9th International Conference on
Molecular Electronics

Paris, France
December, 17-20th 2018

# Ninth international edition of Molecular Electronics

December 17-20th, 2018, Paris, France.

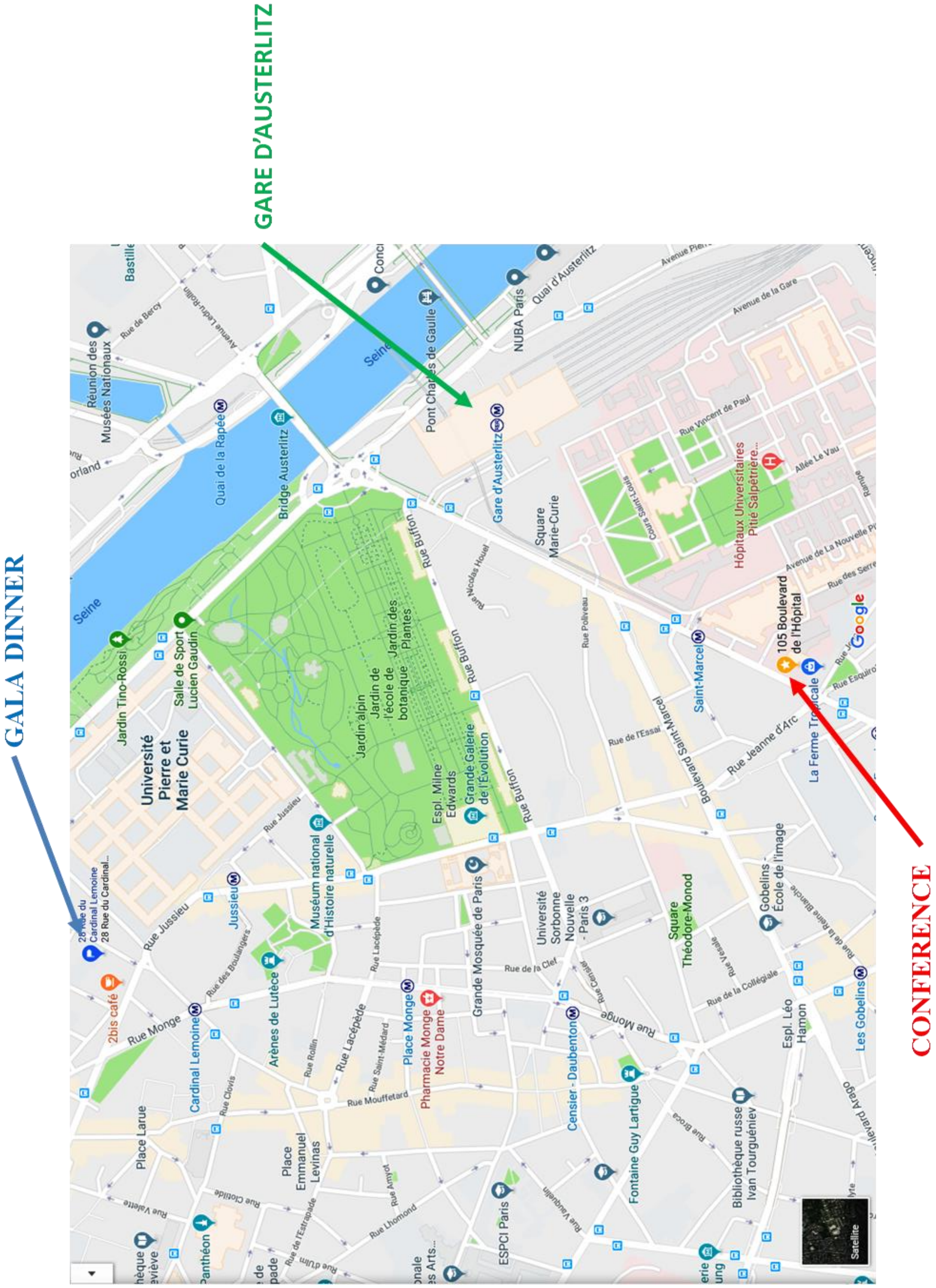
Following the success of the previous editions of **ElecMOL 1-8** (2002, 2004, 2006, 2008, 2010, 2012, 2014 and 2016), the researchers of the “Interfaces, Traitements, Organisations et DYnamique des Systèmes” (ITODYS) and of “Matériaux et Phénomènes Quantiques” (MPQ) laboratories are happy to organize the 9th edition of the international conference **ElecMol,** held in Paris at Sorbonne University from **December 17 to 20th 2018**.

The main purpose of the conference is an up-to-date scientific exchange on recent advances in the field of molecular electronics, gathering researchers from all over the world around top-level plenary speakers. This reunion is also an opportunity for the development of national and international collaborations between academic and private partners at the highest level. The conference will focus on recent advances in molecular and organic electronics in the fields of:

**T1** - Single Molecule & Large Area: Junctions/Memories & Switches
**T2** - Organic Electronics and Spintronics: Materials & Devices
**T3** - Organic Optoelectronics & Photonics: Materials & Devices
**T4** - 2D materials, Nanotubes & Nanowires
**T5** - Self-Assembly & Supramolecular Architectures
**T6** - Scanning Probe Microscopies & Near Field Approaches
**T7** - Molecular Theoretical Modelling
**T8** - Bioinspired Approaches & Biomimetic Devices

**On behalf of the scientific committee and the local organizers we welcome you in Paris and we wish you a successful meeting !!!**

# MAP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Maria Luisa Della Rocca, *MPQ*, University of Paris Diderot

# MONDAY 17TH

## Session 1

| | |
|---|---|
| 13.40-14.20 | **Rudoplh MARCUS (keynote lecture)**<br>Recent Developments in Transfers of Electrons and other Transfers |
| 14.20-14.40 | **Dominique VUILLAUME**<br>Charge Transport through Electro-Active Layers of Polyoxometalates |
| 14.40-15.00 | **Olivier FONTAINE**<br>Molecular electrochemistry in ionic liquids for better supercapacitors |
| 15.00-15.20 | **Rémi AVRILLER**<br>Charge-transfer chemical reactions for molecular populations confined inside a nanofluidic Fabry-Perot cavity |
| 15.20-15.35 | **Megumi AKAI KASAYA**<br>Stochastic Conductance Switching of Single Polyoxometalate Molecule at a Junction in Carbon Nanotube Device |
| 15.35-15.50 | **Omer SHER**<br>Comparative study of molecular place exchange in nano molecular electronic device |

