PROGRAMME







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Axe 1 - Systèmes molécule unique, mémoires et switches

Pr. Elke Scheer University of Konstanz Allemagne



Dr. Francesca Moresco TU Dresden Allemagne



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

Dr. Gabor Molnar LCC Toulouse France



Axe 3 - Matériaux & Ingénierie moléculaire

Dr. Jerome Lagoute MPQ University Paris Cité France



Dr. Xiaocui Wu MPI Stuttgart Allemagne



Axe 4 Transverse - Outils de caractérisation et de modélisation

Dr. Pavel Jelinek Institute of Physics Czech Academy of Sciences Tchéquie



Dr. Daniel Hernangomez CIC nanoGUNE Espagne



Lundi 14 octobre 2024

13h00	Accueil		
14h00	Introduction		
14h15	Invité – Jérôme Lagoute		
	Modification and manipulation of charge density waves in 2D materials		
14h55	Xiaonan Sun		
	Electric field induced conductance switching of single-molecule junctions with non-		
	volatile memory properties		
15h15	Pause café		
15h50	Invité – Pavel Jelinek		
	1D molecular chains: topology and spin crossover		
16h30	Colin Van Dyck		
	Higher-order effects and validity of the point-dipole approximation for conjugated		
	extended molecular emitters near plasmonic nanostructures		
16h50	Session posters et industriel		
	Cocktail de bienvenue		
18h30	Fermeture		

Mardi 15 octobre 2024

09h30	Invité – Elke Scheer		
	Electronic transport in single-molecule junctions of organic radical molecules		
10h10	Emma Aoustin		
	Towards switchable magnetic tunnel junctions based on polyoxometalates monolayer		
10h30	Volodymyr Malytskyi		
	Ultrathin layer deposition of poly redox-active complexes		
10h50	Pause café		
11h25	Invité - Xiaocui Wu		
	Electrospray Ion Beam Deposition and Direct Imaging of Single Molecules and		
	Nanoribbons		
12h05	Samuel Decorps		
	Metamorphic Approaches for On-Surface Switching of Chiroptical Properties		
12h25	Industriel : Nextron		
12h45	Déjeuner		
14h15	Invité - Francesca Moresco		
	Functional molecules synthetized on-surface: Model systems for atomic-scale electronics		
	and molecular machines		
14h55	Stéphane Pons		
	Manipulation of the Magnetic State of Fe-DPyDBrPP molecules on Gold: From Kondo to		
	Quantum Nanomagnet via the Charge Fluctuation Regime		
15h15	Pause café		
15h50	Invité: Daniel Hernangomez		
	Electronic and magnetic properties of single-molecule metallocene junctions		
16h30	Elodie Dureau		
	Molecular wires with new properties for nano-electronics applications		

Mercredi 16 octobre 2024

Invité – Gabor Molnar		
Integration of spin crossover molecules into electronic devices		
Dominique Vuillaume		
Redox switching and plasmonic interactions in a metal/SAM/individual Ag nanocube molecular junction		
Pause café		
Amandin Bellec		
Modifying the spin crossover transition of a molecular layer by epitaxial and oriented growth		
Riu Li		
New Strategies for Functional Devices Through Ultrathin Molecular Layers		
Clôture des troisièmes journées plénières du GDR Nemo		
Déjeuner		

NEXTRON MICRO PROBE SYSTEM

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We sincerely ask for the continuous attention and love of many researchers as we proceed into the future. Thank you.

Integration of cubic switches as active layer into memristor prototypes through electrochemical methods Sofia Frida Russi, Thomas Petenzi, Laure Fillaud, Emmanuel Maisonhaute, Christophe Méthivier, Jessem Landoulsi, Volodymyr Malytskyi, Rodrigue Lescouëzec

Low frequency noise in nanoparticle-molecule networks: a pertinent metric for in-materio reservoir computing.

Cécile Huez, David Guérin, Florence Volatron, Anna Proust, Dominique Vuillaume

Room Temperature Study on Unconventional Growth of Non-Planar Phthalocyanines in the Submonolayer Regime

Victor Vaillant, Edward Dunn, Nesrine Shaiek, Maxime BERTHE, Stéphane Lenfant, Nataliya Kalashnyk

Synthesis and characterization of the switching properties of redox active hybrid polyoxometalates Abdourahim Hammani, Emma Aoustin, Pierre Seneor, Richard Mattana, Anna Proust, Florence Volatron

Thermoelectric Ability of Organo-Ruthenium and Organo-Iron Molecular Junctions

Karine Costuas, Joseane Santos Almeida, Colin van Dyck, Jerome Cornil



Modification and manipulation of charge density waves in 2D materials

Jérôme Lagoute

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Abstract:

Two-dimensional (2D) materials exhibit a fascinating variety of exotic electronic states, including charge density waves (CDWs) observed in transition metal dichalcogenides (TMDs). While the Peierls distortion explains well CDWs in one dimension, understanding their origin in higher dimensions remains a challenge. Beside the question of the physical origin, the control and manipulation of CDW in TMDs offers a rich playground for fundamental physics and possible applications.

Here, recent results will be presented on the modification and manipulation of CDW studied by combining scanning tunneling microscopy and density functional theory calculations. I will show how alkali intercalation can induce a transition from 3D to 2D CDW [1], and how a local excitation with an STM tip can be used to manipulate the CDW in a monolayer TMD [2] (see Figure). These findings showcase the ability to tailor CDWs in 2D materials through different methods.



Figure 1 : Manipulation of CDW in VTe₂ using an STM tip: transition from 4×4 to 4×1 , rotated and translated 4×1 CDW.

- [1] U. Chazarin et al., Adv. Mater. Interfaces, 2201680 (2023).
- [2] U. Chazarin et al., Nano Letters, <u>24</u>, 3470 (2024).



