlak**  
Université de Bale



**Dr. Guillaume Schull**  
CNRS / Université de Strasbourg



**Axe 2 - Jonctions à plus large échelle, mémoires et switches**

**Dr. Mathieu Gonidec**  
CNRS / Université de Bordeaux



**Axe 3 - Matériaux & Ingénierie moléculaire**

**Dr. Jeanne Crassous**  
CNRS / Université de Rennes



**Dr. Clément Merckling**  
IMEC / KU Leuven



**Axe 4 Transverse - Outils de caractérisation et de modélisation**

**Dr. Jérôme Cornil**  
Université de Mons



**Dr. Fabrice Charra**  
CEA / Université Paris Saclay



**Lundi 16 octobre 2023**

13h00		<b>Accueil</b>
13h30		<b>Introduction</b>
13h50	<b>Axe 1</b>	<b>Invité – Rémy Pawlack</b> <i>Probing charge-state, spin and vibrational excitations of radical molecules by low-temperature scanning probe microscopy</i>
14h30		<b>Lihao Guan</b> Conductance switch study of single-molecule junction Au-[Vio-C1]-Pt
14h50		<b>Linsai Chen</b> Spin filtering effects at graphene/molecules interfaces
15h10		<b>Session Poster</b>
16h10		<b>Pause café</b>
16h40	<b>Axe 1</b>	<b>Invité - Jeanne Crassous (en visio)</b> <i>Helicene: chiral platforms with fascinating spin-related properties</i>
17h20		<b>Vivien Andrieux</b> <i>Electron Responsive and Conductive Viologen-Based Supramolecular Gels</i>
17h40		<b>Mélodie Donnart</b> <i>Dual redox and magnetic molecular switches for molecular electronics</i>
18h00		<b>Florence Volatron</b> <i>Assemblies of polyoxometalates: periodicity and individualization</i>
18h20		<b>Cocktail</b>

**Mardi 17 octobre 2023**

09h00	<b>Axe 2</b>	<b>Invité - Mathieu Gonidec</b> <i>A coordination chemistry approach to functional molecular junctions: from switchable molecules to chiral systems</i>
09h40		<b>Kevin Dalla Francesca</b> <i>Fabrication of ferroelectric tunnel nano-junctions in P(VDF-TrFE)-thin layers with conductive-AFM control</i>
10h00		<b>Cécile Huez</b> <i>Polyoxometalate molecular junctions: unveiling the role the redox states and counterions on the electron transport properties.</i>
10h20		<b>Pause café</b>
10h50	<b>Axe 2</b>	<b>Imen Hnid</b> <i>Demonstration of terahertz molecular switches</i>
11h10		<b>Laurette Jerro</b> <i>Magnetic tunnel junctions based on photoswitchable Self-Assembled Monolayers</i>
11h30	<b>Axe 1</b>	<b>Invité – Guillaume Schull</b> <i>Sub-molecular fluorescence microscopy with STM</i>
12h10		<b>Déjeuner</b>

13h30	Axe 3	<b>Vincent Huc</b> <i>A new process for the synthesis of extended, 2D materials</i>
13h50		<b>Fatima Hussein</b> <i>Controlling the formation of organic nanostructures by supramolecular self-assembly and on-surface reactions</i>
14h10		<b>Sofia Frida Russi</b> <i>Electronically active ultra-thin films based on Fe<sub>4</sub>Co<sub>4</sub> cyanide cages</i>
14h30		<b>Invité - Clément Merckling</b> <i>Atomic scaling of CMOS devices: Status, Challenges &amp; Opportunities</i>
15h10		<b>Table Ronde</b>
16h10		<b>Pause café</b>
16h40	Axe 3	<b>Junlong Wang</b> <i>Towards the development of self-assembled monolayers with modulated polarization for the controlled detection of biomarkers</i>
17h00		<b>Nesrine Shaiek</b> <i>Two dimensional Metal-organic Frameworks at a metal surface</i>
17h20	Axe 4	<b>Invité – Jérôme Cornil</b> <i>Theoretical Design of Molecules for Functional Junctions</i>
18h00		<b>Alexander Smogunov</b> <i>Simulation de dynamique quantique de différents porteurs avec interactions dans des jonctions moléculaires</i>
18h20		<b>Fin des exposés</b>
19h00		<b>Diner au restaurant « à l'Assiette du Marché » à Lille</b>

## Mercredi 18 octobre 2023

09h00	Axe 4	<b>Invité – Fabrice Charra</b> <i>Optical functionalization of graphene by self-assembly of conjugated organic molecules.</i>
09h40		<b>Sergio Gonzalez-Casala</b> <i>A C-AFM &amp; SThM study on the thermoelectricity of Fe and Ru based organometallic molecular junctions</i>
10h00		<b>Frédéric Chérioux</b> <i>Unravelling the localization of counter-ions in ionic self-assemblies on a HOPG surface</i>
10h20		<b>Pause café</b>
10h50		<b>Visite des Plateformes de l'IEMN avec les responsables</b>
12h30		<b>Déjeuner</b>
13h30		<b>Réunion Chroniques</b>
16h00		<b>Clôture des deuxièmes journées plénières du GDR Nemo</b>





### **New organometallic molecular wires with thermoelectric and negative differential resistance properties**

Elodie Dureau, Olivier Galangau, Stéphane Rigaut, Karine Costuas, Jérôme Cornil, Dominique Vuillaume.

### **Impact of Molecular Adsorption on the Structural Properties of Several Atom Palladium Clusters**

Ahmed Hewail, Aimeric Ouvrard

### **Switching and in plane rotation of molecular assemblies of azobenzene derivative**

S. Godey, H. Therssen, D. Guérin, Y.J. Dappe, T. Mélin, S. Lenfant

### **Electronic transport of Prussian blue analogue nanocrystals measured by Conductive-AFM**

Hugo Therssen, Talal Mallah, Dominique Vuillaume, Thierry Mélin, Stéphane Lenfant

### **Electronic Structure at the Nanoscale of Molecularly Functionalized MoS<sub>2</sub> Monolayer.**

Kirill KONDRATENKO, Trung Nghia NGUYÊN LÊ, Mariem BEN YOUSSEF, Jean-Christophe LE BRETON, Imane ARBOUCH, Colin VAN DYCK, Jérôme CORNIL, Dominique VUILLAUME, and Bruno FABRE.

### **Ni-centered Coordination-Induced Spin-State Switching Triggered by Electrical Stimulations**

Shaymaa Al Shehimi, Orsola Baydoun, Lhoussain Khrouz, Sandrine Denis-Quanquin, Élise Dumont, Denis Frath, Floris Chevallier and Christophe Bucher

### **Nanometer-Thick Bilayers by Stepwise Electrochemical Reduction of Diazonium Compounds for Molecular Junctions**

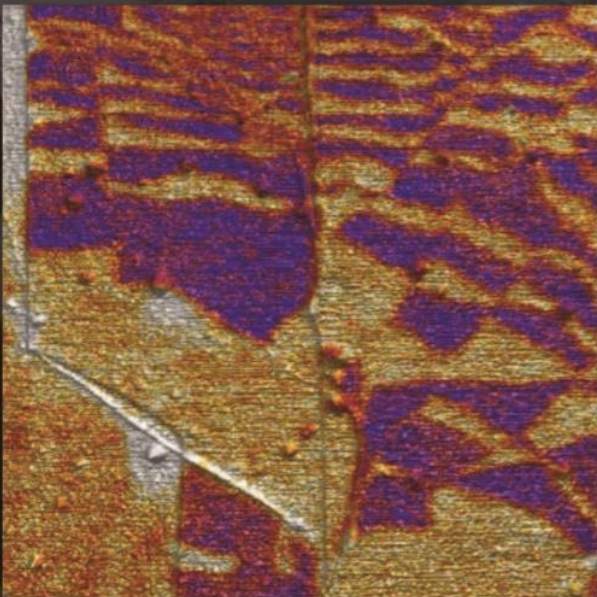
Mingyang Liu, Cecile Huez, Quyen Van Nguyen, Sebastien Bellynck, Philippe Decorse, Jean Christophe Lacroix, Pascal Martin



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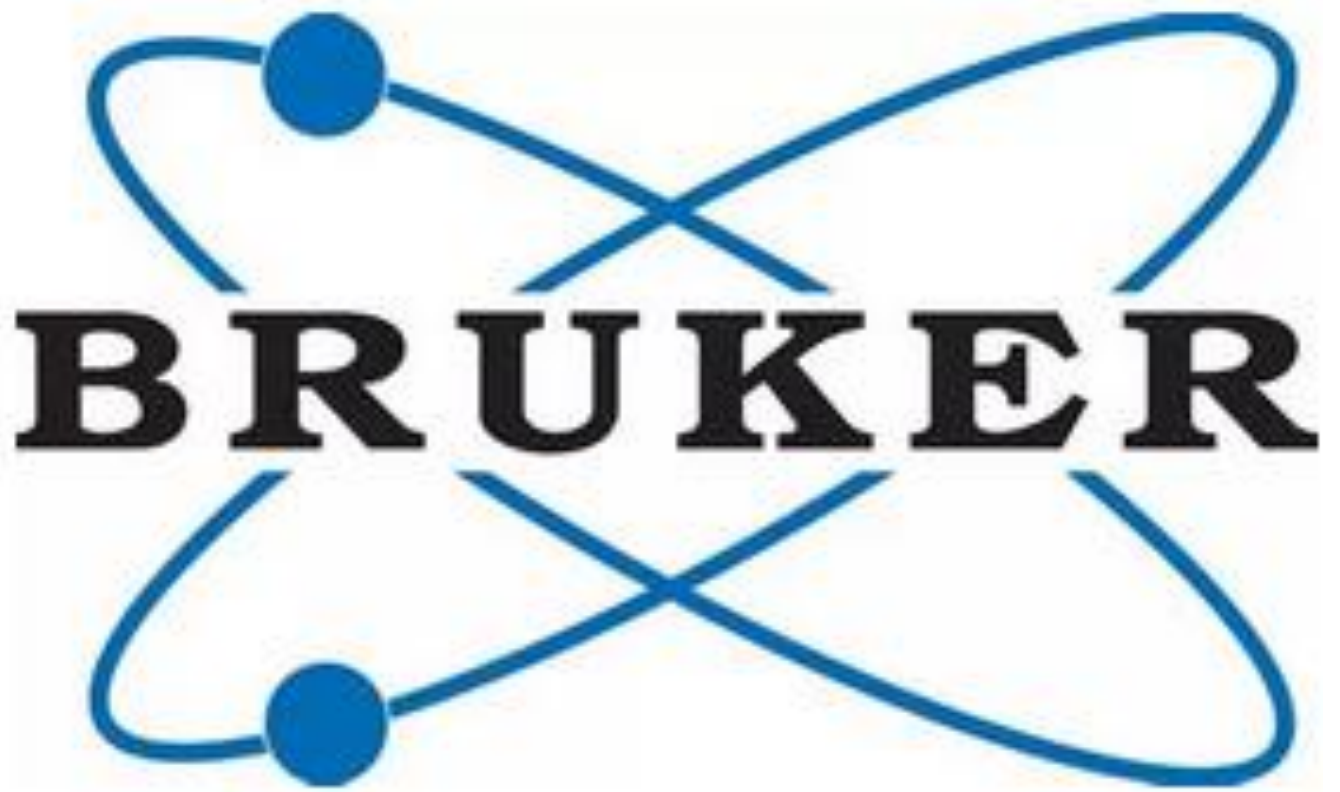


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## Probing charge-state, spin and vibrational excitations of radical molecules by low-temperature scanning probe microscopy

Rémy Pawlak

*University of Basel, Department of Physics, Klingelbergstrasse 82, 4056 Basel, Switzerland*

### Abstract:

Precise control of the charge state of molecules occupied by a single electron (spin) is crucial for their future applications in quantum information platforms. In this contribution, I will show the self-assembly on Ag(111) of tetrabromotetraazapyrene (TBTAP) molecules using scanning tunneling microscopy (STM) and atomic force microscopy (AFM) [1]. Due to their strong electron-accepting character, TBTAP molecules are able to trap an electron transferred from the substrate into an unoccupied molecular orbital. This electron induces a spin  $\frac{1}{2}$  molecular state confirmed by the detection of a Kondo resonance in tunneling spectroscopy ( $dI/dV$ ). Using the local electric field of the tip, we are also able to control the transition from the anionic state (TBTAP<sup>-</sup>) to its neutral counterpart (TBTAP<sup>0</sup>). This transition leads to vibrational excitation of the molecule (Figure 1), which is experimentally reflected by a series of peaks in the  $dI/dV$  spectra. By transferring this precursor to a superconducting Pb(111) surface, I will also show that anionic TBTAP molecules can form an extended two-dimensional electron spin lattice which carries topological edge states [2].

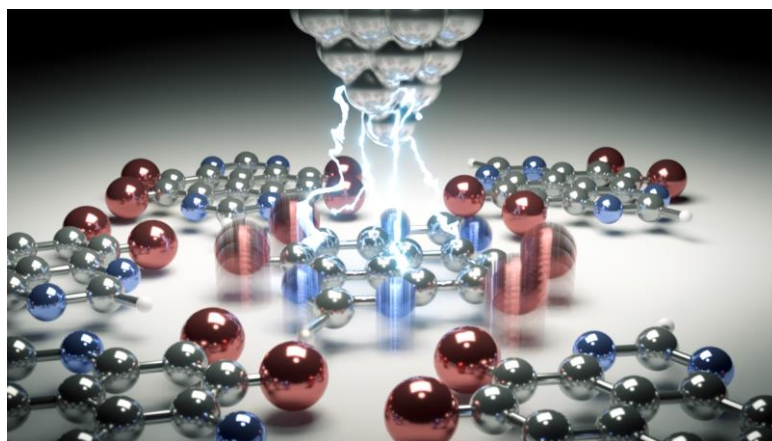


Figure 1 . Illustration of the vibrational excitation of a single molecule following its discharge triggered by the electric field of a STM tip [1].