15.50-16.10 ………COFFEE BREAK

## Session 2

| | |
|---|---|
| 16.10-16.50 | **Christian NIJHUIS (keynote lecture)**<br>Transition from Direct to Inverted Marcus Regions in Highly Efficient Molecular Diodes |
| 16.50-17.10 | **Davide STEFANI**<br>Large Conductance Variations in a Mechanosensitive Single/Molecule Junction |
| 17.10-17.25 | **Zhijin CHEN**<br>Molecular Devices with Novel Electric Function Based on Porphyrin-Imide Single Molecule Rectifier |
| 17.25-18.05 | **Norbert KOCH (keynote lecture)**<br>Energy levels at interfaces with organic semiconductors: Fermi level pinning, doping and heterogenity |
| 18.05-18.25 | **Cyril PORIEL**<br>Dihydroindenofluorenes as hosts for phosphorescent OLEDs |
| 18.25-18.40 | **Clément REYNAUD**<br>Ferrocene-based molecular diodes integrated in plasmonic nanocavities via click chemistry |
| 19.00 | **COCKTAIL** |

# Recent Developments in Transfers of Electrons and other Transfers

Rudolph A. Marcus
Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena CA 91125 USA

## Abstract

In recent years experiments have been made on ultrafast electron transfers with reaction times~ 100 fs or somewhat less and we discuss some of these results. In these short times solvent dynamics plays essentially no role in the reaction rate and vibrational effects are expected to be dominant. There are “electron transfer active vibrations” and “electron transfer inactive vibrations” at these short times, though the data thus far are relatively sparse. We discuss an approximate theory for such systems which are expected to be ”electronically adiabatic” and so independent of the coupling strength when it is sufficiently large.[1] This independence differs from that which arises when the solvent dynamics is so slow that it rather than the electron transfer becomes rate-controlling.

A quite different topic, which we comment on if time permits, is how one can adapt the electron transfer formalism to other types of transfers, such as group transfers in enzymes, and in this way apply the ET formalism to single molecule studies of biomolecular machines.[2]

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1. R.A. Marcus and M.E. Michel-Beyerle, manuscript in preparation
2. Some of our current findings on a rotary motor $F_1$ATPase, in collaboration with Dr. S. Volkan-Kacso, are described in *Quarterly Reviews of Biophysics*, **50**, 2017, no. 14, 1-13.

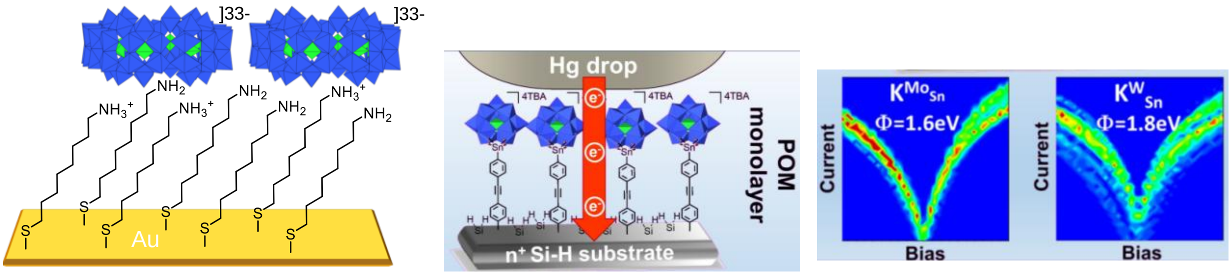
# Charge Transport through Electro-Active Layers of Polyoxometalates

Maxime Laurans, [a] Kevin Dalla Francesca,[a] Florence Volatron,[a] Stéphane Lenfant,[b] David Guerin,[b] G. Izzet, [a] A. Proust, [a] D. Vuillaume,[b]

*[a] Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, IPCM, 4 Place Jussieu, F-75005 Paris, France. Email: anna.proust@sorbonne-universite.fr*
*[b]Institute for Electronics Microelectronics and Nanotechnology (IEMN), CNRS, Lille Univ., Av. Poincaré, F-59652 Villeneuve d'Ascq, France. Email: Dominique.vuillaume@iemn.fr*

## Abstract:

Polyoxometalates (POMs) are nano-scaled molecular oxides endowed with a remarkable structural diversity and outstanding redox properties. This makes them fascinating electro-active molecules to be integrated in functional materials such as multi-level non-volatile memories or other nano-electronic devices.[1-2] Yet the shaping of POMs layers onto electrodes is still a sticking point, albeit essential to improve the control on the POMs/electrode interface and hence the ultimate electrical properties. We have developed several routes to the deposition of POMs: by electrostatic deposition of POMs onto a preformed SAM on Au or by direct covalent grafting of POM hybrids onto n-Si(100)[3], which gives compact monolayers. We will present them together with the transport properties of the resulting molecular junctions.[4-5]



*Left : scheme of the electrostatic deposition of* $[H_7P_8W_{48}O_{184}]^{33-}$ *onto 8-amino-1-octanethiol SAM on Au ; Middle : diazonium route to the covalent grafting of* $[PM_{11}O_{39}\{Sn(C_6H_4)C{\equiv}C(C_6H_4)\text{-}\}]^{4-}$ *(M = Mo, W) onto n-Si(100); Right: 2D-current histograms of Si-POM//Hg molecular junctions and the dependence of the tunneling barrier on the molecular nature of the POM*

## References:

[1] Chen, X. L.; Zhou, Y.; Roy, V. A. L.; Han, S. T., Evolutionary Metal Oxide Clusters for Novel Applications: Toward High-Density Data Storage in Nonvolatile Memories. *Adv. Mater.* **2018,** *30* (3), 1703950.
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# Molecular electrochemistry in ionic liquids for better supercapacitors

C. Bodin,[a,b] D. Zigah,[c] F. Favier, [a,b] O. Fontaine, [a,b]

[a]*Institut Charles Gerhardt Montpellier, UMR 5253, CC 1502, Université Montpellier, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France*
[b]*Réseau sur le Stockage Electrochimique de l'énergie (RS2E), FR CNRSS*
[c] *Univ. Bordeaux, ISM, UMR 5255, F-33400 Talence, France.*

*olivier.fontaine@umontpellier.fr*

## Abstract:

Kinetics of electrochemical reactions are several orders of magnitude slower in solids than in liquids as a result of the much lower ion diffusivity.[1] On the other hand, the solid state maximizes the density of redox species, which is at least two orders of magnitude lower in molecular solutions because of solubility limitations. For such devices the ideal system should endow the liquid state with a density of redox species close to the solid state. Here we report an approach based on biredox ionic liquids (ILs) to achieve towards bulk like redox density at liquid like fast kinetics, Fig. 1a. The cation and anion of these biredox ILs bear moieties that undergo very fast reversible redox reactions.1 As a first demonstration of their potential for high-capacity / high-rate charge storage, we used them in supercapacitors with specific capacitance of 200 F/g and 370 F/g respectively for 0.5 M of biredox ILs in BMimTFSI and for pure biredox ILs at 60°C (Fig. 1b).[2] This new class of functional materials opens up a wide new field in redox materials and their applications in energy storage and beyond.