Electric field induced conductance switching of singlemolecule junctions with non-volatile memory properties

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Abstract:

The global demand for data storage and processing has increased exponentially in the past decade. In-memory computing with logic operations has attracted much attention and been largely used to store data and machine code. The use of memoristic single molecule in molecular electronics aims to fabricate single molecule memoristor with lower cost and optimized functionality with efficient charge transport. The formation of highly stable single-molecular junctions (SMJs) with covalent molecule-bottom electrode contact allows not only conductance measurements but also reliable I/V characterization at room temperature. Under this circumstance, investigations of SMJs with central switchable molecules are of great interest to obtain resistive switches with high on/off ratios for non-volatile memories. We have recently investigated diarylethene (DAE) based SMJs using STM-bj technique by connecting single DAE molecule (pre-grafted using diazonium electroreduction) between two metal electrodes.¹⁻⁴

NH₂-DAE-NH₂ is chosen as a central photochromic unit (for building SMJ) which can switch between its closed and open forms upon UV and visible light irradiation in solution as well as on surface, showing different conjugated structures.¹ Au-[NH2-DAE-NH2]n-Pt (n=1, 2, 3) SMJs are built using STM-bj technique where light-induced high conductance (HC) and low conductance (LC) states are recorded corresponding to conductance switching between the molecular CF and OF states, respectively.



Most importantly, electric field is then used as an external stimulus to trigger the SMJ switching. Cycles of reproducible hysteresis I(V) loops are obtained display a field-generated SMJ non-volatile memory function between their OF and CF states. Repeated cycles of "reading,writing and erasing"⁴ processes are successfully practice showing a XOR logic-in memory effect. Such switchable SMJs may serve as full-electric room temperature memristors that are the keys to the future of molecular storage devices.

- 1. X. Yao, X. Sun*, F. Lafolet, J. C. Lacroix*, Nano Lett. 20, 9 6899–6907 (2020).
- 2. X. Yao, M. Vonesch, M. Combes, J. Weiss, X. Sun*, J. C. Lacroix*, *Nano Lett.* **21**, 15 6540 (2021).
- 3. X. Yao, L. H. Guan, M. Vonesch, J Wytko, J. Weiss, X. Sun*, J. C. Lacroix*, J. Mater. Chem. C 12, 4326-4335 (2024).
- 4. X. Yao, L. H.Guan, F. Lafolet, X, Sun*, J. C. Lacroix*, to be submitted



1D molecular chains: topology and spin crossover

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Recent progress in on-surface chemistry enabled the synthesizing and characterizing of novelconjugated carbon molecules with magnetic properties systems with unprecedented properties [1]. This route, complemented with high-resolution scanning probe imaging (SPM), provides new opportunities to understand their chemical and physical properties, including the emergence of magnetism in such materials [2].

In the first part of the talk, we will discuss the connection between the topological band structure of conjugated polymer introduced in the framework of the Su-Schrieffer-Heeger (SSH) model and their conjugation. We will discuss the quantum phase transition between two topologically distinct phases of the π -conjugated polymer [3]. This quantum phase transition is defined by the length of the polymer, triggered by the transition from topologically trivial to a non-trivial phase above a certain polymer length. We demonstrate that the pseudo-Jahn-Teller effect is the driving mechanism responsible for the quantum phase transition [4].

In the second part, we introduce on-surface synthesis of 1D coordination π -d conjugated polymers, achieved by co-deposition of 2HQDI molecular precursor and various transition metals (Fe, Co, Ni, Cr, Cu) atoms on metal surfaces under UHV conditions. This route enabled us to form magnetic π -d organometallic polymers with lengths up to hundreds of nanometers [4]. We will demonstrate fully reversible multiconfigurational light-driven spin crossover switches in a single π -d organometallic Co-QDI chain suspended between two electrodes [5].

References:

[2] J.Li et al., Nature Communication 10, 200 (2019); N. Pavlicek et al., Nature Nanotechnology 12, 308 (2017); S. Mishra et al., Nature Nanotechnology 15, 22 (2019).

- O. Gröning, et al., Nature 560, 209 (2018); D.J. Rizzo, et al., Nature 560, 204 (2018)
- [3] B. Cierra et al, Nature Nano, 15, 437 (2020)
- [4] H. Gonzalez-Herroro et al Adv. Mat. 33, 2104495 (2021)
- [5] V.M. Santhini et al, Angew. Chem. Int. Ed. 60, 439 (2021).
- [6] A. Cahlik et al, ACS Nano 18, 9576 (2024).

^[1] S. Clair and D. G. de Oteyza, Chemical Reviews **119**, 4717 (2019).



Higher-order effects and validity of the point-dipole approximation for conjugated extended molecular emitters near plasmonic nanostructures

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Abstract:

Recent experiments showed that light emission from a molecule can be triggered by inelastic electron tunnelling through a molecular device. The electronic current promotes the molecule in an excited state, and further deexcitation process leads to photon emission.¹ Very interestingly, the metallic tip is a plasmonic nanostructure. Those specific environments are known to strongly enhance the light emission rate, which is named as the Purcell effect in literature. This strong enhancement effect enables optical detection of single molecule fluorescence or the well-known surface-enhancement effect in Raman spectroscopy.²

Light emission from a molecule is usually approximated as being emitted from an oscillating point-dipole, with the transition dipole moment as a key-property. This approximation generally prevails in the characterization of light emission from molecules, in various environments such as solution but also near plasmonic structures. More recently, it has been suggested that plasmonic nanostructures may confine light to effective wavelengths within the sub-molecular scale.³ Consequently, the question of whether the standard description of a molecular emitter as a point-dipole, i.e., the unique consideration of the transition dipole moment, remains a reasonable assumption.