### References:

- [1] C. Li, C. Kaspar, P. Zhou, J.C. Liu, O. .Chahib, T. Glatzel, R. Häner, U. Aschauer, S. Decurtins, S.-X. Liu, M. Thoss, E. Meyer, R. Pawlak, *Nat. Comm.*, accepted (2023).
- [2] J.-C. Liu, C. Li, H. Chen, C. Drechsel, P. Zhou, R. Häner, U. Aschauer, T. Glatzel, S. Decurtins, S.-X. Liu, D. Loss, J. Klinovaja, W. Wulfhekel, E. Meyer, R. Pawlak. submitted.

## Conductance switch study of single-molecule junction Au-[Vio-C1]-Pt

Lihao Guan, Xiaonan Sun,\* Sebastien Belynyck and Jean-Christophe Lacroix\*

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[lihao.guan@etu.u-paris.fr](mailto:lihao.guan@etu.u-paris.fr)

### Abstract:

The use of single molecules in molecular electronics aims to miniaturize the electronic devices in size and to lower the cost of current nanoelectronics or to develop low power consuming electronics. The formation and the conductance measurement of single-molecular junctions (SMJs) is of great interest to obtain resistive switches with high on/off ratio or to generate non-volatile memories.

Viologens are a set of well-known reversible redox active molecules. They can thus be used as switching building blocks in molecular junctions. In this work, the methyl-viologen (Vio-C1) molecule is connected between two metal electrodes to form the SMJ and the conductance and molecule switch was studied (Figure A). Vio-C1 can be reduced and oxidized stepwise reversibly at around -0.4 and -0.8 V (vs. SCE) with three states ( $V^{2+}$ ,  $V^+$  and  $V^0$ ), respectively.<sup>1</sup> Due to the aniline group, this molecule can be grafted on the gold substrate by a stable covalent gold-nitrogen affinity according to the electrochemical diazonium reduction.<sup>2,3</sup>

By using STM, the SMJ Au-[Vio-C1]-Pt was built by using a Pt tip. Two distinct conductance values  $LC = 4 \pm 1 \times 10^{-4} G_0$  and  $MC = 3 \pm 1 \times 10^{-3} G_0$  are measured by STM break junction technique. LC is attributed to  $V^{2+}$  and MC to  $V^+$ , respectively. Furthermore, long  $I(t)$  curves show stable conductance (G) values corresponding to the G value from STM-bj and the long stability is sufficient for  $I(V)$  measurements. Most importantly, the obtained  $I(V)$  curve shows electric field induced conductance switch (between LC and MC) and hysteresis loop is observed. In the hysteresis loop, the conductance

at 0.2V is calculated to be  $2.6 \times 10^{-4} G_0$  and  $4.3 \times 10^{-3} G_0$  corresponding to the LC and MC, respectively. This conductance switch can be repeated in the same SMJ showing clear ON/OFF behavior.

Therefore, the non-volatile memory effect is achieved at the single-molecule level. This switchable SMJ system is expected to be applied in molecular electronics.

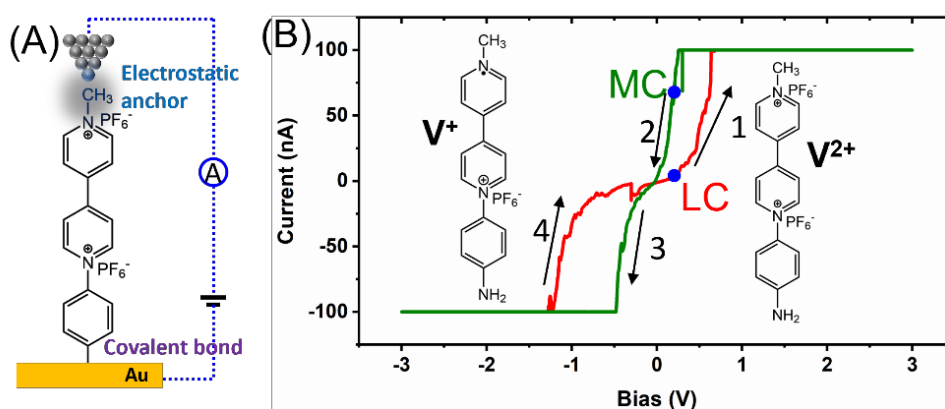


Figure. (A) Scheme of Au-[Vio-C1]-Pt SMJ. (B) Typical  $I(V)$  curve sweep between -3~3V. Inset: molecule structure in MC (left) and LC (right) state.

### References:

1. Nguyen, V. Q.; Martin, P.; Frath, D.; Rocca, M. L. D.; Lafolet, F.; Bellinck, S.; Lafarge, F.; Lacroix J.C., *J. Am. Chem. Soc.* **2018**, 140, 10131-10134.
2. Hnid, I.; Frath, D.; Lafolet, F.; Sun, X.; Lacroix, J.-C., *J. Am. Chem. Soc.* **2020**, 142 (17), 7732-7736.
3. Yao, X.; Sun, X.; Lafolet, F.; Lacroix, J.-C., *Nano Letters* **2020**, 20 (9), 6899-6907.

## Spin filtering effects at graphene/molecules interfaces

L. Chen<sup>3,1</sup>, A. Droghetti<sup>2</sup>, B. Dlubak<sup>4</sup>, P. Martin<sup>3</sup>, R. Mattana<sup>4</sup>, P. Seneor<sup>4</sup> and C. Barraud<sup>1</sup>,

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We present a bias-controlled spin-filtering mechanism in spin-valves including a hybrid organic chain/graphene interface [1]. Wet growth conditions of oligomeric molecular chains would usually lead, during standard CMOS-compatible fabrication processes, to the quenching of spintronics properties of metallic spin source due to oxidation. We demonstrate by X-ray photoelectron spectroscopy that the use of a protective graphene layer fully preserves the metallic character of the ferromagnetic surface and thus its capability to deliver spin polarized currents. We focus here on a small aromatic chain of controllable lengths, formed by nitrobenzene monomers and derived from the commercial 4-nitrobenzene diazonium tetrafluoroborate, covalently attached to the graphene passivated spin sources thanks to electroreduction. A unique bias dependent switch of the spin signal is then observed in complete spin valve devices, from minority to majority spin 84 ABSTRACTS carriers filtering. First-principles calculations are used to highlight the key role played by the spin-dependent hybridization of electronic states present at the different interface [2].

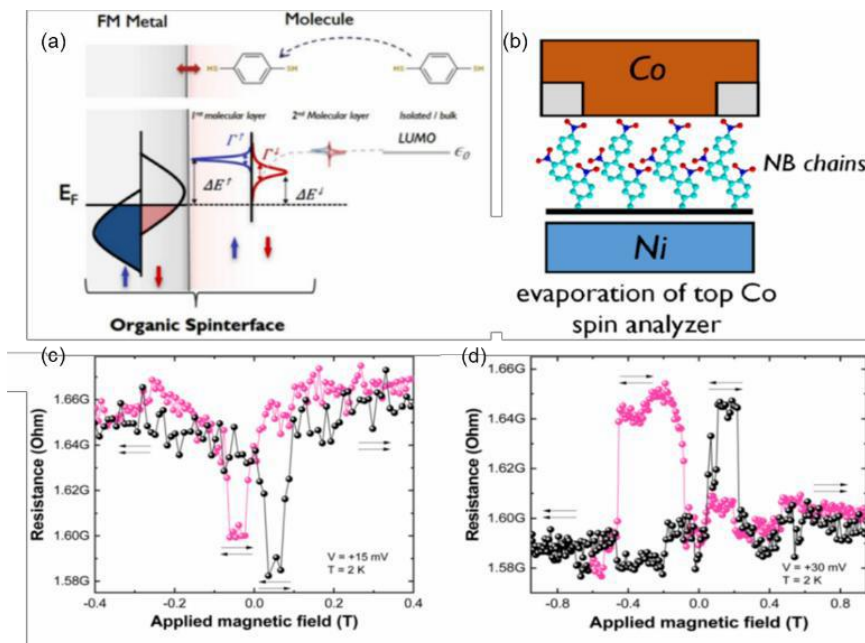


Figure: a). Schematic explaining the hybridization between a ferromagnetic surface and a molecular orbital. b). Schematics of the molecular magnetic junction. c) and d). Magnetoresistive signals measured in Ni/graphene/molecule/Co magnetic junctions.

### References

[1] P. Martin et al., *Nanoscale* **14** (2022) 12692-12702. [2] P. Martin et al., *Adv. Quant. Tech* **5** (2022) 2100166.

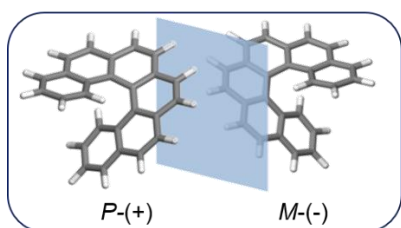
## Helicenes: Chiral Platforms with Fascinating Spin-Related Properties

Jeanne Crassous

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*Ortho*-fused aromatic rings form helically shaped chiral molecules such as carbo[6]helicenes, that wind in a left-handed (*M*) or a right-handed (*P*) sense.<sup>1</sup> The helical topology combined with extended  $\pi$ -conjugation provides helicenes with peculiar properties such as strong photophysical and chiroptical properties (high optical rotation values, intense electronic circular dichroism and circularly polarized emission). The molecular engineering of helicenes using organometallic and heteroaromatic chemistries offers a convenient way to tune the properties of these helically shaped  $\pi$ -ligands. Indeed, their combination with metallic or organic assembling units leads to chiral materials with appealing properties (circularly polarized phosphorescence, magnetochirality, spin selectivity) for applications in materials science (Circularly Polarized OLEDs, Chiroptical Switches, Spintronics). I will present a set of representative examples.<sup>2</sup>



- **Strong circular dichroism**
- **Circularly polarized emission**
- **Chiral-induced spin selectivity**
- **Magnetochirality**

### References :

1) a) C. -F. Chen, Y. Shen, *Helicenes Chemistry: From Synthesis to Applications*. Springer, Berlin, **2017**; b) M. Gingras, *Chem. Soc. Rev.* **2013**, *42*, 1051; c) K. Dhbaibi, L. Favereau, J. Crassous *Chem. Rev.* **2019**, *119*, 8846; d) J. Crassous, I. G. Stará, I. Starý (Eds) *Helicenes - Synthesis, Properties and Applications*. Wiley, **2022**.

2) a) E. S. Gauthier, L. Abella, N. Hellou, B. Darquié, E. Caytan, T. Roisnel, N. Vanthuyne, L. Favereau, M. Srebro-Hooper, J. A. G. Williams, J. Autschbach, J. Crassous, *Angew. Chem. Int. Ed.* **2020**, *59*, 8394; b) K. Dhbaibi, L. Abella, S. Meunier-Della-Gatta, T. Roisnel, N. Vanthuyne, B. Jamoussi, G. Pieters, B. Racine, E. Quesnel, J. Autschbach, J. Crassous, L. Favereau, *Chem. Sci.* **2021**, *12*, 5522; c) M. Atzori, K. Dhbaibi, H. Douib, M. Grasser, V. Dorcet, I. Breslavetz, K. Paillot, O. Cador, G. L. J. A. Rikken, B. Le Guennic, J. Crassous, F. Pointillart, C. Train, *J. Am. Chem. Soc.* **2021**, *143*, 2671; d) R. Rodríguez, C. Naranjo, A. Kumar, P. Matozzo, T.-K. Das, Q. Zhu, N. Vanthuyne, R. Gómez, R. Naaman, L. Sánchez, J. Crassous, *J. Am. Chem. Soc.* **2022**, *144*, 7709 ; e) K. Dhbaibi, M. Grasser, H. Douib, V. Dorcet, O. Cador, N. Vanthuyne, F. Riobé, O. Maury, S. Guy, Amina Bensalah-Ledoux, B. Baguenard, Geert L. J. A. Rikken, C. Train, B. Le Guennic, M. Atzori, F. Pointillart, J. Crassous, *Angew. Chem. Int. Ed.* **2023**, *62*, e202215558.