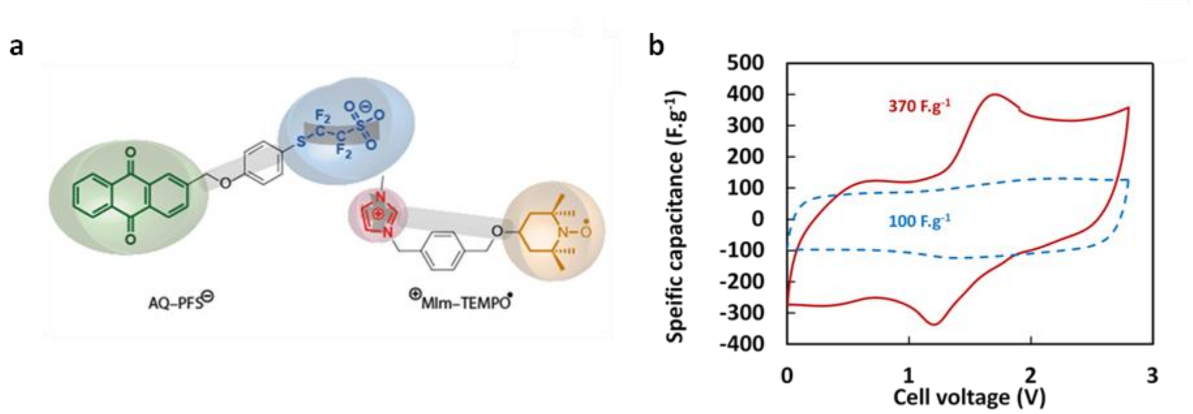

**Figure 1| charge storage in EDLC with the biredox IL enhanced supercapacitor.** a, Structure of the biredox IL comprising a perfluorosulfonate anion bearing anthraquinone (AQ–PFS–) and a methyl imidazolium cation bearing TEMPO (MIm+–TEMPO●). b, Cyclic voltammetry at 5 mV·s-1 with pure biredox IL at 60°C (red solid line) and pure BMImTFSI (blue dashed line) made with PICA activated carbon as electrodes.

## References:

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2. Mourad, et al., Biredox ionic liquids: high-energy supercapacitors through near bulk redox density in the liquid state. *Nature materials,* (2017)

# Charge-transfer chemical reactions for molecular populations confined inside a nanofluidic Fabry-Perot cavity

R. Avriller[a]

[a]*Univ. Bordeaux, CNRS, LOMA, UMR 5798, F-33405 Talence, France*

## Abstract:

Recent progresses in nanotechnology led to a new generation of nano-structures playing the role of electromagnetic cavities, like plasmonic structures [1], organic micro-cavities [2] and *nano-fluidic Fabry-Pérot cavities* [3]. The experimental proof of reaching the *electronic strong-coupling regime* for *cavity-confined molecular populations* was reported recently [2,3]. The confinement has important consequences on the physico-chemical properties of the embedded molecules, with remarkable effects on *the kinetics of chemical reactions* [2].

In this work, we propose to use a nano-fluidic Fabry-Pérot cavity as an original and innovative *chemical nano-reactors,* in order to *initiate, probe* and *modulate* the rate of chemical reactions at the nanoscale (see Fig.1). We develop a *generalized-form* of *Marcus theory* [4] for charge-transfer chemical reactions, taking into account the coupling to a non-equilibrium hybrid-polariton mode of the cavity [5]. We show that despite *strong dissipation* and *dephasing* due the solvent molecules, the light-matter coupling is strong enough to alter significantly the *reaction landscape* of the chemical reaction. Depending on the *concentration of reactants* and *detuning of the cavity* with respect to the molecular transition, we show the possibility of either slow-down or increase the rate of the chemical reaction.

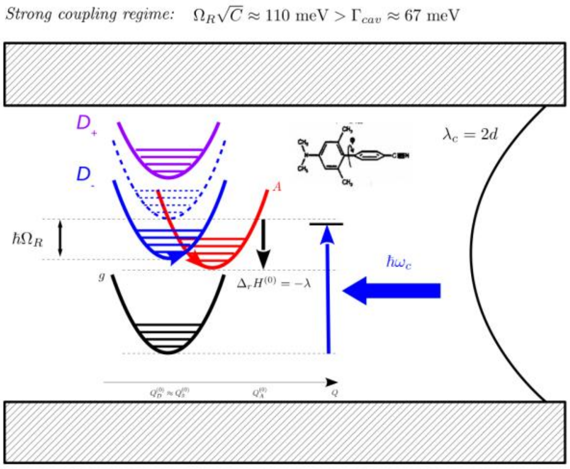

*Fig.1: Scheme of a chemical reactor made of a nano-fluidic Fabry-Perot cavity. A solution of reactants undergoes a charge transfer chemical reaction inside the optical cavity.*

## References:

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# Stochastic Conductance Switching of Single Polyoxometalate Molecule at a Junction in Carbon Nanotube Device

○Megumi Akai-Kasaya[a,b], Goh Kian Lian[b]

[a] Graduate School of Engineering, Osaka University, *2-1 Yamadaoka, Suita, Osaka 565-0871, Japan.*
*:e-mail: kasaya@prec.eng.osaka-u.a.cjp*
[b] PROSTO-JST, 4-1-8, Honcho, Kawaguchi-shi, Saitama 332-0012, Japan.

## Abstract:

Fluctuation of molecule is intrinsic phenomena in nature and considered to be an origin of life. For example, in living cells, molecular fluctuations are a source of heterogeneity among cells sharing a common genetic background. We have investigated discrete-charge-fluctuation dynamics of a single molecule adsorbed on a single walled carbon nanotube (SWNT) in room temperature [1] and demonstrated a week signal detection in a stochastic resonance SWNT device by utilizing internal spontaneous noise that is superimposition of respective fluctuation of additive polyoxometalate (POM) molecules [2]. Moreover, we found generation of spontaneous spikes, which is similar to nerve impulses of neurons, from an extremely dense and random SWNT/POM network [3]. Stochastic fluctuation and state dynamics of nanomaterials are now attracted much attention from in terms of development of bio-inspired technology and neuromorphic engineering.

Here we show a stochastic conductance switching of single POM molecule, where the molecule is at junction between SWNT and metal electrodes in a device structure. It is known that charge transport through the single molecule is influenced by charge states of redox-active molecule, which in turn affect the conductance of the molecule. POM molecule is redox active with high multiple-redox ability, which means that a POM is capable of having multiple charges. We fabricate a bottom contact SWNT device with single or few numbers of SWNT bridging between gold electrodes. POM molecule was inserted into junction between SWNT and gold after the device was soaked into a solution with POM dissolved. Figure 1 (a) shows current flows between electrodes with applied DC voltage of 50mV measured at room temperature in air. We consider that the conductance switching showing clear zero "OFF state" and a certain maximum "ON state" result from a current path through single POM and single SWNT path as shown in Figure 1 (b). The ON/OFF state difference was always more than three orders of magnitude, though ON state conductance depends on samples as it varied 0.004–0.3$G_0$. State change are various, such as abrupt and continuous, and sometime shows stepwise middle states. The fluctuation is very slow and robust against change of applied voltage. We are trying to control the switching by external force to clarify the fluctuation phenomena and open possibility to utilize the state dynamics of single molecule.