In this presentation, we introduce a theoretical framework to explore the limits of this standard description. It allows us to calculate the fluorescence emission rate of a quantum emitter, described at the TD-DFT level, within a nanoplasmonic environment, described by solving Maxwell equations. It is used to characterize the emission rate of different conjugated emitters : (i) an H2Pc molecule within an STM tip-substrate nanogap and (ii) oligothiophenes of different chain lengths (0.8, 1.6 and 2.4 nm) near gold nanospheres. Significant deviations from the point-dipole approximation are predicted for those elementary structures and environments. This result is due to complex high-order multipolar effects. Consequently, the usual description of a molecule using the transition dipole moment breaks down. This paves the way toward high-order photochemistry, with, for example, the activation of dipole-forbidden transitions revealing usually dark spectroscopic features.¹



H₂Pc molecular emitter lying on a substrate and optically coupled to a plasmonic STM tip

- ¹ S. Jiang, et al, Science **379**(6636), 1049–1054 (2023).
- ² G. Sun, et al, Phys. Rev. A **85**(6), 063410 (2012).
- ³ N. Rivera, et al, Science **353**(6296), 263–269 (2016).



Electronic transport in single-molecule junctions of organic radical molecules

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The possibility to fabricate electronic devices with molecules as functional building blocks is a central goal of molecular electronics. Tuning the electronic transport properties by magnetic fields opens the route to use them as functional elements in molecular spintronic devices. Of particular interest are organic radical molecules. The presence of an unpaired electron may give rise to intrinsic magnetic properties that are preserved even when coupled to nonmagnetic electrodes. In this talk I will report on single-molecule transport experiments using the mechanically controlled break junction technique carried out at low temperatures down to 1.5K. I will discuss recent observations of magnetic-field tunable transport in three different classes of organic radical molecules. We have observed very high positive [1,3] and negative magnetoresistance [2,3] up to 200% for a magnetic field of a few Tesla applied perpendicular to the current direction. We furthermore observe an interplay between Kondo peaks and magnetoresistance in perchlorotrityl [2] and Blatter [3] radicals, the origin of which is still unknown and open for further investigation.



- [1] R. Hayakawa et al., Nano Letters 16, 4960 (2016)
- [2] G. Mitra et al., Nano Letters 22, 5773 (2022)
- [3] G. Mitra et al., in preparation. (Calibri, 10)



Towards switchable magnetic tunnel junctions based on polyoxometalates monolayer

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Abstract:

Spintronics has revolutionized modern electronics by introducing new possibilities for data storage and magnetic sensing technologies. As its core, are magnetic tunnel junctions (MTJs) consisting of two ferromagnetic electrodes separated by a thin insulating barrier. It has been shown that molecules could be integrated into MTJs giving rise to molecular spintronics that combines the principles of spintronics with the properties of organic molecules. Thanks to the spin-dependent hybridization at ferromagnetic electrode/molecule interfaces, spin polarization and thus tunnel magnetoresistance can be tailored by molecules [1]. However, up to now, mainly passive molecules such as alkane chain or aromatic rings have been integrated into MTJs [2-3].

In this presentation, we will present molecular MTJs integrating complex molecules, called "active" molecules, which can be switched by an external stimulus (light, pressure, electric field...). The energy gap/coupling strength to the electrodes depending on the molecule state, its modification can hence lead to modulation of the spin polarization of the interface. Consequently, MTJs properties can be expected to be tuned by switching the molecule. Among the large variety of these "active" molecules [4], electrically addressable molecules are particularly interesting for future applications. Here, we focus on polyoxotungstate (PW₁₁O₄₀(SiC₃H₆SH)₂) redox switchable molecules, from the polyoxometalate (POM) family. We will first present the multiple challenges we have faced to fabricate NiFe/POMs/Co MTJs (see Fig.1). Next, we will show the characterizations of the interface which confirm the grafting of molecules onto the electrodes. We will then focus on the investigation of the electrical switching of the molecules by conductive-tip AFM. Finally, we will present the preliminary electrical characterization of the NiFe/POMs/Co MTJs which demonstrate that switchable polyoxometalate monolayer can be successfully integrated in MTJs. This opens the way to develop multifunctional spintronic devices.



Figure 1. (Left) Representation of the magnetic tunnel junction (MTJ) integrating POM molecules. (Right) Current-voltage and conductance curves measured in a NiFe/POM/Co junction at T=100K.

- [1] C.Barraud et al., Nat.Phys. 6, 615 (2010)
- [2] J.R.Petta et al., Phys. Rev. Lett., 93, 136601 (2004)
- [3] M.Galbiati et al., Adv. Mater. 24, 6429 (2012)
- [4] W.Liu et al., WIREs Comput Mol Sci. 11 :e1511 (2021)



Ultrathin layer deposition of poly redox-active complexes

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Abstract:

Interested in polymetallic complexes, our group has recently developed a family of octametallic compounds. These are of cubic geometry with corners occupied by metal cations linked by cyanide anions edges. Each metal is additionally capped by a *fac*-tridentate ligand, typically of scorpionate type. This structure confers remarkable stability to assemblies, making them the first family of solution-stable cyanido-bridged complexes. The π character of the cyanide bridge ensures electronic communication between the metal centers. The stability in solution has offered us the opportunity to study their electrochemical and optical properties and we have found up to nine distinguishable redox states in such compounds,¹ without notable decomposition of a system.

In order to exploit the properties of these compounds in the simplest electronic devices, we have studied their surface deposition. To achieve this, cubic complexes were functionalized with specific scorpionate ligands bearing thiol groups for metal surface grafting or thiophene cycles capable of electropolymerization.