## Electron Responsive and Conductive Viologen-Based Supramolecular Gels

Vivien Andrieux,<sup>a</sup> Julien Bauland,<sup>b</sup> Thibaut Divoux,<sup>b</sup> Sébastien Manneville,<sup>b</sup> Floris Chevallier,<sup>a</sup>

Thomas Gibaud,<sup>b</sup> Denis Frath,<sup>a</sup> Christophe Bucher<sup>a</sup>

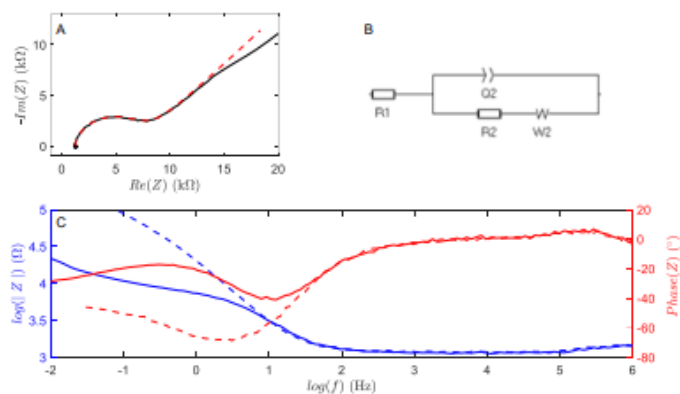
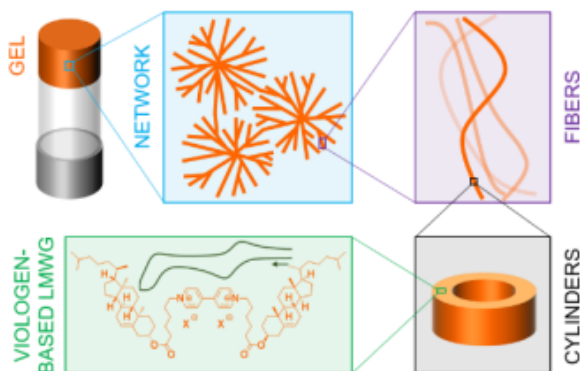
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### Abstract:

The incorporation of photo/redox-active units based on N,N'-disubstituted 4,4'-bispyridinium salts, commonly known as viologens, in the structure of supramolecular assemblies has been shown to confer interesting electron-accepting and photo/electrochromic properties to the materials. These responsive units have already been used as key elements for the development of electrochromic devices, molecular machines and organic batteries. Recently, there has been a renewed interest in the use of viologens as redox-responsive components in molecular junctions showing great promises for uses as conductive material in molecular and organic electronics.<sup>[1]</sup> Our research efforts in this field have led us to focus on molecular and supramolecular architectures involving viologens as key electron-responsive building elements. In particular, we have developed different strategies allowing to exploit the ability of viologen derivatives to form  $\pi$ -dimers in their reduced state to achieve a remote control over their organization within supramolecular assemblies. Among our recent achievements, we have reported a sol/gel transition triggered by light-irradiation of a viologen-based coordination polymer formed in the presence of palladium ions.<sup>[2]</sup> We now report the synthesis and detailed characterizations of supramolecular gels obtained by self-assembly of a dicationic low molecular weight gelator based on viologen. These molecules have been shown to self-assemble in pentanol to form chiral hollow core-shell cylinders eventually yielding dendritic clusters inducing gelation. We also showed that the optical, rheological and electrical properties of the gels can be tuned by addition of ionic additives. Careful control of the formation of charge-transfer complexes between viologens and iodides have led to a robust, transparent, conductive and chiral gel.<sup>[3]</sup> Properties of this responsive material can be modulated when submitting it to electrical or light stimulation.



### References:

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## Dual redox and magnetic molecular switches for molecular electronics

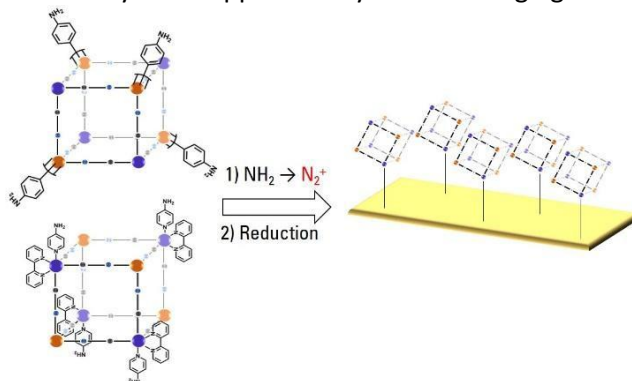
Mélodie Donnat<sup>a</sup>, Volodymyr Malytskyi<sup>a</sup>, Rodrigue Lescouëzec<sup>a</sup>

<sup>a</sup> Institut Parisien de Chimie Moléculaire, CNRS UMR 8232, Sorbonne Université, 4 place Jussieu, 75252 Paris

### Abstract:

Prussian Blue Analogues (PBAs) are three-dimensional inorganic polymers known to showcase interesting electronic properties, such as electrochromism and photomagnetism. Recently, molecular models of PBAs have been developed, granting more control over their electronic properties and a greater scope of applications thanks to their stability in solution. Our group has focused its work on such molecular models, synthesizing multiple types of octametallic cubic complexes of general formula  $A^+ \{ [M(L)(CN)_3]_4 [M'(L')]_4 \}$ . M and M' are metal ions (Fe, Co, Ni, Mn) in a +II/+III oxidation state, usually capped by scorpionate ligands (eg. tris-pyrazolylborate (Tp<sup>-</sup>) or tris-pyrazolylmethane (Tpm) derivatives) and linked by cyanide bridges, forming the cubic cage in which an alkali cation A<sup>+</sup> can be inserted.<sup>1</sup> The cyanide bridges facilitate the electronic communication between the metal centres, giving rise to interesting magnetic and redox properties, such as ETCST (Electron-Transfer Coupled Spin-Transition), multiple accessible redox states or electrochromism<sup>2</sup>. Furthermore, the rational choice of metal, ligand and cation allows to finely tune the electronic properties of the cubes.

Recently, our group has been interested in incorporating new ancillary functions on the capping ligands, allowing us to move toward the cubes' integration into devices. One promising way is diazonium (N<sup>+</sup>) grafting on conductive surfaces, with the aim of maintaining both the redox and magnetic properties of the grafted cubes. To do so, multiple synthetic pathways are being explored. On the one hand, we are developing new types of scorpionate ligands bearing an amino or nitro moiety, which can be readily transformed into diazonium. However, such syntheses proved to be challenging due to their low stability. On the other hand, we have synthesized a new family of cubes bearing a monodentate (eg. 4-aminopyridine) and a bidentate (eg. 2,2'-bipyridine or 1,10-phenanthroline) ligand instead of a scorpionate. Bypassing the scorpionate allows us to use simpler ligands, and to mix and match them to fine-tune the ligand field on the M' metal ion while preserving an amino moiety. Both approaches yield encouraging results.



Two approaches to diazonium grafting of cubes on conductive surfaces

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## Assemblies of polyoxometalates: periodicity and individualization

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Guillaume Izzet,<sup>a</sup> David Kreher,<sup>b</sup> Imad Arfaoui<sup>c</sup>

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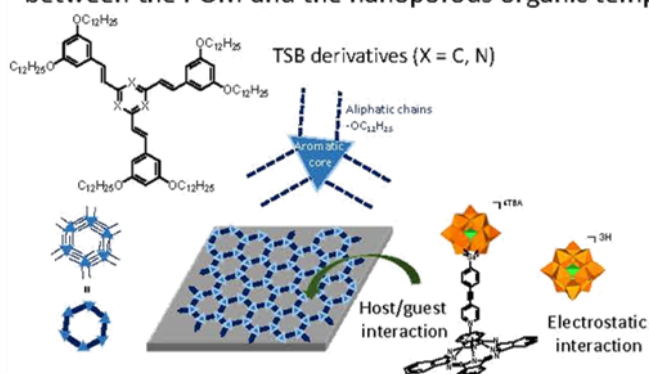
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<sup>c</sup>De la molécule aux nano-objets : réactivité, interactions et spectroscopies (MONARIS), CNRS, Sorbonne Université, 4 place Jussieu, 75005, Paris.

### Abstract:

Polyoxometalates (POMs) are oxo-clusters formed by early transition metals in their highest oxidation state (general formula  $\{X_pM_xO_y\}^{m-}$  with  $M = W^{VI}, Mo^{VI}, V^V, \dots$ ;  $X = \emptyset, P^V, Si^{IV}, Al^{III}, \dots$ ). They have been studied for decades in a large panel of applications in catalysis, biology, medicine, energy storage, information storage... In particular, they display remarkable redox and magnetic properties that have retained attention in the molecular electronics and spintronics fields.<sup>1</sup> Constituted by metallic atoms with empty d-orbitals, they are easily reduced and have the ability to switch their redox state under electrical or even optical stimuli. Transition metals can also be part of the structure and induce two stable magnetic states, switchable by a magnetic field. Those robust nanometer-sized molecules have thus been thoroughly studied these last two decades, to be integrated into molecular electronic devices and study their properties at the metal-molecule interface. A wide diversity of systems has been described, from thick films, more sophisticated monolayers, to the ultimate individualized POMs (random deposition from ultra-diluted solutions, break-junctions).<sup>2</sup> However, one approach is still missing: a periodical organization of individualized POMs on the substrate to i) control the density in the 2D assembly ii) facilitate the addressing of the single molecules. This is probably due to the difficulty to manipulate individually the polyanions that tend to aggregate by cation exchange. In this presentation we will present our last results about the periodical organization of individualized POMs of the Keggin family using nanoporous organic templates based on tristilbene derivatives self-assembled on HOPG.<sup>3</sup> We have explored several modes of interaction between the POM and the nanoporous organic template: i) host/guest interaction, which implies the



use of a hybrid POM bearing a pendant anchoring group to drive their insertion into the pores and ii) electrostatic interaction, which imposes chemical modification of the organic template to allow cation exchange with the POM.<sup>4</sup>

*Scheme of the tristilbene derivatives, their self-assembly on HOPG and the strategies adopted to periodically individualize Keggin-type polyoxometalates.*

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## A coordination chemistry approach to functional molecular junctions: from switchable molecules to chiral systems

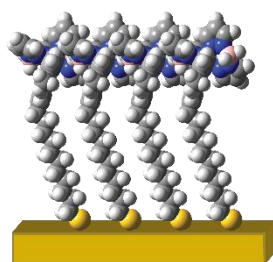
Rebecca Rodrigues de Miranda,<sup>a</sup> Margaux Pénicaud,<sup>a</sup>  
Lorenzo Poggini,<sup>a,b</sup> Mathieu Gonidec<sup>a</sup> and Patrick Rosa<sup>a</sup>

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### Abstract:

Molecular junctions have been a big focus in our community for decades, and the extensive work over the years has allowed to derive a good understanding of most of the fundamental aspects governing charge transport in or across molecular thin films and monolayers. Coordination chemistry is a great tool to allow to alter almost at will the electronic structure of molecular systems. While this allows to design interesting switching molecules, it can also be used as a tool to prepare series of isostructural systems for the study of behavioral trends across rational series of compounds. Over the last few years, our group has been working to implement molecular junctions based on Spin-crossover (SCO) compounds, a class of coordination compounds exhibiting reversible spin state switching, which are targets of high interest for the development of switchable molecular electronic and spintronic devices. For “simplicity” reasons, our journey started initially with sublimated thin films of SCO, which allowed us to demonstrate that it is possible to maintain the reversible temperature-driven spin crossover at the nanoscale in junctions. As expected, we could show that upon SCO, the reconfiguration of the electronic structure induces significant changes in the current density flowing through the junction. More recently, we have designed a series of stable self-assembled monolayers based on Fe(II) compounds on coinage metals that exhibit reversible temperature-driven SCO, and even some photo-switching activity. Those results open a whole panel of experiments to test them in vertical junctions or break-junctions, with interesting prospects in molecular spintronics. As a final opening perspective, in this presentation, we will also outline how we plan to implement a coordination chemistry approach to the study of one of the hot topics of the moment, the CISS effect.



**Figure 1** Self-assembled mono-layer of  $[Fe(H_2B(pz)_2)_2(bipy-alkanethiol)]$  on  $Au^{TS}$

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## Fabrication of ferroelectric tunnel nano-junctions in P(VDF-TrFE)-thin layers with conductive-AFM control

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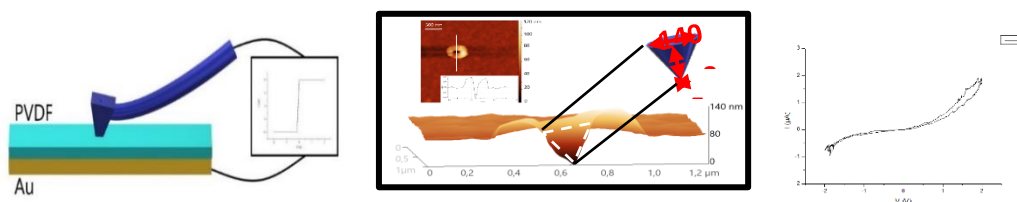
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### Abstract:

Start In the frame of the FEOrgSpin project (Ferroelectric control of organic/ferromagnetic spinterface) funded by the National French Research Agency (ANR), one of the objectives is to control the hybrid ferroelectric organic/ferromagnetic metal interface, as known as “spinterface”, for the development of future advanced data storage devices based on spin electronics. For example, the spin polarization of spinterface at the Fermi level can be different or even of opposite sign to that of the adjacent ferromagnetic electrode, annihilating the spin properties of the device.

Recently, we demonstrated the possibility of modulating the spin polarization at the poly(vinylidene fluoride) (PVDF)/Co interface by changing the direction of the ferroelectric polarization within the PVDF material [1]. We obtained important results regarding the surface morphology, the conduction properties as well as piezo-/ferroelectric behavior of these organic ferroelectric barrier layers by using different techniques/tools of Atomic Force Microscopy (AFM), such as piezoelectric force microscopy, for nanoscale investigation. Now, in order to optimize the parameters of spin transfer, it becomes necessary to develop nanometric-size organic tunnel junctions to improve the effects of both electroresistance (TER) [2] and magnetoresistance (TMR). The solution chosen consists in the development of tunnel nano-junctions indentation by the use of conductive-AFM probes (CT-AFM) [3]. Here the feedback control of the process is operated by the current measurement during indentation and allows for a sub-nanometer control of the thickness of the junction (Fig. 1)



**Figure 1.** (left) Schematic representation of the nano-indentation step using the CT-AFM technique. (center) AFM image showing the indented area. (right) Local I-V curve showing the evolution of the electrical properties of the nano-junction during indentation.