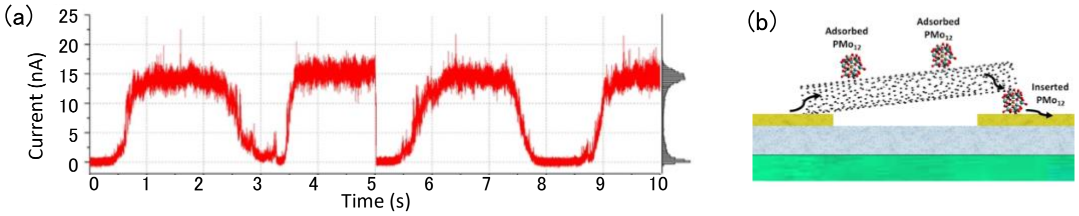

Figure 1 (a) Current showing stochastic conductance fluctuation of single POM molecule with 50mV DC voltage apply. (b) Schematic view of SWNT device with single POM junction.

[1] A. Setiadi, H. Fujii, M. Akai-Kasaya et al., "Room-temperature discrete-charge-fluctuation dynamics of a single molecule adsorbed on a carbon nanotube", *Nanoscale* **9**, 10674 (2017)

[2] H. Fujii, A. Setiadi, Y. Kuwahara, and M. Akai-Kasaya, "Single walled carbon nanotube-based stochastic resonance device with molecular self-noise source", *Appl. Phys. Lett.* **111**, 133501 (2017)

[3] H. Tanaka, M. Akai-Kasaya, T. Asai et al., "A Molecular Neuromorphic Network Device consisting of Single-Walled Carbon Nanotubes complexed with Polyoxometalate", *Nature Communication* **9**, 2693 (2018)

# Comparative study of molecular place exchange in nano molecular electronic device

Omer Sher[1], Yuanyuan Han[1], Aqib Hayat[1], Andreas Orthaber[2], Francois Calard[3], S. H. M. Jafri[1], Françoise Serein-Spirau[3], and Klaus Leifer[1]
*[1]Applied Materials Science, Department of Engineering Sciences, Uppsala University, 75120 Uppsala, Sweden.*
*[2]Department of Chemistry, Ångstrom Laboratories, Uppsala University, PO box 534,75120 Uppsala, Sweden.*
*[3]Institut Charles Gerhardt de Montpellier, UMR CNRS 5253, Architectures Moléculaires et Matériaux Nanostructurés, Ecole Nationale Supérieure de Chimie de Montpellier, 8, rue de l'Ecole Normale, 34296 Montpellier Cedex, France.*
*Omer.sher@angstrom.uu.se*

The nano molecular electronic device (nanoMOED) platform is a sub-20nm device with extremely low power consumption and it is the first few molecular electronic device operating at ambient conditions[1]. The core of the nanoMOED device consists in nano-electrodes that are connected by functionalized gold nanoparticles (AuNPs). The key fabrication elements to bring this platform to the desired electrical properties and performance are the functionalization of the AuNPs with organic conductive molecules[2,3] and the establishment of conductive junctions between the Au surface and the short chained (1-5nm) molecule.

In this work, we analyze ligand or place exchange in the nanoMOED devices for two cases: A) using same molecules for place exchange (type 2 molecules), but different functionalization shells (type 1 molecules), B) use of the same functionalization molecule but different molecules used for place exchange. For (A), the AuNPs were functionalized with 3 types of molecules type 1, with alkane-thiol molecules, with trityl terminated octane molecules and with a mixture of alkane-thiol and so called stopper molecules (ω-trityl substituted alkanedithiol)[4]. These 3 types of functionalized AuNPs are then positioned in between the nanogaps. These molecules are isolating molecules, and are replaced in the place exchange reaction, with conductive molecules, here biphenyl-dithiol (BPDT). In the case B, we use different molecules containing phenyl rings to replace the molecules of type 1.

We have shown by electrical measurements that place exchange reaction is successful. From a comparison of the efficiency of the place exchange reaction for both cases A and B we find that the place exchange reaction sensitively depends on the length of the place exchange molecules, on the morphology of the functionalization shell of the AuNPs and on the measured AuNP interparticles distances.

These findings are an important corner stone to build a molecular electronic device where one up to a few molecules determine the electrical properties of the device. In its current form, the device is ready to be introduced into a real application.

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# Transition from Direct to Inverted Marcus Regions in Highly Efficient Molecular Diodes

Christian A. Nijhuis
*National University of Singapore. Department of Chemistry and Centre for Advanced 2D Materials,*
*3 Science Drive 3, Singapore 117543, Singapore*
chnmca@nus.edu.sg

The mechanisms of charge transport can be, generally speaking, described by two theories: activationless coherent tunnelling processes which can be described by the Landauer theory [1], or thermally-activated charge transfer which can be described by the Marcus theory [2]. In molecular junctions with redox-active molecules, the mechanism of charge transport may be in between these two extremes [3]. For example, low activation energies are frequently observed in molecular junctions but cannot be readily explained, and activationless transport has been reported for very long molecules [4].

We have been studying the mechanisms of charge transport across molecular diodes inside EGaIn junctions based on self-assembled monolayers of with redox-active ferrocenyl (Fc) groups [5]. This system has been well-characterized and yields molecular diodes with exceptionally large rectification ratios [6]. Here, the Fc units oxidize only in one direction of bias and the Fc$^+$ interaction with the negatively charged top-electrode is much stronger than in opposite bias when the Fc units are neutral. This bias dependent change in the electrostatic interaction results in highly efficient molecular diodes with rectification ratios of nearly $10^6$. We used this system to demonstrate experimentally the transition from the Marcus to the inverted Marcus region via intra-molecular orbital gating [7]. In the inverted Marcus region, charge transport is incoherent yet virtually independent of temperature; these findings fit well to a theoretical model that combines Landauer and Marcus theories [3]. As a group, these findings demonstrate that molecular junctions can operate in the grey zone in between pure electrochemical and tunnelling extremes which can be used in the future design of molecular junctions.