In this communication, we will discuss the synthesis of those functionalized cubes, their surfacedeposition followed by electrochemistry study, surface analysis by AFM, XPS and XAS and finally, the simplest electronic dispositive consisting of thin polymeric film of cubes exhibiting a memristive-like behavior. (figure below.)



(a) Structure of the cube before polymerization. (b) Device configuration. (c) i-V curve response.

^{1.} a) J. Glatz, L.-M. Chamoreau, A. Flambard, J.-F. Meunier, A. Bousseksou and R. Lescouëzec *Chem. Commun.*, 2020, 56, 10950; b) J. Jiménez, J. Glatz, A. Benchohra, G. Gontard, L. Chamoreau, J. Meunier, A. Bousseksou, R. Lescouëzec *Angew. Chem. Int. Ed.*, 2020, 59, 8089–8093.



Electrospray Ion Beam Deposition and Direct Imaging of Single Molecules and Nanoribbons

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Molecular electronics aims to use single molecule as the fundamental building blocks for electronic devices, enabling components with unprecedented miniaturization and functionality. Organic semiconductors, bridged typically by biomolecules such as DNA, proteins and peptides play an important role in the development of the field (1). However, their structural complexity pose challenges for present analytical methods in characterizing their individual molecular structures, hindering the understanding of their structure-property relationships. Ensemble-averaged measurement on molecules with extensive structural variation leads to loss of structural information for individual molecules.

We address this problem by using Electrospray Ion Beam Deposition (ESIBD), a technique that transfers molecules into the gas-phase, mass-selects, and soft-lands them onto a cold single-crystal metal surface. This is followed by their imaging using Scanning Tunneling Microscopy (STM) and Scanning Transmission Electron Microscopy (STEM), correlated with DFT calculations to reveal their individual structures on surface. We successfully applied our approach to conjugated polymers (2), biomolecules (3-5), as well as MoS₂ nanoribbons (6). This method opens a new avenue to access individual structures of increasing complexity that can be electrosprayed and deposited onto a surface.

- [1] T. Li, et. al. Adv. Mater. 35, 2209088 (2023)
- [2] J. Vanderspikken, Z. Liu, X. Wu, et. al. Adv. Funct. Mater. 33, 2309403 (2023)
- [3] X. Wu, et. al. Nature 582, 375 (2020).
- [4] K. Anggara, et. al. JACS 142, 21420 (2020).
- [5] K. Anggara, et. al. Science 382, 219 (2023).
- [6] X. Zhang, et. al. Adv. Mater. 36, 2310817 (2024)



Metamorphic Approaches for On-Surface Switching of Chiroptical Properties

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Abstract:

One great challenge nanoscience is facing is the difficulty to transpose molecular-scale phenomena into macroscopic properties finding application in everyday-life devices. A way to address this issue is to develop metamorphic molecular systems for which an external stimulus triggers a drastic structural reorganization. Based on this strategy, our project bridges the gap between chiroptical properties observed in solution for Circularly Polarized Luminescence (CPL) switches¹ and their use in device-like systems as major breakthrough.

This work is focused on synthesis and investigation of new boron-based chiral fluorophores and their implementation on bis-viologen hinges to create stimuli-responsive CPL switches with metamorphic properties (see Figure 1). Chirality is either induced on the boron based fluorophores^{2–4} using BINOL⁵ or helicene-like subunits. Different strategies are also currently being developed to incorporate these chiroptical dyes on molecular switches. Once fluorophores are synthesized using new synthetics pathways, their photophysical and chiroptical properties are firstly studied in solutions before addressing on-surface properties.



Figure 1. Schematic representation of metamorphic processes associated with modulation of chiroptical properties.

References:

[1] J.-L. Ma, Q. Peng and C.-H. Zhao, Chem. – Eur. J., 2019, 25, 15441–15454.

- [2] D. Frath, S. Azizi, G. Ulrich, P. Retailleau and R. Ziessel, Org. Lett., 2011, 13, 3414–3417.
- [3] D. Frath, A. Poirel, G. Ulrich, A. De Nicola and R. Ziessel, Chem. Commun., 2013, 49, 4908.
- [4] D. Frath, J. Massue, G. Ulrich and R. Ziessel, Angew. Chem. Int. Ed., 2014, 53, 2290–2310.

[5] R. Hachem, S. Decorps, R. Devienne, T. Baron, O. Maury, B. Baguenard, S. Guy, E. Janneau, F. Chevallier, C. Bucher, L. Guy, D. Frath, manuscript in preparation



Functional molecules synthetized on-surface: Model systems for atomic-scale electronics and molecular machines

Francesca Moresco

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Scanning tunneling microscope (STM) experiments permit a deep insight into the electronic properties of molecular and atomic systems. Furthermore, on-surface synthesis is presently developing as a powerful strategy for the generation of complex functional molecules on a surface and opens new perspectives for the development of technology at the atomic scale. In this talk, recent low-temperature scanning tunneling microscopy experiments will be reviewed, where on-surface reactions are applied to investigate the electronic and mechanical properties of designed molecular systems.



Manipulation of the Magnetic State of Fe-DPyDBrPP molecules on Gold: From Kondo to Quantum Nanomagnet via the Charge Fluctuation Regime

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Abstract:

We demonstrate how the magnetic state of Fe-porphyrin-based molecules is influenced by surface charge fluctuations using density functional theory (DFT) calculations and scanning tunneling microscopy (STM) measurements. We investigated Fe-DPyDBrPP molecules deposited on Au(111) surface decorated with Br adatoms which produces molecular chains at the surface of gold (Figure 1). When a molecule in the chain is positioned above the Br site, it enters a non-magnetic quantum Kondo regime. In other positions, the molecule remains magnetic and behaves as an S = 1 nanomagnet. By using the STM tip to move the molecules, we tracked the transition between the magnetic state and the Kondo effect through several intermediate states. This transition is driven by enhanced charge fluctuations within the molecule, caused by increased hybridization of the molecular orbitals with the conduction electrons as the molecule approaches the Br site. This hybridization and low magnetic anisotropy yield the Kondo effect in the molecule while maintaining S = 1 spin state. This study provides valuable insights into the control of molecular spin states, which is critical for advancing spintronics, nanoelectronics, and quantum electronics.