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## Polyoxometalate molecular junctions: unveiling the role the redox states and counterions on the electron transport properties.

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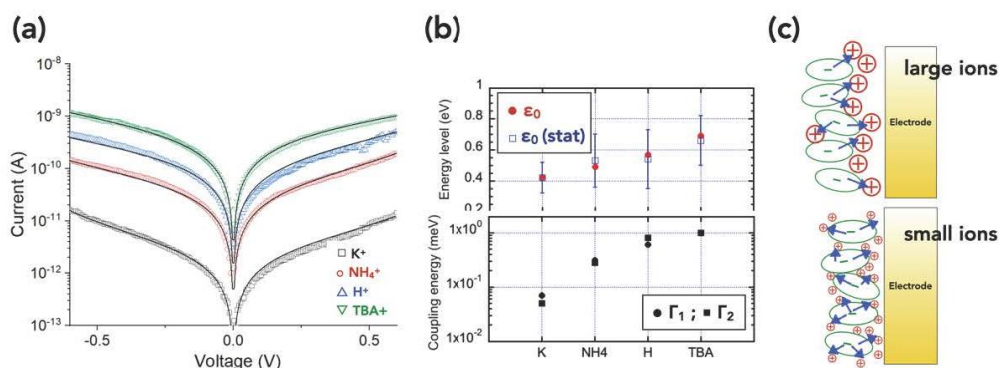
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Polyoxometalates (POMs) are nanometric molecular oxides with remarkable redox properties that can be explored in the context of advanced molecular devices (MDs). However, the precise relationship between the electrical conductance of the MDs, the redox state and the nature of the counterions remains to be clarified [1,2]. Here, we demonstrate the reversible in situ photoreduction of phosphomolybdate  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  monolayer self-assembled on Au electrodes. The conductance (C-AFM measurements) is increased by  $\sim 10$ , and the analysis of large current-voltage (I-V) datasets by unsupervised machine learning and clustering algorithms allows us to correlate this increase with the evolution of the I-V shape (symmetric vs. rectifying) and the energy of the molecular orbitals in the MDs: LUMO at 0.6-0.7 eV above  $\epsilon_F$  for  $\text{PMo}_{12}(\text{O})$  vs. SUMO at  $\sim 0.3$  eV for  $\text{PMo}_{12}(\text{I})$  [3]. This result also illustrates a rare example of a stable open-shell molecular junction at room temperature.

To unravel the role of counterions, we synthesized a series of Preyssler POMs  $[\text{NaCP}_5\text{W}_{30}\text{O}_{110}]^{14-}$  stabilized with four different counterions,  $\text{H}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$  and tetrabutylammonium ( $\text{N}(\text{C}_4\text{H}_9)_4^+$  or  $\text{TBA}^+$ ). The low-bias conductance gradually increases over two decades with changing the counterion in the order  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{H}^+$  and  $\text{TBA}^+$  (Fig. a). Albeit the LUMO of the  $\text{P}_5\text{W}_{30}$  (with respect of Au  $\epsilon_F$ ) increases from  $\sim 0.4$  eV to 0.7 eV, the electrode coupling energy evolves from  $\sim 0.05$  to 1 meV depending on the nature of the counterion in the order  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{H}^+$  and  $\text{TBA}^+$  (Fig. b) in correlation with the MD conductance [4]. We suggested that these variations could be due to a counterion-dependent POM/electrode interface dipole and a molecule/electrode hybridization mediated by the counterions (Fig. c). These non-trivial POM-counterion-metal electrode interactions clearly require further theoretical studies to elucidate the influence of the counterions on the electron transport properties of POM-based molecular devices.



(a) Mean current-voltage curves and fits (solid lines) of the SEL (single energy level) model. (b) Energetics of the molecular junction (LUMO position and electrode coupling energies). (c) Hypothesis on the organization of the molecules and ions at the electrode interface.

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## Demonstration of terahertz molecular switches

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### Abstract:

We study the electron transport properties under a terahertz (THz) irradiation of three molecules that consist of two conjugated systems, which are coupled through a non-conjugated linker. Due to this non-conjugation between them, each molecule can be seen as two weakly coupled sites in series and a resonant transport occurs only when the energy of the two sites are aligned leading to negative differential resistance (NDR) behaviors<sup>1</sup>. Moreover, it has been theoretically suggested that switching in such systems, between different current states in transport through molecules, is possible and may be triggered by a passing electromagnetic pulse in the THz range<sup>2</sup>. This mechanism relies on a THz-induced resonant electron transfer between the pair of neighboring subunits. As a consequence, the energy of the two sites are misaligned and therefore, the passage of current is turned off by the irradiation pulse and the NDR behaviors are eliminated.

Three molecules that differ by the spacer (phenyl vs. thiophene) and the anchor group (thiol vs. cyanide) were synthesized and corresponding SAMs were formed on very flat template-stripped gold electrodes (RMS<0.5nm). Solid-state molecular junctions (MJs), in which a C-AFM (Conducting- Atomic Force Microscopy) Pt/Ir tip is used as the top electrode, were formed. The electronic properties of the resulting MJs were investigated under an in-situ THz irradiation (30THz), and will be presented for the three molecules.

When the THz irradiation is OFF, NDR behaviors at the nanoscale (for few tens of molecules) were observed. To gain more insight into the origin of the NDR effect, we also investigated these molecules using density functional theory (DFT) and the non-equilibrium Green's function formalism (NEGF). The calculations reproduced well the observed experimental NDR behavior, which is explained by breaking the degeneracy of the HOMO and HOMO-1 levels under the effect of the applied voltage.

When the THz irradiation is ON, the junction is immediately switched and the NDR behaviors are completely suppressed. These phenomena were reproducibly and reversibly observed for all three molecular junctions, whatever the nature of the spacer and anchoring group, and will be presented and discussed.

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## Magnetic tunnel junctions based on photoswitchable Self-Assembled Monolayers

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### Abstract:

Magnetic tunnel junctions (MTJs) are known to be one of the main building blocks of spintronics. In these devices, the integration of molecular layers as tunnel barrier is envisioned as an opportunity to allow the engineering of spintronics at the molecular scale. Actually, thanks to the spin-dependent hybridization at ferromagnet/molecule interfaces, spin polarization and thus tunnel magnetoresistance can now be tailored by molecules [1]. However, up to now, only basic “passive” self-assembled monolayers (SAMs) such as alkane chain have been integrated into MTJs [2-3].

In this presentation, we will present molecular MTJs integrating “active” photoswitchable molecules of diarylethenes. These molecules can be switched by light between two stable states corresponding to an open and a closed form. After presenting the fabrication process of the molecular MTJs, we will show some characterization techniques (Raman, XPS, XAS) that validates the grafting protocol of the SAMs between the permalloy and the cobalt electrodes, avoiding any trace of its oxidization. We will then focus on transport results. We will show that we have been able to obtain the signature of a tunneling current passing through the SAMs. In addition, we have performed inelastic electron tunneling spectroscopy (IETS) in order to detect molecular vibrations inside the tunnel barrier. We will also show the first magnetoresistance curves (up to 50%) obtained with an “active” molecular barrier for both open and closed forms of diarylethenes. Lastly, the impact of molecular switching on MTJs properties has been investigated. Change of resistance and TMR sign have been observed. This type of device could be used to build multifunctional molecular spintronic devices electrically and/or optically controllable.

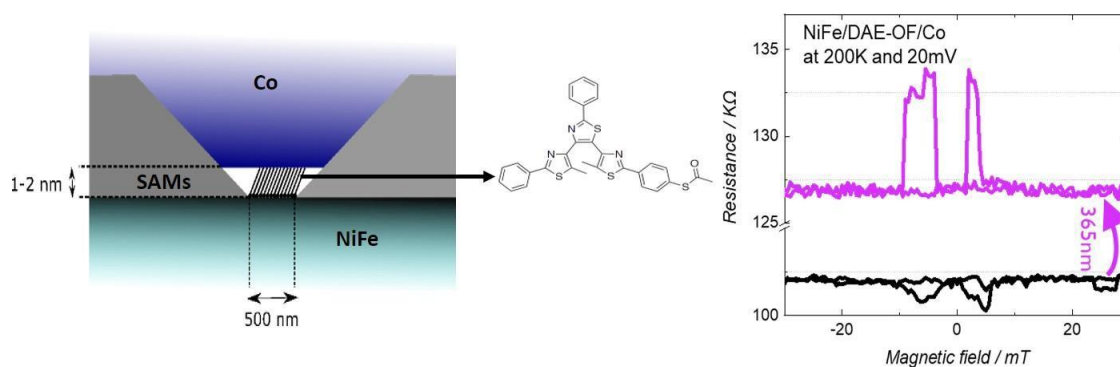


Figure 1. (left) Representation of the magnetic tunnel junction (MTJ) formed by two ferromagnetic electrodes of NiFe and Co separated by a self-assembled monolayer of diarylethenes. (Right) Magnetoresistance curves obtained before and after irradiation of the open form of diarylethenes.

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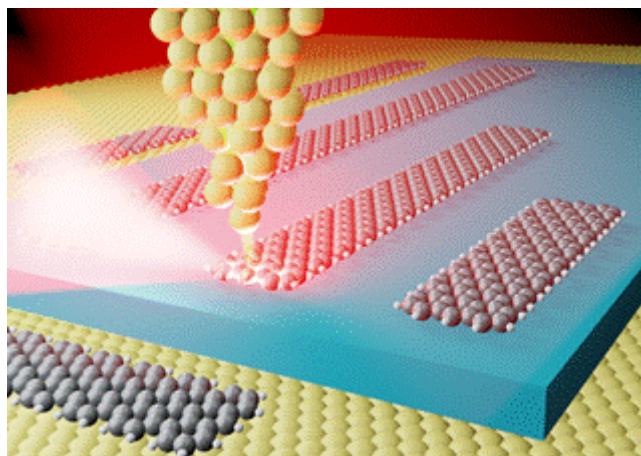
## Sub-molecular fluorescence microscopy with STM

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The electric current traversing the junction of a scanning tunneling microscope (STM) may lead to a local emission of light that can be used to generate sub-molecularly resolved fluorescence maps of individual molecules. Combined with spectral selection and time-correlated measurements, this hyper-resolved fluorescence microscopy approach allowed us to characterize the photonics properties of individual [1,2], or interacting molecules [3]. The presentation will describe the underlying mechanisms giving rise to sub-molecular resolution in STM-induced fluorescence [4, 5], and will discuss recent results obtained with this approach with graphene nanoribbons (GNRs) [6] and 2D materials [7].



*Exciting the fluorescence of dark states in GNRs with an STM.*

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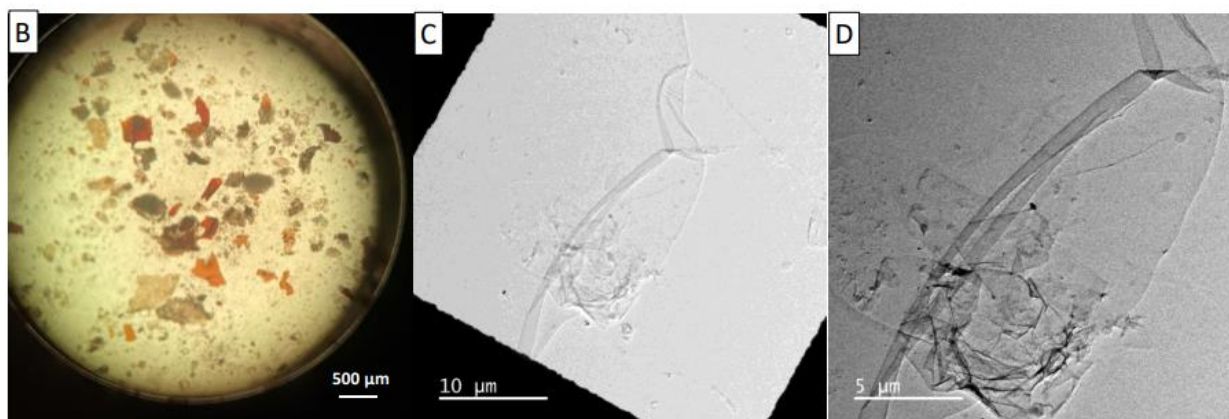
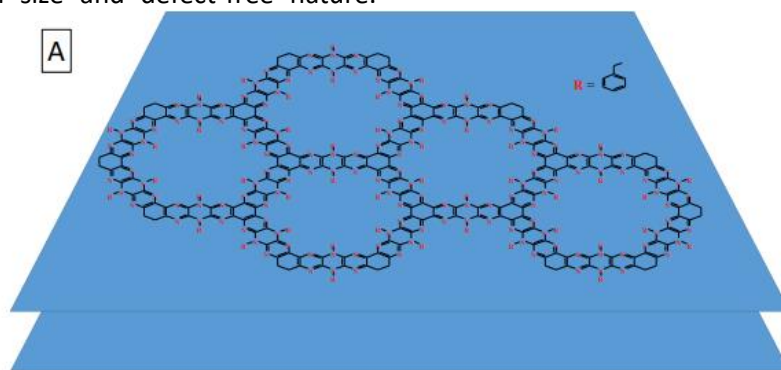


## A new process for the synthesis of extended, 2D materials

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### Abstract:

The first preparation of graphene by Geim and Novoselov in 2004 sparked an ever-increasing interest in 2D materials. Indeed, along with graphene, dichalcogenides such as MoS<sub>2</sub> or WS<sub>2</sub>, silicene, phosphorene, hexagonal boron nitride etc... are also being investigated all over the world, due to their fascinating physical and chemical properties. More recently, 2D COFs (Covalent Organic Frameworks), a family of 2D materials, has received a growing interest. These are obtained by assembling small molecular building units using the rich toolbox of molecular chemistry. We describe here a new process for the synthesis of very high quality 2D Covalent Organic Frameworks (COFs), such a C<sub>2</sub>N, CN and C<sub>4</sub>N<sub>3</sub> carbon nitrides. This wet process relies on the use of a metallic surface as both a reagent and a support for the coupling of small halogenated building blocks. The conditions of the assembly reaction are chosen so as to leave the inorganic salts by-products on the surface, to further confine the assembly reaction on the surface and increase the quality of the 2D layers. Very high quality flakes are obtained, in terms of lateral size and defect-free nature.