**References**

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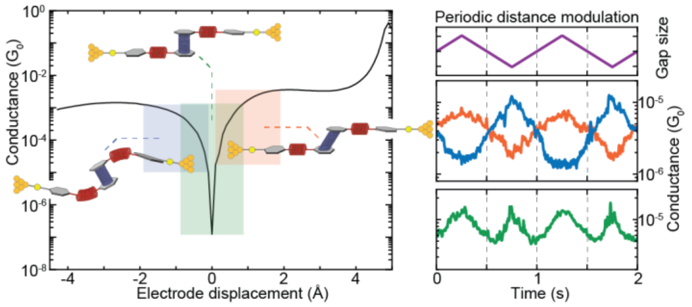
# Large Conductance Variations in a Mechanosensitive Single–Molecule Junction

Davide Stefani,[a] Kevin J. Weiland,[b] Maxim Skripnik,[c,d] Chunwei Hsu, [a] Mickael L. Perrin, [a,e] Marcel Mayor,[b,f,g] Fabian Pauly, [c,d] and Herre S. J. van der Zant [a]

*[a] Kavli Institute of Nanoscience, Delft University of Technology, 2600 GA Delft, The Netherlands*
*[b] Department of Chemistry, University of Basel, 4056 Basel, Switzerland*
*[c] Okinawa Institute of Science and Technology Graduate University, Onna-son, Okinawa 904-0395, Japan*
*[d] Department of Physics, University of Konstanz, 78457 Konstanz, Germany*
*[e] Empa, Swiss Federal Laboratories for Materials Science and Technology, Transport at Nanoscale Interfaces Laboratory, 8600 Dübendorf, Switzerland*
*[f] Karlsruhe Institute of Technology (KIT), P.O. Box 3640, 76021 Karlsruhe, Germany*
*[g] Lehn Institute of Functional Materials, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, China*

## Abstract:

The appealing feature of molecular electronics is the possibility of inducing changes in the orbital structure through external stimuli. This can provide functionality on the single molecule level, which can be employed for sensing or switching purposes, if the associated conductance changes are sizable upon application of the stimuli. Here, we show that the room-temperature conductance of a spring-like molecule can be mechanically controlled up to an order of magnitude by compressing or elongating it. Quantum chemistry calculations indicate that the large conductance variations are the result of destructive interference effects between the frontier orbitals that can be lifted by applying either compressive or tensile strain to the molecule. When periodically modulating the electrode separation, a conductance modulation at double the driving frequency is observed, providing a direct proof for the presence of quantum interference. Furthermore, oscillations in the conductance occur when the stress built up in the molecule is high enough to allow the anchoring groups to move along the surface in a stick-slip-like fashion. The mechanical control of quantum interference effects results in the largest gauge factor reported for single-molecule devices up to now, which may open the door for applications in, e.g., a nano-scale mechanosensitive sensing device functional at room temperature.



*(Left) Possible behaviour of the molecule under the force applied by the electrodes: compression (left) relaxed (center) and elongation (right). The simulated conductance as a function of the applied mechanical stress is displayed as the black line; (Right) Experimental distance-modulation traces. The blue, orange and green lines (middle and bottom panel) represent three different conductance measurements; the purple line (top panel) represents the gap size. The conductance responds to the modulation either in-phase (orange), in antiphase (blue), or with double the modulation frequency (green). This is related to the junction configuration at the start of the modulation (stretched, relaxed and compressed), represented by the same colour areas in the left panel.*

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# Molecular Devices with Novel Electric Function Based on Porphyrin-Imide Single Molecule Rectifier

Zhijin Chen,[a] Yosuke Tani,[b] Ken-ichi Yamashita,[b] Takuji Ogawa.[b]
[a]*Department of Chemistry, School of Science, Osaka University, Osaka, Japan*
*Email: chenz14@chem.sci.osaka-u.ac.jp*
[b] *Department of Chemistry, School of Science, Osaka University, Osaka, Japan.*

## Abstract:

Molecular rectifier is one of the most important elementary components which conducts in only one direction. In previous study, perpendicularly connected porphyrin-imide (PorIm) has been studied as a molecular rectifier[1] (Fig1.a). In PorIm, highest occupied molecular orbital (HOMO) localizes in porphyrin part and lowest unoccupied molecular orbital (LUMO) localizes in imide part. Unlike the original molecular rectifier proposed by Aviram and Ratner[2], which localizes HOMO and LUMO by introducing insulator between them, PorIm is the first molecule that localizes its HOMO and LUMO by perpendicular spatial configuration between porphyrin plane and imide plane (Fig1.b).

The rectifying behaviour of PorIm was confirmed experimentally by scanning tunnel microscopy (STM), and the rectifying direction of electron flow is from porphyrin (donor) to imide (acceptor) (Figure 1c, d). This rectifying direction is found to be opposite to the direction of Aviram and Ratner's model, which indicates a different molecular orbital matching mechanism. By using molecules utilizing the rectifying behaviour of porphyrin-imide rectifier, functional materials with novel functionalities can be realized. These functional materials are expected to give huge impact to electric circuits because they can reduce the size of electric circuits. For example, by using AgS based atomic switch which shows memory functionality by one molecule, the occupying area of one memory unit can be reduced to one quarter of conventional silicon-based devices.

Here in this presentation the synthesis and measurement of molecular devices with novel electric functions utilizing porphyrin-imide molecular rectifiers will be introduced. Electric properties will be measured by break junction method or point-contact current imaging atomic force microscopy (PCI-AFM).

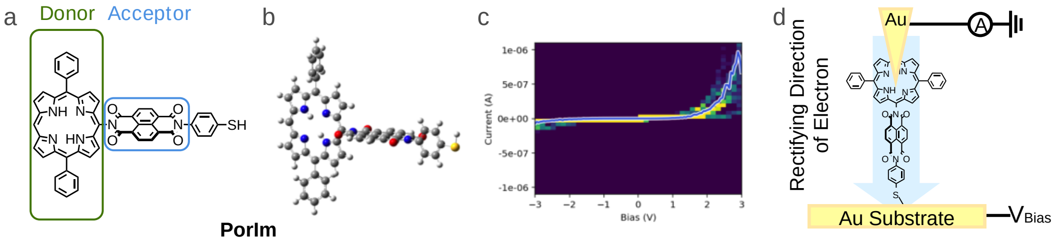

*Figure 1 (a) Structure of Porphyrin-imide donor-acceptor molecule. (b) Stable conformation of PorIm. (c) 2D histogram of single molecule I-V characteristic of PorIm.*

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# Energy levels at interfaces with organic semiconductors: Fermi level pinning, doping, and heterogeneity

Norbert Koch[a,b]

[a]Humboldt-Universität zu Berlin, Institut für Physik, Berlin, Germany. Email: norbert.koch@physik.hu-berlin.de
[b]Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany.

Abstract:

The electronic properties of interfaces with organic semiconductors are crucial for the functionality and efficiency of electronic and optoelectronic devices. Therefore, a comprehensive understanding of interfacial phenomena is needed to push the development of superior deices. A key mechanism that can induce interfacial charge transfer, even in the absence of chemical interactions, is Fermi level pinning of the occupied/unoccupied frontier energy level manifold of the organic semiconductor. As shown for prototypical contacts with inorganic semiconductors and electrode materials, this helps realizing ohmic contacts as well as tuning the interface energy levels over extremely wide ranges. While doping of inorganic semiconductors has become a standard technological component, doping of organic semiconductors remains challenging. The impact of doping an organic layer in a hybrid inorganic/organic pn-junction is analyzed and can be rationalized within established semiconductor physics, yet considering the particularities of the organic compound.

Surface and interface lateral homogeneity is a key for determining the ionization energy of an organic semiconductor, and for robust device functionality. In practice, however, inhomogeneities are difficult to eliminate. The consequence of work function inhomogeneity of a substrate used for organic semiconductor deposition on the interface energy levels is presented, and pitfalls for reliable ionization energy determination with photoemission spectroscopy are identified.