Figure 1. (a) Iron(II) 5,15-(di-4-bromophenyl)-10,20-(di-4-pyridyl)porphyrin molecules chemical composition. (b)
STM topography: the molecules group in threes to form a chain. The leftmost molecule in the chain placed by manipulation with the microscope tip above a Br atom. V=125mV, I=20pA. Image size: 7x7 nm². (c & d)
Corresponding tunneling conductance maps showing the location of spin-flip excitations at 3 meV and 10 meV, respectively. The presence of a Br atom beneath the left molecule facilitates spin flipping. V_{stab}=30mV, I_{stab}=200pA. V_{mod}=0.2mV, f=750Hz. T=1.3K

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Electronic and magnetic properties of single-molecule metallocene junctions

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Metallocenes, a well-known family of organo-metallic molecules in which a transition-metal atom is sandwiched between two organic ring-like ligands, have been recently attracting a renowned interest in view of their utility as robust functional building blocks in molecular-scale devices. In this talk, I will present several recent theoretical aspects associated to these molecules. First, I will show that the configurational degree of freedom of ferrocene (where the metal is iron - Fe) allows to mechanically-tune its conductance in single-molecule junctions. Using ab initio transport calculations and simple models, I will prove that ferrocene displays destructive quantum interference effects. By rotation of the ligands, the nature of the quantum interference can be mechanically controlled and the conductance modulated. Next, I will show that these devices also allow for direct interfacial contact between iron and a gold contact at room temperature in the absence of supporting coordinating ligands. This occurs only when the metal center is oxidized to a Fe^{3+} center, which can be induced *in-situ* by a photo-redox reaction, thus laying the foundation for light-switchable ferrocene-based single-molecule devices with potential mechanistic functionality. Finally, I will present a methodological study of how electric fields can be used to control the magnetic moments by non-magnetic means through spin-orbit torques. I will show first-principles calculations of this observable at a single-molecule level in a vanadocene (where the metal is vanadium) - copper single-molecule junction under bias, beyond the linear response regime. Invoking a selfconsistency scheme between density functional theory and non-equilibrium Green's functions formalism, we compute the change of magnetization, as well as the associated spin-orbit torque. Our findings lay the foundational work to study spin dynamics at the single-molecule level in this and other promising molecular complexes.

The research presented here was performed in collaboration with M. Camarasa-Gómez (Universidad del País Vasco/CFM, Spain), F. Evers (Universität Regensburg, Germany), the group of L. Venkataraman (Columbia University NYC, USA), M. S. Inkpen (University of Southern California, USA).



Vanadocene-copper single-molecule junction, taken from Ref. [3]

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MOLECULAR WIRES WITH NEW PROPERTIES FOR NANO-ELECTRONICS APPLICATIONS

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Abstract:

Molecular junctions (MJ) with molecular self-assembled monolayers (SAM) (Figure 1a) may bring a tangible response to the achievement of electronic system miniaturization with specific molecular design¹.

Although, the conductance of MJ is in principle controlled by the frontier orbitals (FO) correlated to the molecular scaffold, FO pinning to electrodes levels-off the orbital energy levels and results in similar conductance values for SAM of electron rich or poor molecules in a given series². In this first part we present our molecular design and the synthesis of molecules that will allow us to study in depth the pinning effect in SAM by varying the anchoring group of the molecule with its FO energy levels (Figure 1b).



Figure 1 : a) SAM representation. b) New molecular wires for pinning effect investigation.

Importantly, it is well-known that MJ cannot currently compete in terms of electrical conductance with silicon-based technologies. However, via dedicated organic molecular systems, new original functionalities could be introduced like thermoelectric behaviour or negative differential resistance (NDR)³, the latter being characterized by a decrease of intensity with voltage increase at some point.

Theoretical calculations indicated that insertion of silicon atoms within the conjugated path of a molecular wire may result in pronounced NDR effect, through silicon hyperconjugation. Therefore, we choose to add silane and disilane functions to an organic molecular wire in order to break the π -conjugation by allowing hyperconjugation of the silicon with the π -conjugated part. It is anticipated that the second one will increase conductivity with respect to the first one while maintaining the NDR properties of the molecular wires Figure 2 : Molecular wire for NDR effect. (Figure 2) which synthesis will be described.





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Integration of spin crossover molecules into electronic devices

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Molecular spin crossover compounds present a special technological interest for their roomtemperature bistability leading to a sizeable variation of different physical properties (HOMO-LUMO gap, dielectric permittivity, magneticmoment, heat capacity, elasticmodulus, ...) [1]. As a result, when integrated into electronic devices, a potentially huge impact of the spin-state switching on the device properties can be foreseen. In this talk, I will present a review of research conducted in our team on electrical and charge transport properties of molecule-based spin crossover complexes. The presentation covers different size scales from bulk materials to thin films and nanoparticles, including their device integration, and embraces the topic of hybrid materials/systems with coupled (electrical and spin crossover) properties as well.



Figure 1. (a) Scheme and SEM image of the cross-section of an $ITO/[Fe(HB(tz)_3)_2]/AI$ junction [2]. (b) I - V curves of the junction acquired in the low-spin (low resistance) and high-spin (high resistance) states. (c) Scheme and SEM image of the cross-section of a [Fe(Htrz)_2(trz)]BF4@PVP/P3HT bilayer inside an OFET [3]. (d) Drain-source current of the transistor recorded for ten successive thermal cycles through the spin transition.