A)- the newly obtained C<sub>4</sub>N<sub>3</sub> carbon nitride; optical microscopy (B) and TEM observation (C and D) of C<sub>4</sub>N<sub>3</sub> flakes

### References:

A simple and efficient process for the synthesis of 2D carbon nitrides and related materials; Cora Moreira Da Silva et al. Scientific Reports | (2023) 13:15423 | <https://doi.org/10.1038/s41598-023-39899-5>. <https://cnrs.hal.science/hal-03874253/>

## Controlling the formation of organic nanostructures by supramolecular self-assembly and on-surface reactions

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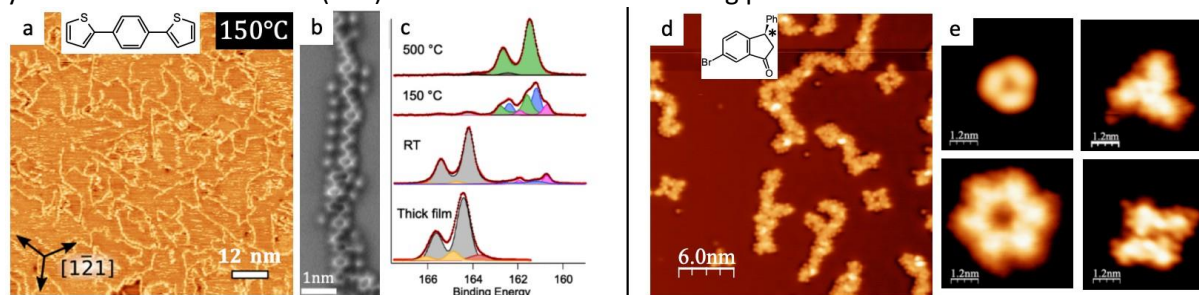
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The controlled formation of new objects at the nanoscale is an important challenge for the development of new materials and electronic devices. On surfaces, the formation of organic nanostructures is based on the concepts of supramolecular self-assembly and on-surface synthesis taking use respectively of non-covalent and covalent intermolecular interactions. The control of these nanostructures is affected by various factors and parameters such as the choice of the substrate used, thermal annealing, etc. In this work, we propose new strategies to control the formation of nanostructures on surfaces and investigate their properties. In a first part, we studied the polymerization of 1,4-di(thiophen-2-yl)benzene (DTB)<sup>[1]</sup> on Cu(111) under ultra-high vacuum (UHV) by STM and photoelectron spectroscopy (XPS), supplemented by non-contact atomic force microscopy (nc-AFM) and theoretical modelling based on the density functional theory (DFT). The results show the formation of unsaturated hydrocarbon chains based on C-S activation. Then, we demonstrated by STM and XPS under UHV that the use of the bifunctional chiral precursor (*R*)-6-bromo-3-phenyl-2,3-dihydro-1*H*-inden-1-one (BrPhINDO)<sup>[2]</sup> leads to the formation of different covalently bonded structures on Cu(111) with chiral inversion inducing partial racemization.



**Figure 1:** (a) RT-STM images revealing the on-surface reaction of DTB on Cu(111) after annealing at 150 °C. (b) High-resolution AFM images of the polymeric chains obtained after annealing at 130 °C. (c) XPS S2p core level spectra obtained after different annealing temperatures. (d) LT-STM images obtained after deposition of *R*-BrPhINDO molecule on hot Cu (111) surface ( $T_{Cu} = 100$  °C) and after annealing at 200 °C. (e) STM images of all observed isolated structures.

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## Electronically active ultra-thin films based on $\text{Fe}_4\text{Co}_4$ cyanide cages

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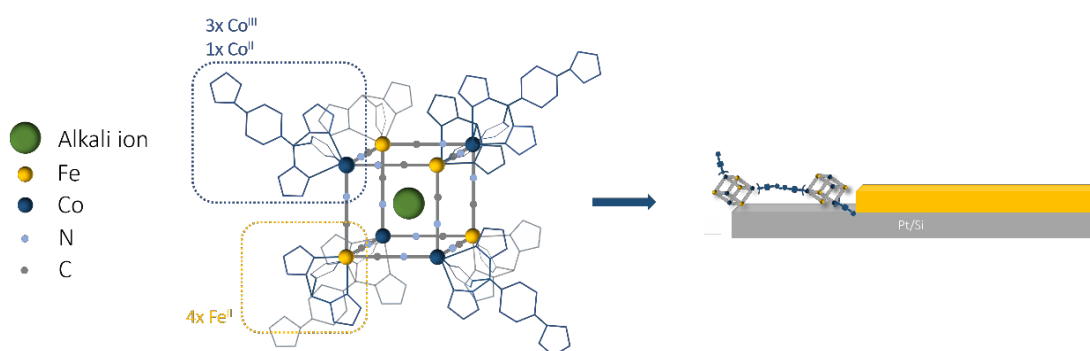
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Prussian blue analogues (PBAs) are well-known 3D inorganic polymers that have gained significant attention in the field of material science due to their tuneable electronic properties and nanoporosity. However, like many polymeric materials, PBAs often pose challenges due to their insolubility in organic solvents and difficulty in integration into microelectronic devices.

In this context, in order to overcome these problems, our group is working on molecular scale PBAs based on octametallal cages with cubic geometries,  $\text{Cs} \llbracket [\text{Fe}(\text{Tp})(\text{CN})_3]_4[\text{Co}(\text{R}^{\text{Tp}})]_4 \rrbracket$ , in which metal ions are connected through a cyanide bridge ( $\mu_2\text{-CN}^-$ ), and are blocked by capping ligands. The latter ensure the stability of the polymetallic complex and can be specifically designed to enable the use of the switches in molecular materials with the desired application<sup>1</sup>.

More specifically, we employed a modified  $\text{R}^{\text{Tp}}$  ligand that was functionalized with thiophene to design electropolymerizable cubic switches. The electropolymerization of these cages results in the creation of hybrid materials, where cubes are interconnected with thiophene oligomers. This wet-chemistry approach is characterized by its simplicity, obviating the need for expensive deposition techniques, while ensuring the controlled formation of thin films on various electrodes. Similar to the polymeric Fe-Co PBA parent compound, our system demonstrates switchable properties, featuring photo-induced metal-to-metal Electron Transfer Coupled to Spin Transition (ETCST). Furthermore, these compounds display noteworthy redox behaviour, showing up to nine accessible redox states<sup>2</sup>.



$\{\text{Fe}_4\text{Co}_4\}$  cages deposited through electropolymerization on Pt/Si.

<sup>1</sup> J. Jiménez, J. Glatz, A. Benchohra, G. Gontard, L. Chamoreau, J. Meunier, A. Bousseksou, R. Lescouëzec, *Angew. Chem. Int. Ed.* **2020**, 59, 8089–8093.

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## Atomic scaling of CMOS devices: Status, Challenges & Opportunities

Prof. Dr. Clement MERKCLING

*Imec & KU Leuven*

The Silicon semiconductor technology has been the main driver in the last 60 years in the advancement of our daily life. The development of electronics devices, sensors, automation, computers, cameras and smartphones based on this material will reach soon ultimate limits due to the continuous downscaling of the physical size of devices and wires to the nanometer scale. The miniaturization of circuits seems to have reached a possible halt, since transistors can only be shrunk down to a certain size and not further beyond. Thus, there is a pressing need to complement Si CMOS technology with new materials to fulfil the future computing requirements as well as the needs for diversification of applications.

In this framework, two-dimensional (2D) materials offer prospects of unprecedented advances in device performance at the sub-nanometer scale. Their amazing potential has proven to be a possible solution to overcome the limitations of silicon technology, where the combination of 2D materials with silicon chips promises to surpass the current technological limitations. With that vision, imec investigates their integration, in particular for beyond silicon CMOS and advanced memory technologies. However, many challenges still remain to unlock their incorporation into the Si-technology, especially the growth, the gate oxide and contact module at the source/drain area in a Field-Effect Transistor device. The quest towards 2D devices is today the main focus to boost current device performances.

## Towards the development of self-assembled monolayers with modulated polarization for the controlled detection of biomarkers

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### Abstract:

The specific detection of antibodies within biosensors based on antibody/antigen binding interactions has been the subject of numerous studies [1-3]. Among the different approaches, a promising functional ON/OFF system has been proposed based on the reversible modification of the conformation of a charged oligopeptide by the application of an electrical potential on the surface, thus making it possible to control the activity of the antigen [4]. On the other hand, triggering detection at a given time, and controlling on-demand the nature of the biomarker to be identified remain problematic. Indeed, this system can only respond to a single electrical stimulus, thus limiting its use to a single antibody/antigen pair. In order to overcome this scientific obstacle, we propose in this study to develop a system allowing the detection of the binding interaction of several antibody/antigen pairs within a single platform.

For this purpose, we are considering an original approach based on the use of “push-pull” chromophores in order to control the potential allowing the conformation of the oligopeptide to be switched between the OFF state (antibody-antigen interaction not allowed) and the ON state (interaction permitted). Push-pull molecules are composed of an attractor group and an electron donor group separated by a  $\pi$ -conjugated bridge. This particular structure gives them a modular electric dipole depending on the nature of the donor and attractor groups, and the  $\pi$ -conjugated bridge. The idea is to add push-pull chromophores presenting different polarizabilities - each one associated to a specific electrical potential value - between the surface and the oligopeptide supporting a given antigen, and to insert this active system within a matrix of an inert molecular compound of polyethylene glycol (PEG).

Therefore, in this work original uncharged push-pull (PP) chromophores comprising a thiol anchoring group were specifically synthesized and analyzed, and their self-assembled monolayers (SAMs) on a gold surface studied using various solvents. In parallel, we studied the formation of SAMs of thiol-terminated PEG (mPEG12-SH) as the host matrix, of 4KC cysteine oligopeptide, and various strategies to obtain isolated domains of 4KC & PP in the PEG matrix. We will present here the first results of grafting of the different compounds and the morphological analyzes using scanning probe microscopy (AFM/STM) and spectroscopy such as Surface Enhanced Raman Spectroscopy.

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## Two dimensional Metal-organic Frameworks at a metal surface

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Akreml<sup>c</sup> and M. Abel<sup>a</sup>

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### Abstract:

Two-dimensional materials (2D) are the favored appropriate material, which has attracted a great scientific interest, due to their several important and excellent electrical properties. In a similar way to the transition metal dichalcogenide materials, the combination of metal and organic species (preserving the pi-delocalization) allows to obtain not only a particular electronic structure of 2D materials but also unique magnetic properties. In this context, the new class of conductive

2D -MOF has emerged in 2009<sup>[1]</sup> and are particularly attractive because of their ability to form

stable 2D materials for application in spintronic (spinvalve ferrimagnet), superconductivity, or electrochemistry.

Herein the growth of 2D conductive MOF composed of Tetrahydroxy-1,4-benzoquinone (THBQ) and metal atoms of manganese and copper have been studied under UHV on Ag(111) substrate. The surface is studied by complementary methods of Scanning tunneling microscopy (STM), low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) to optimized the growth conditions (fluxes, temperatures...).

### References

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## Theoretical Design of Molecules for Functional Junctions"

Prof. Jérôme Cornil

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This lecture will illustrate how theoretical modelling can contribute to the design of functional molecular junctions. We will only consider here calculations performed at the quantum-chemical level using Density Functional Theory (DFT) coupled to the Non-Equilibrium Green's Function (NEGF) formalism since the DFT/NEGF method is widely used in the field of molecular electronics. We will start by describing the general principle of this methodology with a critical discussion of its limitations. We will then define some key theoretical concepts, in particular the factors controlling the shape of the transmission spectrum and by extension the I/V curves. In a next step, the DFT/NEGF approach will be applied to design molecules for specific functionalities (such as a diode behavior characterized by a high rectification ratio, molecular switches with high ON/Off ratio triggered by light or chemical reactions, magnetoresistance in presence of ferromagnetic electrodes,...). A key message that will be conveyed is that: (i) attaching molecules to electrodes in a strong coupling regime (i.e., by a strong orbital hybridization) can strongly perturb the intrinsic electronic properties of the isolated molecule, leading to situations where the impact of chemical modifications on isolated molecules is not recovered in the junction; (ii) cooperative effects based on electrostatic interactions in dense medium should also be accounted for in SAM-based junctions to rationalize experimental data.