# Dihydroindenofluorenes as hosts for phosphorescent OLEDs

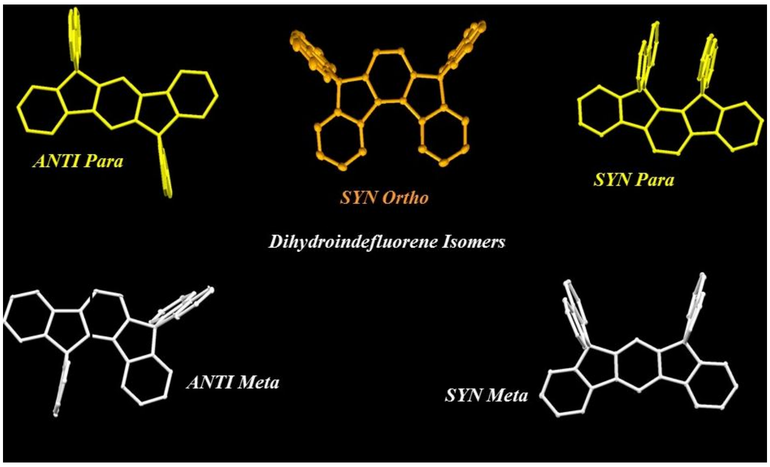
Cyril Poriel,[a] Joelle Rault-Berthelot,[a] Maxime Romain,[a] Bernard Geffroy,[bc] Denis Tondelier[b]

[a] Univ Rennes, CNRS, ISCR- UMR 6226, F-35000 Rennes, France [b] *LPICM, CNRS, Ecole Polytechnique, Université Paris Saclay, 91128, Palaiseau, France;* [c]*LICSEN, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif-sur-Yvette Cedex, France.*

E-mail: cyril.poriel@univ-rennes1.fr

## Abstract:

Regioisomerism, also called positional isomerism, is an important concept in organic chemistry which can have remarkable consequences on the properties of molecules.[1-4] Indeed, a simple structural modification can drastically influence the electronic and physical properties of an organic semi-conductor (OSC), which in turn strongly modifies the performance and stability of the corresponding electronic device.[5-6] Although very promising, this concept remains nevertheless rarely used in optoelectronics. In this work, we demonstrated the impact of regioisomerism to finely tune the singlet and triplet energies of a key class of materials, ie dihydroindenofluorene isomers, leading to efficient optoelectronic devices.[2-3, 7-8] This work reports hence the first structure-properties relationship study of the 5 positional isomers of dihydroindenofluorenes, ie *ortho* [2,1-*c*], *meta* [1,2-*a*] and [2,1-*b*] and *para* [1,2-*b*] and [2,1-*a*] dihydroindenofluorenes, highlighting the key influence of the bridge rigidification and of the linkages on the electronic properties.



This study has allowed combining within an extended $\pi$–conjugated molecule a high $E_T$ and excellent thermal/morphological stabilities. The proof of concept has been demonstrated through the first use of dihydroindenofluorenes as host in sky blue PhOLEDs.

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# Ferrocene-based molecular diodes integrated in plasmonic nanocavities via click chemistry

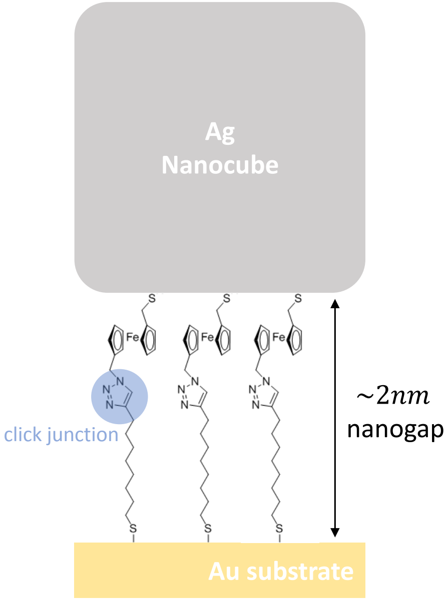
C. Reynaud[1], D. Duché[1], F. Pourcin[2], O. Margeat[2], J. Ackermann[2], D. Brunel[3], F. Dumur[3], D. Gigmes[3], C. Lebouin[4],R-M. Sauvage, G. Berginc, J-J. Simon[1] and L. Escoubas[1]

[1] Aix Marseille Univ, Univ Toulon, CNRS, IM2NP, Marseille, France
[2] Aix Marseille Univ, CNRS, Cinam, Marseille, France
[3] *Aix Marseille Univ, CNRS, Institut de Chimie Radicalaire, UMR7273, F-13397 Marseille (France)*
[4] *Aix-Marseille Univ, CNRS, MADIREL, Marseille, France*
[5] *4DGA/DS/MRIS, 75015 Paris, France*
[6] *Thales Optronics, Elancourt, France*

## Abstract:

Ferrocene-based molecules have been extensively studied during the past decade[1][2] and have already proven current rectification capabilities with measured rectification ratio $R = J(\frac{|-1V|}{|+1V|})$ above $10^3$.[3] Beside this electronic feature, SAM-based metal-insulator-metal (MIM) junctions are appealing because of their reduced thickness and simple processing compared to other expensive atomic layer deposition methods. One of these MIM approach consists into nanopatch antennas made of colloidal metallic nanoparticles deposited on another metallic substrate. These plasmonic structures are known to exhibit quasi total absorption of light at a given wavelength related to the size, shape, and material of the nanoparticles, leading to electric field enhancements up to two order of magnitude in the nanocavity created between the particle and the substrate.

In this work, we demonstrate that SAMs can be especially convenient to create nanopatch antennas based on silver nanocubes for two main reasons : i) they offer a very thin control of the nanogap which enhances the reproducibility of samples ii) they allow for downsizing of these gaps below the usual 3 nm limit imposed by the silver nanocube polymer surfactant, which triggers nonlocal effects that are now easier to study experimentally. Moreover, we synthetized and self-assembled dithiolated ferrocene-based molecules to be integrated in nanogaps where they act both as optical spacers and electronically active compounds. Because of their rectifying properties, we aim to measure optical rectification performed by the association of these molecular diodes plugged into resonating nanocavities where the light induces an alternative current in the form of surface plasmons. Because the orientation of the molecular diodes matters[2] , we worked on click chemistry methods to be able to self-assemble the dithiolated chains in a specific direction.