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Redox switching and plasmonic interactions in a metal/SAM/individual Ag nanocube molecular junction.

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Plasmonic nanostructures can be used in light-harvesting systems to increase the efficiency of solar cells by concentrating light¹ or to improve the efficiency of light harvesting by nano-rectennas.² In the field of molecular electronics, by incorporating molecules with specific chemical functions into plasmonic nanostructures, we can create devices that respond selectively to different stimuli with foreseen applications for highly sensitive sensors, photonics and optoelectronics.³



Here, we report the redox switching of ferrocene moieties (Fc) embedded in a double tunnel barrier plasmonic cavity fabricated from a click-chemistry self-assembled monolayers (SAMs) of Fc-alkylthiol on ultra flat gold surfaces,⁴ connected to silver nanocubes, AgNCs, which are capped by an ultra-thin layer of poly(vinylpyrrolidone) (PVP).⁵ A single Au-Fc-alkylthiol/AgNC is contacted by the tip of a conductive-AFM, figure (a), and we study the electron transport properties of this molecular device in the dark and under light irradiation at the plasmonic resonance

wavelengths. We demonstrate a dual behavior in the current-voltage (I-V) characteristics in the dark: a large hysteresis loop at positive voltages and an hysteretic negative differential conductance (NDC) at negative voltages, figure (b). These features are due to the redox switching of Fc between its neutral (Fc⁰) and oxidized (Fc+) states and the double tunnel barrier structure of the device (alkyl chains and PVP layer) leading to a weak coupling of the Fc with the electrodes, increasing the lifetime of the Fc⁰ state, making it observable. The I-V curves are analyzed by the Landauer model when the transport is dominated by a single energy level or by a combined Marcus and Landauer approaches for parts of the I-V curves when Fc redox switching comes into play.⁶ We determine the HOMO of the Fc+ and Fc⁰ states at 0.54 and 0.42 eV below the Fermi energy, respectively, figure (c), with a weak reorganization energy < 0.1 eV upon switching. The hysteresis and NDC behaviors are no longer observed under a plasmonic light excitation, figure (d), and the I-V curves of the molecular junctions are similar as those for the same SAMs directly contacted by the C-AFM tip. A virtual molecular orbital due to the plasmon-induced coupling (fast electron transfer) between the two redox states of the Fc is determined at 0.46 eV.

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Modifying the spin crossover transition of a molecular layer by epitaxial and oriented growth

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Abstract:

Spin crossover (SCO) molecules present two spin states that can be controlled by external stimuli such as light or temperature. Their ability to switch makes them promising candidates for incorporation in molecular spintronic devices. In this purpose, it is mandatory to understand how the properties of spin crossover molecules are modified when in direct contact with metallic substrates and how the growth of molecular films is governed by the substrate. Additionally, the bistability, i.e. the ability to reversibly switch between two stable states in the hysteretic temperature range, is an important property that needs to be controlled at the nanoscale.

Grazing incidence x-ray diffraction measurements on monolayer of Fe[HB(3,5-(CH3)₂Pz)₃]₂ (Pz=pyrazolyl) adsorbed on Au(111) and Cu(111) substrates enabled us to evidence that an epitaxial relationship between the molecular layer and the substrates exists (1). This has a direct consequence on the conversion from one spin-state to the other either by using temperature (2,3) light (4,5) or electric field (6) as external stimuli. Here, we will discuss in detailed the molecular structure of Fe[HB(3,5-Me2Pz)₃]₂ ultra-thin films adsorbed on Cu(110). For sub-monolayer coverage, the molecules form a perfectly epitaxial network on the Cu(110) substrate. For larger thicknesses, the film evolves due to the release of the epitaxial strain. Interestingly, the thicker molecular film structure resembles the one of the bulk molecular crystal with a growth along the (100) plane. By XAS measurements, we demonstrated that for a one-monolayer-high layer, the molecules are locked in the high spin state; while for a six-monolayer-high layer the molecules recovered their spin-crossover properties.

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New Strategies for Functional Devices Through Ultrathin Molecular Layers

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Abstract:

Molecular Electronics (MEs) are driven by the dream of expanding Moore's law to the molecular level for next-generation electronics by incorporating molecules into electronic circuits. Compared to traditional silicon-based electronic devices, MEs offer unparalleled advantages, such as faster performance, higher packing density, and exceptional functional diversity. As one of the essential components of MEs, Molecular Junctions (MJs) comprising a single molecule or an assembly of many molecules between two conducting electrodes, have garnered substantial research interest.

In this study, ultrathin layers (7-10nm) of 4,4'-diamino-2,2'-stilbenedisulfonic acid (DAS) oligomers were grafted on gold strip electrodes by electrochemical reduction of in-situ generated diazonium salts (**Figure 1**. a)¹. Then, a Ti/Au top contact was deposited to complete a solid-state MJ^2 . These fabricated devices exhibit robust and reproducible rectification, with the current at +2 V (positive bias on the gold strip electrode) exceeding that at -2 V by more than 2000 times (**Figure 1**. b).

Furthermore, to investigate the role counterions play in the conductivity of DAS-basted MJs, Li⁺ ions were incorporated into DAS layers through ion exchange. Compared to parallelly fabricated DAS-based MJs, Li⁺-inserted DAS MJs exhibit a remarkable 1000-fold increase in current, with a current density of 0.2 A/cm² at 1V (**Figure 1**. c).