## Simulation de dynamique quantique de différents porteurs avec interactions dans des jonctions moléculaires

Alexander Smogunov, Omar Lahrache (SPEC, CEA Saclay)

Nous développons une méthodologie générale pour modéliser la propagation et la dynamique quantique de différents porteurs, tels que des électrons ou des phonons, à travers des jonctions moléculaires. L'approche est basée sur des calculs DFT ("Density functional theory") effectués avec le code d'ondes planes Quantum-ESPRESSO et utilise en plus les codes Wannier90 et EPW pour extraire des paramètres nécessaires tels que des Hamiltoniens ou des matrices d'interactions. Cela nous permettra de construire un modèle efficace de type "liaisons fortes" à grande échelle pour simuler en suite une évolution des paquets d'onde en temps réel en utilisant soit directement l'équation de Schrödinger soit l'approche des polynômes de Chebyshev.

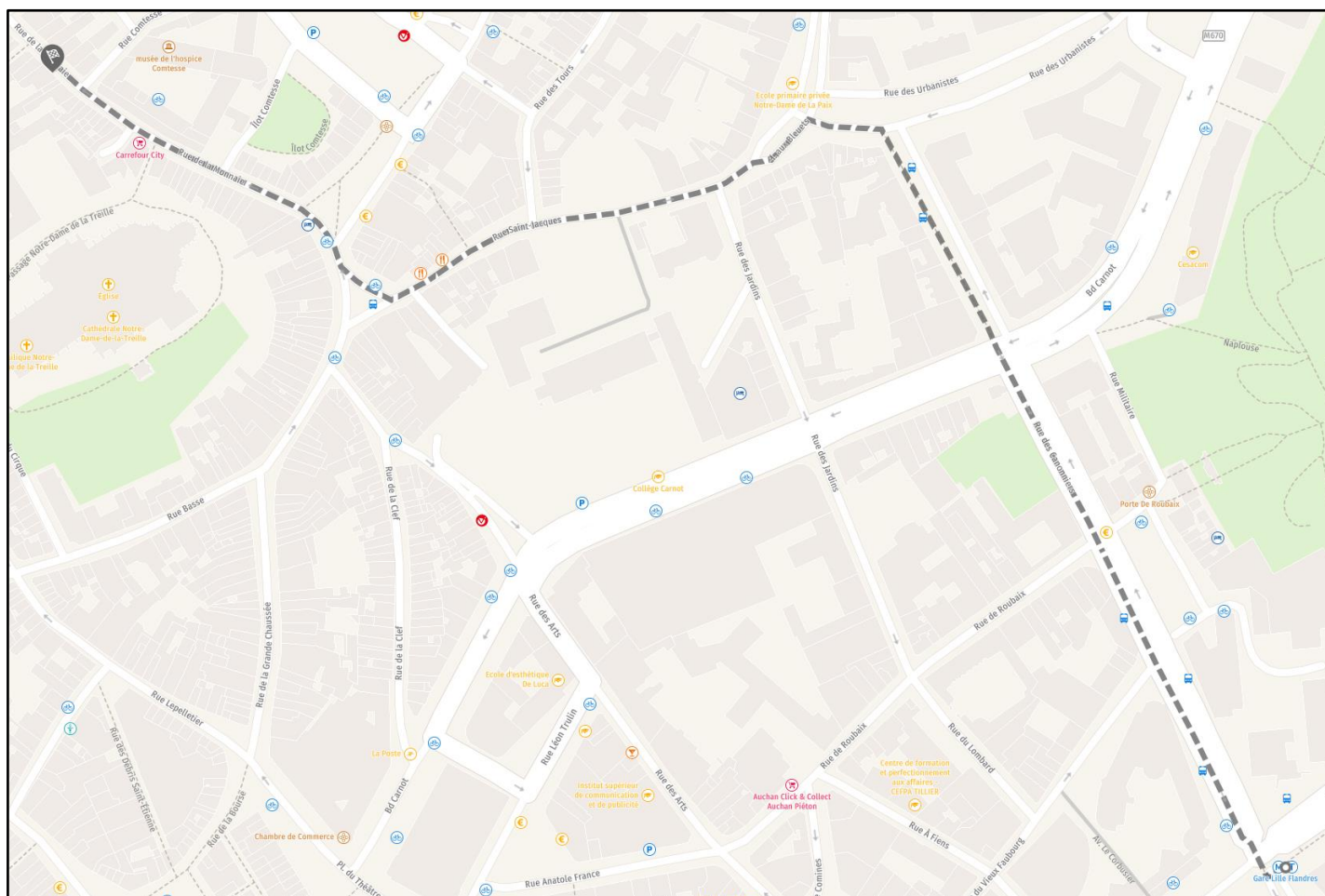
Différents types d'interactions entre porteurs dans la jonction peuvent être en plus pris en compte et traités de façon exacte en rajoutant des termes supplémentaires dans l'Hamiltonien total du système. Ces interactions sont responsables des effets inélastiques et portent aux plusieurs phénomènes intéressants comme un échange d'énergie, une intrication quantique ou encore une décohérence quantique dans des canaux de transport individuels. Nous allons présenter des premiers tests de notre méthode sur deux systèmes modèles composés de chaînes d'Ag reliées par une molécule de benzène (non-magnétique) ou de vanadocène (magnétique) ou les interactions électron-phonon ou spin-spin sur la molécule ont été pris en considération dans le premier et deuxième cas, respectivement.



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## Optical functionalization of graphene by self-assembly of conjugated organic molecules.

G. Creutzer\*, Q. Fernez\*\*, C. Fiorini-Debuisschert\*, S. Vassant\*,

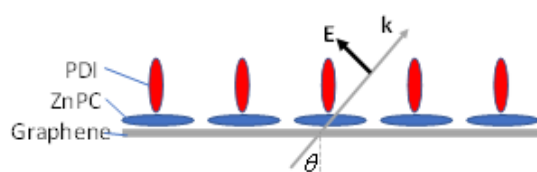
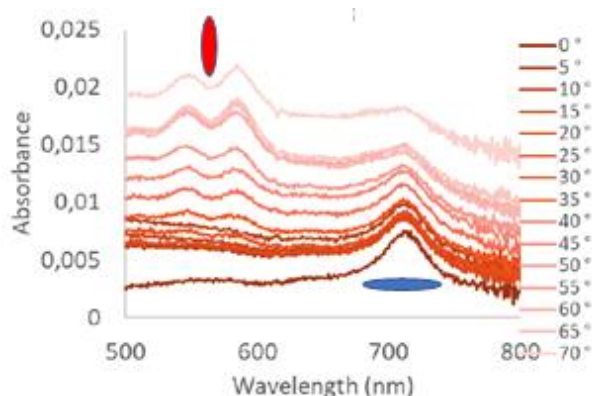
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The design of van-der-Waals (vdW) heterostructures based on two-dimensional (2D) materials is evolving as a credible route to the fabrication of new materials with original electronic and photonic responses tailored at the nanoscale. A strong limitation results from the limited choice of easily processible 2D materials with complementary properties, beyond graphene. However, graphene properties can be tuned through its functionalization by specific conjugated molecules. We have recently developed original molecular-engineering concepts for designing molecular building blocks spontaneously adsorbing on graphene according to various preprogrammed patterns.[1] We shown that such “augmented graphene” layers can be stacked on each other to form original vdW heterostructures.[2] We have realized and probed the photonic responses of such single or bi-layer structures embedding one or several molecular or polymeric building blocks. The scanning tunneling microscopy and spectroscopy permit an accurate structural analysis of molecular organization induced by the atomic-scale template of graphene. The self-organization has a clear influence on optical properties, as observed by absorbance, fluorescence and Raman micro-spectroscopy. These experiments permit to distinguish the influence of the various molecule-molecule and molecule-graphene interactions of either electronic or near-field optical origins. Finally, the possibility of assembling different molecules with perpendicularly-oriented transition dipole moments ([3], see figure) opens new perspectives *e.g.* in the domain of hyperbolic metamaterials.



*Incidence-angle resolved absorption of an organized monolayer of in-plane Zinc Phthalocyanine derivatives (ZnPC, in blue, absorption peak at 710nm) and out-of-plane perylene derivatives (PDI, in red, 540-600nm) formed by self-assembly onto monolayer graphene.*

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## A C-AFM & SThM study on the thermoelectricity of Fe and Ru based organometallic molecular junctions

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<sup>b</sup> Institut des Sciences Chimiques de Rennes (ISCR), CNRS, Rennes, France.

<sup>c</sup> Laboratoire de Chimie des Matériaux Nouveaux, U. Mons, Belgique

### Abstract:

Molecular electronics allow the tailored design of molecular systems for nanoelectronic devices. In this context, molecules with thermoelectric<sup>1</sup> properties could be used for applications such as electricity nanogenerators or thermal regulators that could address current electronics problems with heat dissipation. More specifically, organometallic molecules should present highly efficient thermoelectric effect, which is desirable for this type of application.

In this work, we designed, synthesized Fe-cyclam and Ru-dppe (Fig. 1a) and fabricated molecular junctions (MJs) using self-assembled monolayers (SAM) on template-stripped Au electrodes. We measured their electronic and thermal conductivity by conductive atomic force microscopy (C-AFM) and null point scanning thermal microscopy (NP-SThM)<sup>2</sup>, respectively. The Fe-cyclam MJs have a lower electrical conductivity (Fig. 1a-b), that is understood by a HOMO level at  $0.76 \pm 0.18$  eV below the Fermi energy of the Au electrodes (vs.  $0.32 \pm 0.06$  eV for the Ru-dppe MJs), in good agreement with ab-initio calculations<sup>3</sup> (0.23 eV for Ru-dppe, 0.73 eV for Fe-cyclam, if Fe<sup>III</sup>). The thermal conductivity is almost the same ( $0.2\text{-}0.3 \text{ Wm}^{-1}\text{K}^{-1}$ ) in both cases, which corresponds to a thermal conductance of the SAM  $\approx 20$  nW/K on a par with the values reported for several other MJs based on alkylchains and short  $\pi$ -conjugated oligomers.<sup>4</sup> The Seebeck coefficient for these organometallic MJs is theoretically predicted to be larger ( $\approx 100 \mu\text{V/K}$ ) than for the  $\pi$ -conjugated MJs (few tens  $\mu\text{V/K}$ ). Their measurements with a modified SThM set-up are in progress. A large figure of merit  $ZT \approx 0.3\text{-}0.4$  is theoretically expected for these organometallic MJs.<sup>3</sup>

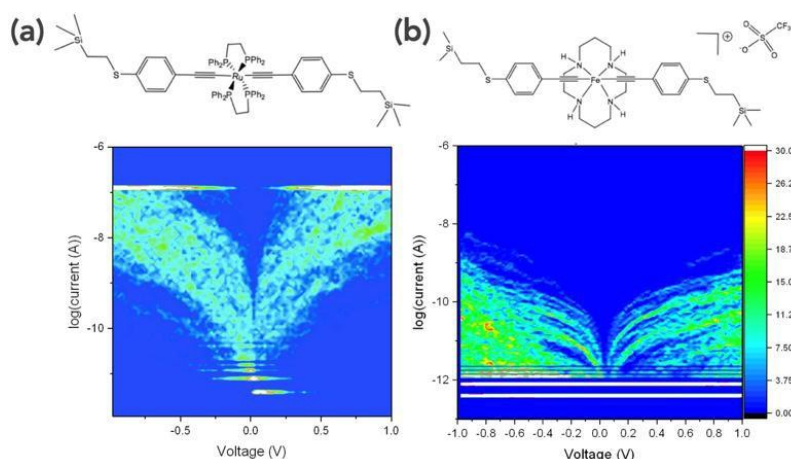


Figure 1: (a) 2D histogram of hundreds of current-voltage ( $I$ - $V$ ) curves measured by C-AFM on the Ru-dppe SAMs. (b) 2D histogram of hundreds of  $I$ - $V$  measured by C-AFM on the Fe-cyclam SAMs.

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## Unravelling the localization of counter-ions in ionic self-assemblies on a HOPG surface

Jean Joseph,<sup>a</sup> Frank Palmino,<sup>b</sup> Judicaël Jeannoutot,<sup>b</sup> Jésus Raya,<sup>a</sup> Mathilde Berville,<sup>a</sup> Jean Weiss,<sup>a</sup> Jennifer A. Wytka<sup>a</sup>, and Frédéric Chérioux\*<sup>b</sup>

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### Abstract:

Adsorption of supramolecular networks is considered a useful technique to tune the electronic properties of the underlying surfaces. Organic molecules with the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) at suitable positions with respect to the Fermi level of underlying surfaces can be used to dope surfaces. The degree of doping is strongly driven by the on-surface organization of adsorbed molecules. Among all  $\pi$ -conjugated molecules, redox-active viologens (or 4,4'-bipyridiniums) with low-lying LUMOs have emerged as promising candidates to address this major challenge.

Atomic force microscopy (AFM) is a commonly used method to investigate the self-organization of molecules on surfaces under ambient conditions at the sub-molecular level. However, in the case of organic salts, such as viologens, the position of the organic cations is well determined whereas the position of the corresponding anions has been less investigated mainly because these anions are often smaller than organic cations. The role of electrostatic interactions between anions and cations is essential to the understanding of on-surface organization. These electrostatic interactions strongly depend on the relative positions of the charged species and require the precise determination of the positions of both the cations and the anions. Whereas attempts to combine solid state NMR (ssNMR) with optical microscopy have been successfully reported for liquid crystalline viologen derivatives, the complementarity of ssNMR and AFM was neither established nor reported. This work describes an original strategy, based on a combination of AFM images and ssNMR, to unravel the position of anions and cations in organic salts deposited on a highly-oriented pyrolytic graphite (HOPG) surface. This simple strategy shows that ssNMR can quickly indicate the tendency of building blocks to organize efficiently prior to AFM studies.