*Nanocube assembly via clickable ferrocene-based molecular diodes ensuring both proper orientation of the rectification and strong anchoring of the particle*

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# TUESDAY 18TH

| | |
|---|---|
| **Session 3** | |
| 8.30-9.10 | **Richard McCREERY (Keynote lecture)**<br>Photocurrents and Photoemission in All-Carbon Molecular Electronic Junctions |
| 9.30-9.30 | **Jan MOL**<br>Progress in graphene-based single-molecule electronics |
| 9.30-9.45 | **Michal VALASEK**<br>Spatial and Lateral Control of Functionality by Rigid Molecular Tripods: Towards Surface Mounted Devices |
| 9.45-10.00 | **Linda ZOTTI**<br>The Role of Oligomeric Gold-Thiolate Units in Single Molecule Junctions of Thiol-Anchored Molecules |
| | 10.00-11.00 POSTER SESSION & COFFEE BREAK |
| 11.00-11.40 | **Luisa TORSI (Keynote lecture)**<br>Single Molecule detection of Markers with a Label-free bio-electronic sensor |
| 11.40-12.00 | **Sébastien PECQUEUR**<br>Materials' Variability enabling Neuromorphic Pattern Recognition in Organic Electrochemical Transistors Networks |
| 12.00-12.20 | **Vincent FORGE**<br>Self-Assembling Proteins for Bio-Inspired NanoElectronics |
| 12.20-12.30 | **Sponsors presentation** |
| | 12.30-14.00 LUNCH |
| **Session 4** | |
| 14.00-14.40 | **Dan FRISBIE (Keynote lecture)**<br>Imaging Defects and Electronic Disorder in Organic Semiconductors |
| 14.40-15.00 | **Kamal LMIMOUNI**<br>Multilevel charge storage in Flexible Organic Nano-Floating gate Memory |
| 15.00-15.20 | **Yutaka NOGUCHI**<br>Electrical and optical properties during doping relaxation process in light-emitting electrochemical cells studied by extended displacement current measurement |
| 15.20-15.35 | **Scott SMITH**<br>Large-area, Photosensitive, Molecular Devices with Tunable Electronic Behaviour Achieved through a Multilayered Architecture |
| 15.35-15.50 | **Florian LEBON**<br>Robust ultra-thin electrografted molecular layers for high yield vertical metal-molecules-metal junctions |
| | 15.50-16.10 ………COFFEE BREAK |
| 16.50-17.30 | **Alberto CREDI (keynote lecture)**<br>Processing signals with (supra)molecular devices and machines |
| 17.30-17.50 | **Jean Pierre LAUNAY**<br>The challenge of unidirectional motion in molecular machines |
| 17.50-18.10 | **Jean WEISS**<br>Light Triggers Molecular Shuttling in Rotaxanes: Control over Proximity and Charge Recombination |
| 18.10-18.25 | **Jovana MILIC**<br>Supramolecular Engineering and Molecular Modulation for Highly Efficient and Stable Perovskite Solar Cells |
| 18.25-18.40 | **Catherine ADAM**<br>Electroactive Helical Foldamers: Self-Assembled Monolayers and their Anion Recognition Properties |

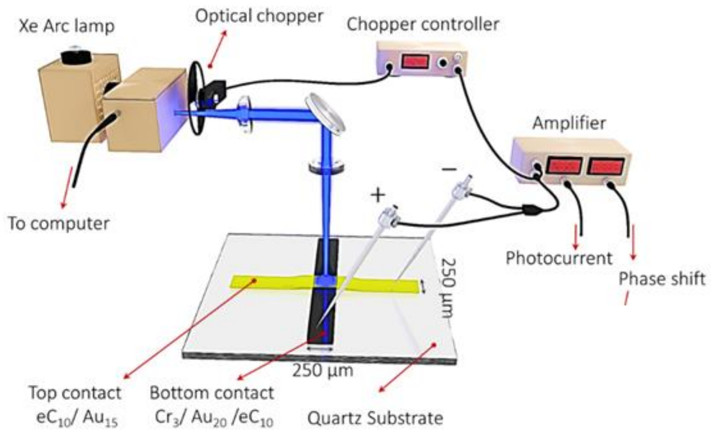
# Photocurrents and Photoemission in All-Carbon Molecular Electronic Junctions

Richard McCreery, Amin Morteza Najarian, Ushula Tefashe, Scott R. Smith

*University of Alberta*
*Edmonton, Alberta, Canada*
*Email: mccreery@ualberta.ca*

## Abstract:

Molecular electronic junctions consisting of 2-10 nm thick conjugated oligomers between conducting carbon contacts show distinct electronic behaviors from conventional semiconductors or thicker organic films, and often involve distinct physical principles. Interactions with light provide a means to probe internal device energy levels in order to better understand the charge transport mechanisms and provide a basis for rational design of unusual electronic devices. Illumination of molecular junctions with UV-Vis light through partially transparent electrodes produces stable photocurrents with zero applied bias, or photovoltages at open circuit. If the molecules do not absorb light, internal photoemission underlies the transport mechanism. [1-2] For absorbing molecules, the sign of the photocurrent indicates which orbitals are nearest in energy to the Fermi level, and the photocurrent spectrum approximately tracks the in-situ absorption spectrum of the molecular layer inside the junction. [3] Analysis of the bias, thickness, and temperature dependence of the photocurrent under an applied bias reveal a distinct mechanism compared to the dark current, with near-resonant transport and inverse temperature dependence compared to typical activated transport mechanisms. Light emission from molecular junctions is also a useful probe of conduction mechanisms, and may involve both "hot electron" photoemission [4-5] and photons from bias-induced exciton formation. [6]



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# Progress in graphene-based single-molecule electronics

Jakub K. Sowa[a], Achim Harzheim[a], John Cully[a], Pawel Puczkarski[a], James O. Thomas[a,b], Bart Limburg[a,b], Pascal Gehring[c], G. Andrew D. Briggs[a], Harry L. Anderson[b], Jan A. Mol[a,d]

[a] *Department of Materials, University of Oxford, Oxford, UK*
[b] *Department of Chemistry, University of Oxford, Oxford, UK*
[c] *Kavli Institute of Nanoscience, Delft University of Technology, Delft, The Netherlands*
[d] *School of Physics and Astronomy, Queen Mary University of London, London, UK. Email: j.mol@qmul.ac.uk*

## Abstract:

Five years ago we started to investigate the use of graphene nanoelectrodes for contacting individual molecules [1]. Graphene nanoelectrodes allow for non-covalent bonding of molecules [2], effective electrostatic gating, and large-scale fabrication [3] and integration with other nanoelectronic components [4]. The great success of this approach is only lessened by the fact that, unlike in the case of for example gold nanoelectordes, the graphene nanoelectrodes cannot simply be thought of as ideal, semi-infinite metal leads [5]. As the electronic and thermal properties of the graphene nanoelectrodes significantly influence the behaviour of the graphene-based single-molecule devices, the graphene-molecule-graphene junction needs to be considered as a whole. Here, I will present a broad overview of the challenges and progress in understanding and controlling the interactions between individual molecules anchored to graphene nanoelectrodes and their environment. I will focus on the influence the unique material properties of graphene – its two-dimensional nature, electronic band structure, and long mean-free path – have on potential single-molecule device applications such as transistors [6], heat engines [4], and sensors [7].