Figure 1. (a) Schematic representation of DAS and its electrochemical grafting through diazonium salt reduction on a gold electrode. (b) Average current-density vs applied voltage (JV) curves of Au/DAS/Ti/Au MJs. Inset: Schematic illustration of a molecular junction. (c) Logarithmic plots (log₁₀ |J|) of current density vs. voltage for DAS MJs and Li⁺-inserted DAS MJs.

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Integration of cubic switches as active layer into memristor prototypes through electrochemical methods

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Abstract:

Prussian blue analogues (PBAs) on molecular scale PBAs, octametallic units based in our case on Fe₄Co₄ cages, are robust in solution and can be therefore integrated in nanomaterials. Similarly to the polymeric parent compound PBAs, the π -character of the cyanide bridge ensures the electronic communication between the metal centres resulting in the occurrence of a photo- or thermally-induced metal-to-metal Electron Transfer Coupled to a Spin Transition (ETCST). Moreover, differently from the polymer, the cube assembly can be studied by electrochemical methods, for which it shows interesting redox behaviour with up to nine oxidation states¹. The stability in solution of the molecule is due to the capping of each cation by organic *fac*-tridentate ligands. In our group we are using scorpionates ligands like tris-pyrazolylborate (Tp) and tris-pyrazolylmethane (Tpm) which can also act as "linkers" among cubes thanks to their functionalization with electropolymerizable groups (e.g. thiophene derivatives)². Such connection is made by cyclic voltammetry, a wet chemistry approach, permitting the growth of a film with controlled thickness. CV, AFM, XPS and XAS analysis confirm the stability of the cage after deposition and the preservation of the properties of the bulk. Finally, with the aim of integrating these obtained films into prototypes of two-electrodes devices, a top electrode was deposited to measure the electric activity of the film, which showed memristive-like effect.



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Low frequency noise in nanoparticle-molecule networks: a pertinent metric for in-materio reservoir computing.

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Nanoparticles-molecules-networks (NMNs) are 2D arrays of molecularly functionalized nanoparticles connected on their periphery by several electrodes, which are used as a versatile platform to study the basic electron transport and optical properties in molecular electronics.¹ Several studies have demonstrated their potentiality to implement devices for unconventional computing like reconfigurable logic gates and neuro-inspired reservoir computing (RC).² The spatiotemporal dynamics inside the RC network generate noise that can be measured at the output electrodes. In recent implementations of physical reservoir computing (RC) with various nanometarials and nanodevices, the relationship between the low-frequency noise (LFN, *i.e.* flicker noise, also referred to as 1/fⁿ noise) and the computational ability of the RC was assessed with the objective to optimize the RC performances.³



Here, we compare the LFN behaviors of NMNs hosting the alkyl chains (octanethiol), fatty acid oleic acids (oleylamine), redox molecules (polyoxotungstate) and photoisomerizable molecules (azobenzene).⁴ The LFN of octanethiol-NMNs and oleylamine-NMNs obeys the Hooge law⁵ with a frequency exponent n close to 1 and 1.2, respectively. The slight difference between the two NMNs is ascribed to the different molecule/gold bonding (thiol vs. amine groups). A larger frequency exponent, $n \approx 1.4-1.5$ is

observed for the polyoxotungstate-NMNs and azobenzene-NMNs (in the *cis* isomer). In the case of the azobenzene-NMNs, we interpret this behavior as a consequence of the inelastic scattering of electron transport by the azobenzene vibrational modes.⁶ In the case of polyoxotungstate-NMNs, we propose a current-driven stochastic redox switching of the molecules inserted between the gold nanoparticles.⁷ From these results, we conclude that the polyoxotungstate-NMNs and *cis*-azobenzene-NMNs are the most suitable for the implementation of in-materio reservoir computing devices.

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Room Temperature Study on Unconventional Growth of Non-Planar Phthalocyanines in the Submonolayer Regime

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Abstract:

Non-planar metal-phthalocyanines (MPcs) are highly promising molecules for the development of various devices such as sensors [1] or light-emitting diodes [2] due to their exceptional stability in air and vacuum, along with their ability to absorb visible light. In addition, these MPcs possess a permanent dipole, oriented either up or down, which can be modified by external stimuli such as annealing [3], applied bias voltage [4], and ultraviolet radiation [5]. This dipole modulation alters the contact potential difference [3], offering a foundation for exploring molecular switches. The ability to control these stimuli paves the way for future research in this area.

In this ultra-high vacuum (UHV) study, room temperature scanning tunneling microscopy (RT-STM) reveals, in contrast to previous findings [6,7], that chloroaluminium phthalocyanine (CIAIPc) submonolayers are predominantly composed of molecules with their Cl atoms facing the substrate (Cldown or dipole-up orientation, visualized as 4-lobed features in Fig. 1a,b), and are stable enough to be imaged on Au(111) at RT. Additionally, an alternative molecular conformation, appearing as a triangular feature in STM images, was also observed at both low and high coverages (Fig. 1 a,c). This phthalocyanine imaging mode likely indicates a tilted molecular orientation, previously reported for CIAIPc on Ag(111) and VOPc on Au(111), but not for CIAIPc on Au(111) [5,8]. Upon annealing at 150°C, the Cl-down and tilted molecules switch to a Cl-up (dipole-down, square feature with central bright protrusion, Fig. not shown) conformation. Notably, as molecular coverage increases, we observed the unexpected formation of a bilayer structure (Fig. 1d), consisting of Cl-up molecules in the bottom layer and Cl-down molecules in the top layer, prior to completing the first monolayer.