We have combined ss-NMR spectroscopy and AFM topography images to obtain a complete picture of the supramolecular self-assemblies of organic salts on an HOPG surface. This original, simple and efficient method paves the way to the construction of supramolecular self-assembled nanostructures with promising electronic properties.

## New organometallic molecular wires with thermoelectric and negative differential resistance properties

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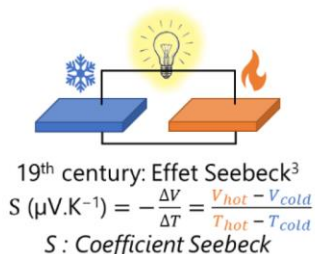
<sup>b</sup>Institut de recherche en Sciences et Ingénierie des Matériaux de l'UMONS, B-7000 Mons, Belgique.

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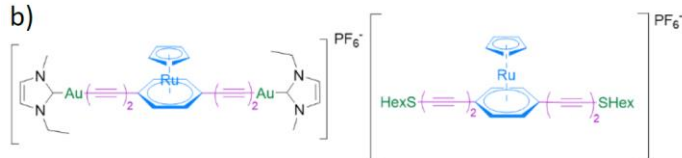
### Abstract:

Molecular electronics, or the idea of using a molecule or assemblies of molecules to manufacture electronic compounds at the nanoscale, is a viable approach to meet the growing demand for miniaturization of electronic systems.<sup>1</sup> Today, this new technology cannot compete in terms of electrical conductance and miniaturization with silicon-based technologies. However, *via* dedicated organic molecular systems, new original functionalities could be introduced like thermoelectricity or negative differential resistance.<sup>2</sup> The objective of my PhD is to design molecular wires that show i) promising seebeck effect thanks to quantum interferences due to the presence of the metal center (scheme a and b) and ii) strong negative differential resistance because of the insertion of heteroatoms into the conjugation path (scheme 1c and 1d).

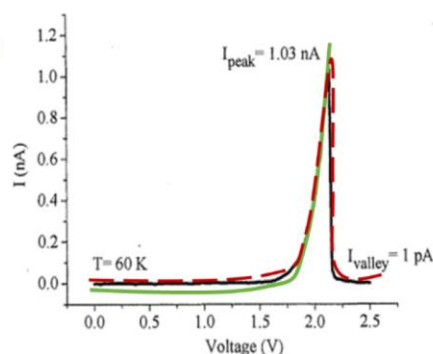
a)



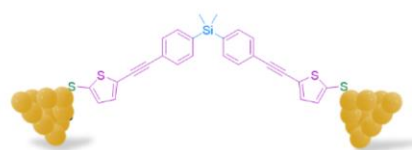
b)



c)



d)



Scheme: (a) Scheme of seebeck effect, (b) Target molecule for seebeck effect; (c) Intensity as a function of current showing an ohmic effect in green and a negative differential resistance effect in red (d) Target molecule for NDR effect.<sup>4</sup>

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## Impact of Molecular Adsorption on the Structural Properties of Several Atom Palladium Clusters

Ahmed Hewail,<sup>a,b</sup> Aimeric Ouvrard<sup>a</sup>

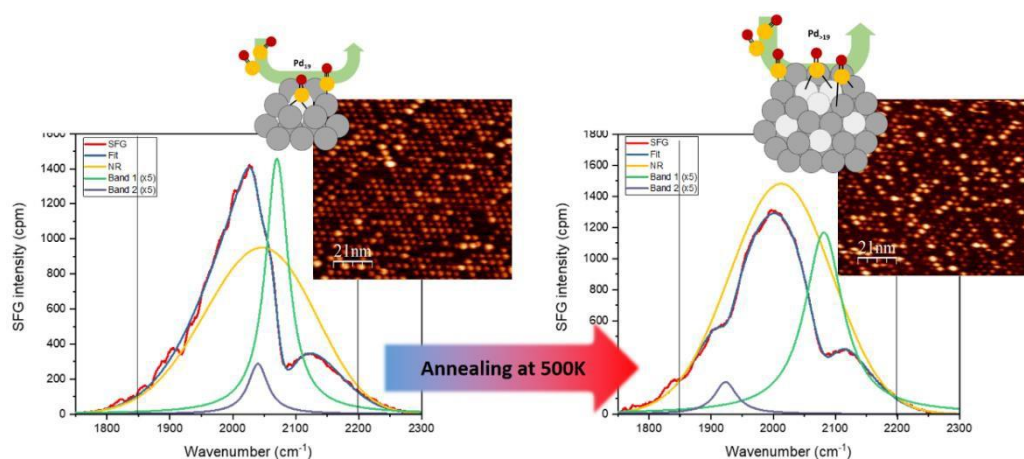
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### Abstract:

Understanding the strong coupling between molecules and plasmonic nanoparticles (NPs) exhibiting is of great relevance for photo-catalyze chemical reactions or enhanced charge transfer in optoelectronic devices. Few-atom model catalysts have gathered significant attention due to their unique catalytic properties as well as their tunable electronic structure to match with molecular orbital levels. Their electronic structure regarding catalytic activity depends strongly on their size, composition, adsorption site coordination, or support.

Here, we present the study of the geometry of 19 atom Pd nanoparticles (NP) and their structural changes upon CO and oxygen adsorption and sample annealing. For that, we have combined high surface sensitivity tools [1], such as scanning tunneling microscopy and vibrational sum frequency generation (SFG) spectroscopy, to study high-density Pd NP arrays grown in ultrahigh vacuum on a strained alumina bilayer on Ni<sub>3</sub>Al(111) [2]. This system has already shown its capability to serve as a template to form dense hybrid ordered assemblies of metallic NPs and organic molecules [3]. Here, we have been able to reveal the NP geometry and their stability regarding adsorption and surface temperature for very small clusters. SFG spectroscopy has proven to be highly sensitive in identifying the adsorption sites of CO on NPs containing as few as ~19 atoms, providing insights into their geometric properties and stability. CO and O<sub>2</sub> co-adsorption were also studied and suggest that edge atoms are the main active sites for molecular adsorption and the most reactive, revealing their different electronic structure. Future work will focus on smaller clusters made of less than 10 atoms.



**Figure:** SFG spectra showing CO adsorption sites at edges ( $>2000\text{ cm}^{-1}$ ) and facets ( $<2000\text{ cm}^{-1}$ ) and STM topography images ( $100\times 100\text{ nm}^2$ ,  $10\text{ pA}$ ,  $1\text{ V}$ ) of ~19 atom Pd cluster array on Al<sub>2</sub>O<sub>3</sub>/Ni<sub>3</sub>Al(111), before and after sample annealing at 500 K. In inset sketches of Pd cluster deduced from SFG and STM investigations.

### References:

- [1] N. Alyabyeva, A. Ouvrard, A.-M. Zakaria, B. Bourguignon, *J. Phys. Chem. Lett.*, **10**, 624, 2019
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- [3] N. Alyabyeva, A. Ouvrard, R. Lazzari, B. Bourguignon, *J. Phys. Chem. C*, **123**, 19175, 2019

## Switching and in plane rotation of molecular assemblies of azobenzene derivative

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### Abstract:

In recent years, molecular switches such as azobenzene adsorbed on metal surfaces have attracted considerable attention due to their potential use in nanotechnology, information storage or molecular electronics [1,2]. In particular, the 3,3',5,5'-tetra-tert-butylazobenzene (TBA) molecule is a promising candidate for such studies, due to the four lateral tert-butyl-groups which act as "spacer leg" to reduce the electronic coupling between the active part of the molecule (azobenzene) and the metal surface. This azobenzene derivative switches reversibly between the two isomeric states (trans-TBA and cis-TBA; Fig. 1a). This isomerization has already been demonstrated by STM using either the electric field induced by a STM tip [3] or by exposure to UV or blue light [4].

Here we report an other effect of electric field for one monolayer TBA coverage on Au(111). After the TBA evaporation, molecules are organized in the trans isomer in the plane of the surface with four lobes corresponding to the 4 "legs", with an apparent height of  $0.25 \pm 0.02$  nm (Fig. 1b 1c 1e). STM imaging at 77K reveals domains only visible in negative polarity; by scanning these TBA domains at -2V (Fig. 1b) bright spots appear, with an apparent height of  $0.36 \pm 0.05$  nm confirmed by nc-AFM. These spots are usually associated to the formation of cis-TBA molecules, induced by the trans-TBA to cis-TBA isomerization under the presence of an electric field<sup>3</sup>. For domains imaged by STM with both polarities, an in plane rotation of TBA network is observed in STM and nc-AFM images, after scanning at a negative polarity (-1V). The origin of this in plane rotation will be discussed. These results show how crucial are the intramolecular and molecular-substrate forces control and understanding in the perspective of molecular electronics.

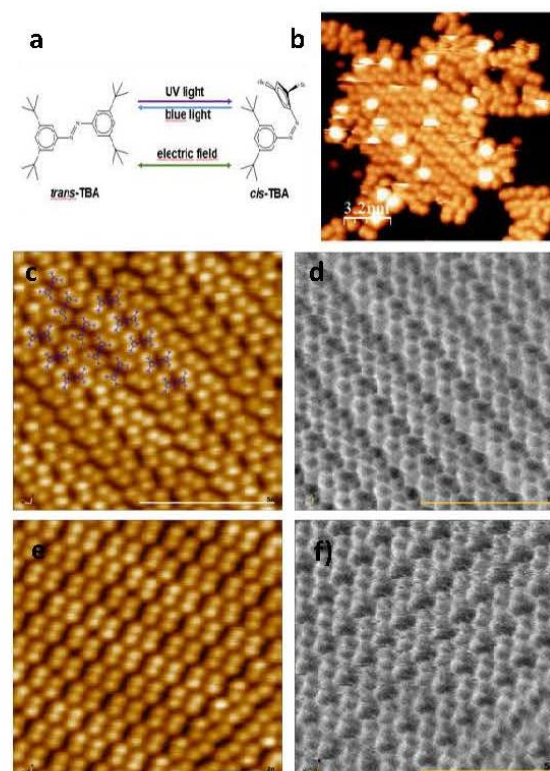


Figure 1: a) Isomerization of the TBA molecule with light or electric field between the two isomers trans-TBA and cis-TBA; b) STM image of TBA on Au(111),  $V = -2.0$  V,  $I = 20$  pA showing bright spots corresponding to cis isomers; c) e) STM images (+1V- 3pA) and d) f) constant height nc-AFM images of the same TBA domain before and after scanning in STM mode at -1V (3pA) respectively.

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## Electronic transport of Prussian blue analogue nanocrystals measured by Conductive-AFM.

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Prussian blue analogue (PBA) nanocrystals (NCs) are nano-objects at the frontier between molecules and bulk materials. These NCs have properties that can be used for a variety of applications, from information storage to biomedical applications [1], or molecular electronics [2]. Here we present a study of the nanoscale electronic transport properties measured by Conductive-AFM (Figure 1b) of these individual cubic NCs of CsCo<sup>III</sup>Fe<sup>II</sup> PBA (Figure 1a) deposited on a graphite substrate (highly ordered pyrolytic graphite -HOPG-) as a function of their size (15 nm, 30 nm and 50 nm).

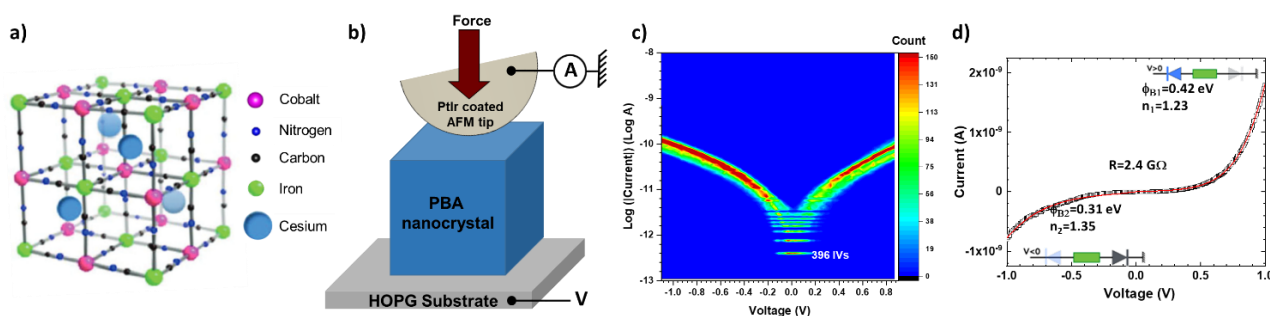


Figure 1: (a) Scheme of the unit cell of the fcc structure of CsCoFe PBA NCs. The cell parameter is close to 10 Å. (b) Scheme of the conducting AFM experiments performed, in which an individual PBA NC with a characteristic size around 50 nm deposited on a freshly cleaved HOPG substrate is addressed, and statistics of  $I(V)$  characteristics are recorded using a given AFM tip force around 20 nN. The AFM PtIr coated tip is grounded, the voltage  $V$  is applied on the HOPG substrate. (c) Example of 2D current-voltage histogram  $I(V)$  measured by Conductive-AFM on a 15 nm nominal size CsCoFe PBA NC. (d) Average  $\bar{I}(V)$  curve (black squares) corresponding to the 2D histogram, fitted by a model of two Schottky diodes in series with a resistor (red line). The inset shows the equivalent electrical circuits, with the diodes in the forward mode highlighted.