Fig. 1: (a) Large scale STM image of AICIPc molecules deposited on Au(111) at sub-molecular coverage (50x50 nm^2 , $V_{tip} = -1.4V$, $I_t = 5.6pA$), (b,c) close-up views of domains composed of Cl-down (5x5 nm^2 , $V_{tip} = -1.11V$, $I_t = -1.11V$ 11pA) and tilted (5x5 nm², V_{tip} = -1.9V, I_t = 7.5pA) molecular conformations, respectively, (d) bilayer structure built of Cl-down and Cl-up molecules in the 2^{nd} and 1^{st} layers, respectively (30x30 nm², V_{tip} = -0.8V, I_t = 5pA).

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Synthesis and characterization of the switching properties of redox active hybrid polyoxometalates

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Abstract:

Polyoxometalates (POMs), are nanometric oxoclusters composed of transition metals in their highest oxidation state with remarkable redox properties,^{1,2} which make them promising for numerous applications, as for example in spintronics. Indeed, integration of these electrically switchable molecules into magnetic tunnel junctions (MTJs) could open perspectives for next-generation spintronic devices³. In this presentation, we will show the synthesis of two types of hybrid POMs: those from the Keggin family (TBA)₃[PW₁₁O₄₀(SiC₃H₆SH)₂] and those from the Lindqvist family (TBA)₂[V₆O₁₃{(O-CH₂)₃-CNHCO-(CH₂)₄-C₃H₅S₂)₂] (TBA stands for tetrabutylammonium).^{4,5} They both display the required physical and morphological features to be integrated in a MTJ. The characterization of their redox and photoredox properties in solution and at the solid sate will be presented. Additionally, we will expose how we control the organization of the hybrid POMs in monolayers on gold substrates to gain a deeper understanding of their behavior at the nanoscale.

The ultimate goal of this project is to integrate these redox-active POM layers into MTJs to explore how redox state changes, induced by an electric field or optical irradiation, affect the electronic levels and, consequently, the TMR measured in the device. This approach could pave the way for multifunctional spintronic devices with innovative in situ control of properties.



Figure : (left) Scheme of the $(TBA)_3[PW_{11}O_{40}(SiC_3H_6SH)_2]$ and cyclic voltammetry recorded at a glassy carbon electrode, 1mM in acetonitrile with TBAPF_61M (0.1 V.s⁻¹) (right) Scheme of the $(TBA)_2[V_6O_{13}\{(O-CH_2)_3-CNHCO-(CH_2)_4-C_3H_5S_2\}_2]$ and formation of the reduced form by UV light irriadation of a 0.5 mM solution in DMSO

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T Thermoelectric Ability of Organo-Ruthenium and Organo-Iron Molecular Junctions

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Abstract:

Quantum mechanical investigations of the thermoelectric properties of organometallic molecular junctions were performed. They reveal that the single-level tunnelling model used to interpret the electronic transmission properties can lead to erroneous results when several molecular levels are present near the Fermi energy.¹ The localisation of some of these levels on the metal centre and pendant ligands can induce quantum interference. This has a direct effect on the thermoelectric ability of the molecular junction.



Top: lateral view of the computational unit cell of the $Au | Fe(cyclam)(C \square C-Ph-S)_2 | Au junction.$ Bottom: calculated transmission functions at zero bias of flat (blue) and tip (orange) configuration-type $Au | Fe(cyclam)(C \square C-Ph-S)_2 | Au (left) and Au | Ru(dppe)(C \square C-Ph-S)_2 | Au) (right) junctions (dppe = diphenyl$ diphosphino-ethane.

The density functional non-equilibrium Green's function (DFT-NEGF) methodology was used to study the electrical transport properties. Several factors such as functional, Fermi energy dependence, kpoint sampling, bias voltage, electrode shape and partial coordination were evaluated. Junctions based on charged molecules were also investigated implying a specific computational protocol. This work is directly linked to the experimental work performed by the groups of S. Rigaut (Univ. Rennes), E. Scheer (U. Konstanz) and D. Vuillaume (IEMN, Villeneuve d'Ascq) (syntheses and characterizations of the molecular precursors, fabrication and physical measurements of the molecular junctions).

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NEXTRON MICRO PROBE SYSTEM

	Lundi 14 octobre 2024	Mardi 15 octobre 2024	Mercredi 16 octobre 2024
10h			
-ų -ų		Invité - Elke Scheer	Invité - Gabor Molnar
11 1		Emma Aoustin	Dominique Vuillaume
10h-		Volodymyr Malytskyi	10h30 à 11h10 Pause café
		10h50 à 11h25 Pause café	Amandine Bellec
11h-12h			Rui Li
		Invité - Xiaocui Wu	Clôture
ų		Samuel Decorps	
12h-13		Industriel Nextron	
13h-14h	13h à 14h Accueil	12h45 à 14h15 Déjeuner	
14h-15h	Introduction		
	Invité - Jerome Lagoute	Invité Francesca Moresco	
	Xiaonan Sun	Stéphane Pons	
15h-16h	15h15 à 15h50 Pause Café	15h15 à 15h50 Pause Café	
17h			
47h	Invité - Pavel Jelinek	Invité - Daniel Hernangomez	
16h-17h	Invité - Pavel Jelinek Colin Van Dyck	Invité - Daniel Hernangomez Elodie Dureau	
17h-18h 16h-17h	Invité - Pavel Jelinek Colin Van Dyck 16h50 à 18h30 Session poster & indus	Invité - Daniel Hernangomez Elodie Dureau	
-19h 17h-18h 16h-17h	Invité - Pavel Jelinek Colin Van Dyck 16h50 à 18h30 Session poster & indus Cocktail de bienvenue	Invité - Daniel Hernangomez Elodie Dureau	
18h-19h 17h-18h 16h-17h	Invité - Pavel Jelinek Colin Van Dyck 16h50 à 18h30 Session poster & indus Cocktail de bienvenue	Invité - Daniel Hernangomez Elodie Dureau	







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