Figure 1c shows an example of an IV current-voltage characteristic measured on a 15 nm CsCoFe PBA NC. The 2D current-voltage IV histograms show current values with little dispersion, indicating reproducible and controlled acquisition of IVs characteristics with the Conductive-AFM. The IVs measurements performed on several NCs of the same size and for each size are fitted by an electronic conduction model integrating two back-to-back Schottky diodes (corresponding to the NC/Conductive-AFM and HOPG/NC interfaces) in series with a resistor (intrinsic resistance of the NC) (Figure 1d). This analysis shows that these PBA NCs exhibit electron injection barriers that are almost independent of NC size, of around  $0.41 \pm 0.02$  eV and  $0.27 \pm 0.03$  eV at the HOPG/NC and NC/Conductive-AFM interfaces respectively. The resistance obtained with this model gives an intrinsic electronic conductivity of the NC evolving from widely dispersed values between  $\sim 5 \times 10^{-2}$  -  $5 \times 10^{-4}$  S/cm for the 15 nm size, to a less dispersed conductivity between  $2 \times 10^{-2}$  -  $4 \times 10^{-3}$  S/cm for 50 nm NCs. The origins of the inhomogeneity of the conductivity will be discussed in relation to the size of the NCs and the stoichiometric fluctuations of the CsCo<sup>III</sup>Fe<sup>II</sup> NCs.

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## Electronic Structure at the Nanoscale of Molecularly Functionalized MoS<sub>2</sub> Monolayer.

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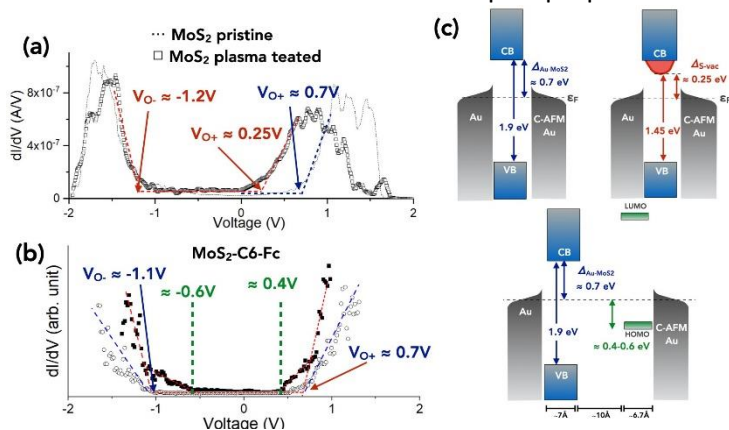
2) CNRS, ISCR (Institut des Sciences Chimiques de Rennes), Univ. Rennes, France

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Molybdenum disulfide MoS<sub>2</sub> is one of the most promising transition metal dichalcogenides (TMDs). It emerged as next-generation materials with high potential for spintronic applications, for example.<sup>1</sup> The combination of its promising properties with the unique modularity of organic molecules opens up new opportunities to precisely tune or to confer new functionality for device perspectives.<sup>2</sup> Here, we report on a detailed understanding of the electronic structure at the nanoscale (conductive-AFM) of a MoS<sub>2</sub> monolayer functionalized by a monolayer of Ferrocenyl-hexanethiol (Fc-C6 for short). The MoS<sub>2</sub> monolayer was deposited on Au by the gold tape exfoliation method.<sup>3</sup> O<sub>2</sub> plasma treatment was used to increase the density of S-vacancies which serve as grafting sites for thiol-functionalized molecules. The Fc-C6 monolayer was deposited in solution. These steps were validated by physico-chemical characterizations: Raman, XPS, C-V. The electron transport properties (I-V and  $\partial I/\partial V$  versus V) were measured by C-AFM. We examined the effects of chemical functionalization of TMDs and determined in detail the electronic transport properties.



(a-b)  $\partial I/\partial V$ -V curves of pristine MoS<sub>2</sub>, plasma-treated MoS<sub>2</sub> and MoS<sub>2</sub>-C6-Fc molecular junctions; (c) corresponding energy diagram.

The figure shows typical  $\partial I/\partial V$ -V curves. For the pristine MoS<sub>2</sub> sample, the two onset voltages:  $V_{O+} \approx 0.7 V$  and  $V_{O-} \approx -1.2 V$  corresponds to the electron transport through the bottom of the MoS<sub>2</sub> CB and VB, respectively (while only direct tunneling is possible between  $V_{O-}$  and  $V_{O+}$ ). After the plasma treatment, the clearly observed reduction of  $V_{O+}$  is due to the creation of S-vacancy states in an energy range of  $\approx 0.45 eV$  below the MoS<sub>2</sub> CB.<sup>4</sup> For the MoS<sub>2</sub>-C6-Fc junctions, we clearly observed the

disappearance of the S-vacancy states ( $V_{O+}$  returned to 0.7V) proving the grafting of thiol-terminated C6-Fc. In addition, two bumps appear at lower onset voltages of  $\approx 0.4 V$  and  $\approx -0.6V$ . We attribute these bumps to electron transport through the Fc HOMO located in the MoS<sub>2</sub> band gap. These conclusions are supported by DFT calculations (S-vacancy at  $\approx 0.5 eV$  below MoS<sub>2</sub> CB, Fc-HOMO at  $\approx 0.4-0.9 eV$  below the Fermi energy, PBE or HSE06 functionals). Implications to device perspectives will be briefly discussed.

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We acknowledge the funding by ANR (project ECOTRAM, # ANR-20-CE09-0018-01).

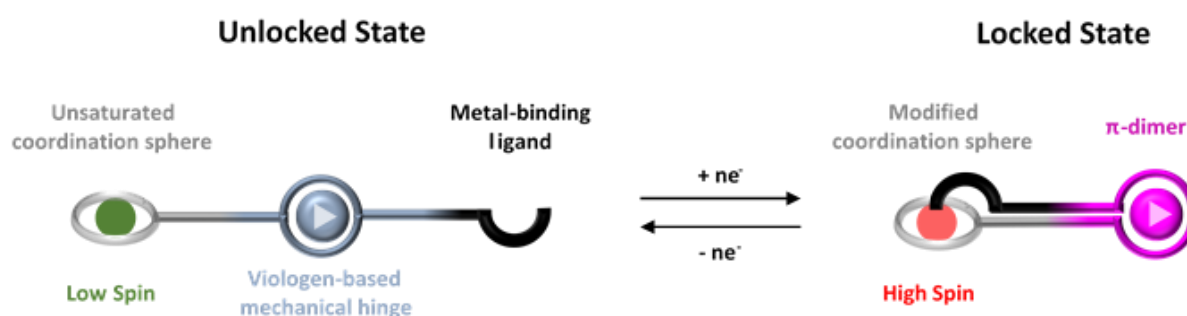
## Ni-centered Coordination-Induced Spin-State Switching Triggered by Electrical Stimulations<sup>[1]</sup>

Shaymaa Al Shehimi,<sup>a</sup> Orsola Baydoun,<sup>a</sup> Lhoussain Khrouz,<sup>a</sup> Sandrine Denis-Quanquin,<sup>a</sup>  
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### Abstract:

The control of magnetic properties by external stimuli has attracted much interest over the past few decades and tremendous work has been achieved thereafter.<sup>[2]</sup> Our contribution to this field is based on the **Coordination-induced Spin State Switching** approach (**CiSSS**)<sup>[3]</sup> which, as its name implies, aims at changing the spin state of a metal center by modifying its coordination sphere. Therefore, based on our expertise in supramolecular chemistry and with the help of theoretical calculations, a well-suited model system was designed and eventually synthesized. In this presentation, the targeted tweezer-like molecule features a redox-responsive viologen-based hinge tethering a high affinity ligand to a magnetically active metal center. In agreement with the concept depicted below, the electrical stimulation of the hinge is expected to trigger a large amplitude molecular motion driven by the reversible, intramolecular  $\pi$ -dimerization of the electrochemically-generated viologen cation radicals.<sup>[4,5]</sup> This fully reversible back and forth self-locking process will enable to control the coordination/dissociation of the ligand to/from the metal center and, consequently, its spin state. The spin-state switching process will be discussed on the grounds of spectroscopic, electrochemical and spectro-electrochemical data supported by quantum calculations.



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## Nanometer-Thick Bilayers by Stepwise Electrochemical Reduction of Diazonium Compounds for Molecular Junctions

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This work describes an electrochemical bottom-up approach for modification of metallic electrode to modulate the electrochemical properties of the layer. The adopted strategy is based on two successive electroreductions of diazonium salt and was successfully used in the fabrication of molecular junction with specific behavior.<sup>1</sup> The deposited ultrathin layers consist of an electron donating oligo (bisthiénylbenzene) (BTB) and an electron acceptor namely oligo (phenyl methylbipyridium) (PMV<sup>2+</sup>). The generated bilayers are studied by AFM, XPS, XPS depth analysis and electrochemical techniques. The study demonstrates the possibility to graft one layer over the initial one to create strongly coupled donor-acceptor or acceptor-donor bilayer systems with minimal interpenetration and overall thicknesses between 5 and 20 nm. The electron transfer towards redox probe in solution and electron transfer in solid state molecular junctions are studied.<sup>2,3</sup> The electrochemical response of several outer-sphere redox probes on such modified electrodes is close to that of a diode, thanks to the easily p-doped oligo (BTB) or easily reducible oligo (PMV) moieties. Moreover, the electron transport in solid state molecular junctions exhibits strong rectification with opposite sign depending on the order of the two layers. Our goal in this work was to control the electronic response through the structuration and the functionality of the organic layer.<sup>4</sup>

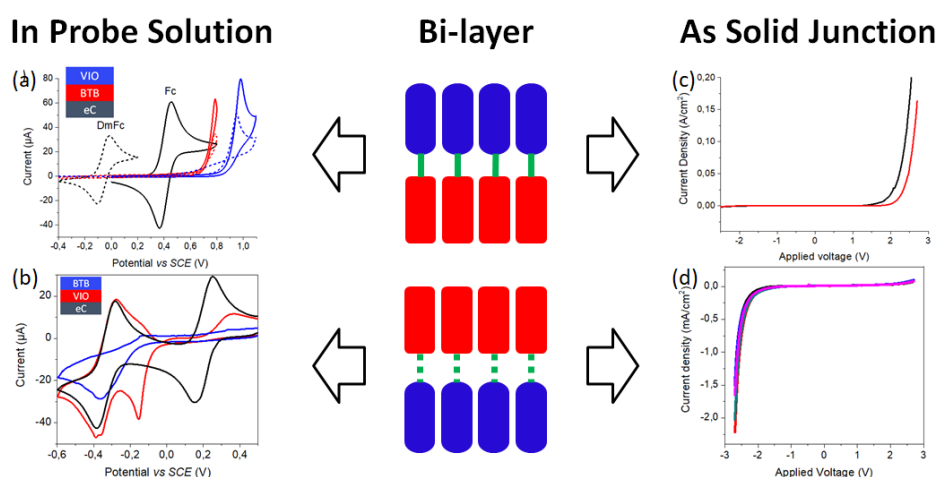


Figure 1: CVs of bare (black curve), single layer modified electrode (red curve) and bilayer modified electrode (blue curve) in Fc solution (5mM), DmFc(5mM) (a) and TCNQ(5mM)(b). Scan rate 100 mV.s<sup>-1</sup>; JV curves for Au/BTB/PMV/Ti(c) and Au/PMV/BTB/Ti (d) junctions.

### Références (Calibri, 11 pts, alignement à gauche)

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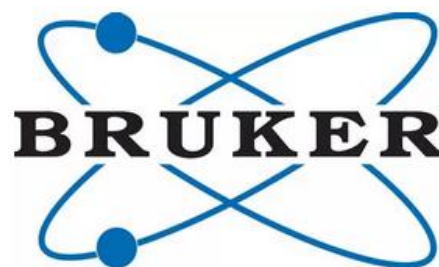
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	Lundi 16 octobre 2023	Mardi 17 octobre 2023	Mercredi 18 octobre 2023
9h-10h		Axe 2 Invité - Mathieu Gonidec Kevin Dalla Francesca Cécile Huez	Axe 4 Invité - Fabrice Charra Sergio González Casal Frédéric Cherioux
10h-11h		10h20 à 10h50 Pause café	10h20 à 10h40 Pause café
11h-12h		Axe 2 Imen Hnid Laurette Jerro	Visite des Plateformes de l'IEMN: Plateforme centrale de micro nano fabrication Plateforme de Caractérisation multi-physiques
12h-13h		Axe 1 Invité - Guillaume Schull	
13h-14h	13h à 13h30 Accueil	12h10 à 13h30 Déjeuner	12h30 à 13h30 Déjeuner
14h-15h	Introduction	Vincent Huc	Réunion Chroniques
15h-16h	Axe 1 Invité - Rémy Pawlack Lihao Guan Linsai Chen	Fatima Hussein Sofia Frida Russi Invité - Clément Merckling	
	Session Poster Stands Industriels	Table Ronde	
	16h-17h	16h10 à 16h40 Pause café	
17h-18h	Axe 3 Invité - Jeanne Crassous (en visio) Vivien Andrieux Mélodie Donnart Florence Volatron	Axe 3 Junlong Wang Nesrine Shaiek	
18h-19h		Axe 4 Invité - Jérôme Cornil Alexander Smogunov	
19h-20h	18h20 à 19h30 Cocktail	Diner au restaurant "l'assiette du marché"	



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