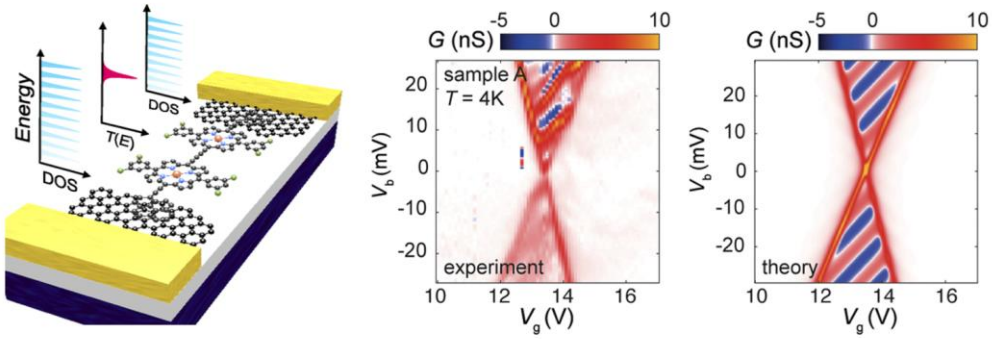

*Figure 1 : The influence of the electronic structure of graphene nanoelectrodes on the sequential electron tunnelling in a single-molecule transistor.*

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# Spatial and Lateral Control of Functionality by Rigid Molecular Tripods: Towards Surface Mounted Devices

Michal Valášek,[a] Marcin Lindner,[a] Lukas Gerhard,[a] Wulf Wulfhekel,[a] Viliam Kolivoška,[b] Magdaléna Hromadová,[b] Marcel Mayor,[a,c]

[a] *Institute of Nanotechnology, Karlsruhe Institute of Technology, P. O. Box 3640, D-76021 Karlsruhe, Germany.*
*Email: michal.valasek@kit.edu*
[b] *J. Heyrovský Institute of Physical Chemistry of ASCR v.v.i., Dolejškova 3, 182 23 Prague 8, Czech Republic*
[c] *Department of Chemistry, University of Basel, St. Johannsring 19, CH-4056 Basel, Switzerland*

## Abstract:

Surface mounted molecular devices have received significant attention in the scientific community because of their unique ability to construct functional materials. The key involves the platform on which the molecular device works on solid substrates to control physical features like the coupling to the surface or the available free space for sterically demanding operations of the protruding functionality atop surfaces. The concept of rigid molecular tripods to immobilize active functionality atop flat metallic surfaces in a controllable manner will be outlined.[1] These tripodal platforms based on tetraphenylmethane or 9,9´-spirobifluorene moieties have three thiol anchoring groups to control the spatial arrangement of the protruding functional moieties and form mechanically stable and electronically tuned contacts to the underlying gold substrate. The effect of the positions (*para* versus *meta*) of anchoring groups relative to the sp$^3$-hybridized central carbon atom was studied in the tetraphenylmethane scaffolds.[2] Whereas *meta*-substituted variant shows well-ordered monolayers, *para*- regioisomer shows multilayer formation. Moreover, the position of the anchoring group did not affect significantly the single molecule conductance values as determined by STM-BJ techniques which might point to the central sp$^3$-hybridized carbon atom controlling the electronic coupling. Our further studies geared towards investigating the dimensions of functionalities that can be mounted to tetraphenylmethanes and finally led to the concept of "molecular graph paper" in which the spatially resolved deprotection of individual molecules is used to write letters by pulses from the STM tip on these self-assembled molecular islands.[3] To combine both a perpendicular arrangement with efficient electronic coupling of the protruding molecular structure, we recently developed the 9,9´-spirobifluorene tripodal platform.[4] Combined experimental break junctions investigations, UHV-STM experiments, IET spectroscopy and theoretical calculations confirmed that these molecules are standing upwards and displayed the expected high conductance value on the order of $10^{-3}$ $G_0$ in contrast to tetraphenylmethane variants.[5,6] Furthermore, extensive low temperature UHV-STM of 9,9´-spirobifluorene platform functionalized with a nitrile group lifted away from the gold surface showed that the formation of a coordinative bond between the nitrile nitrogen and the gold tip of a STM can be controlled by both electrical and mechanical means. The molecular junction became a highly reproducible toggle switch actuated by electrical pulses and shows a hysteretic conductance switching by more than two orders of magnitude.[7]

## References:

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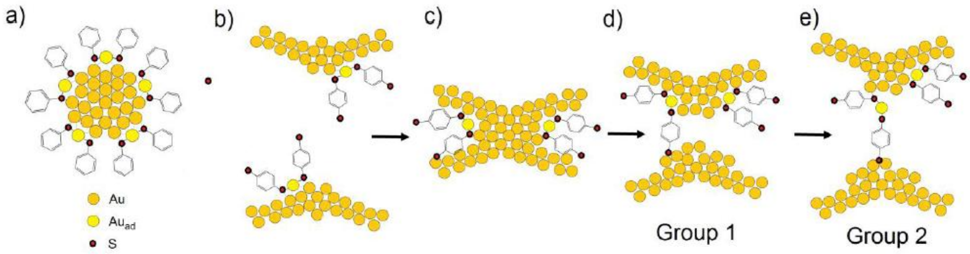
# The Role of Oligomeric Gold-Thiolate Units in Single Molecule Junctions of Thiol-Anchored Molecules

Edmund Leary,[a] Linda A. Zotti,[b] Delia Miguel,[c] Irene R. Márquez,[c] Lucía Palomino-Ruiz,[c] Juan Manuel Cuerva,[c] Gabino Rubio-Bollinger, [d] M. Teresa González, [a] Nicolás Agrait [d]

*[a]Instituto Madrileño de Estudios Advanzados (IMDEA), Calle Faraday 9, Campus Universitario de Cantoblanco, 28049 Madrid, Spain*
*[b]Departamento de Física Teórica de la Materia Condensada and IFIMAC, Universidad Autónoma de Madrid, Madrid, E-28049, Spain; linda.zotti@uam.es*
*[c]Departamento de Química Orgánica, Universidad de Granada, C. U. Fuentanueva, Avda. Severo Ochoa s/n, E-18071, Granada, Spain*
*[e]Departamento de Física de la Materia Condensada, Instituto "Nicolás Cabrera" and Condensed Matter Physics Cen-ter (IFIMAC), Universidad Autónoma de Madrid, E-28049, Madrid, Spain*

Abstract:

We present a combined experimental and theoretical study of the role played by "Au(RS)2" units in thiol-terminated molecular junctions formed on gold in break-junction experiments. By analizing a large number of thiol-terminated compounds, we demonstrate that these units give rise to the lower conductance group [1]. These structural motifs are found on the surface of gold nanoparticles, but they have not before been shown to exist in molecular-break junctions.



*(a) Representation of a thiol-capped gold nanoparticle showing the RS−Au(I)−SR surface motif. (b)−(e) Proposed model of thiol behavior inside a gold-electrode BJ experiment using benzene dithiol as an example.*

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# Single Molecule Detection of Markers with a Label Free Bio Electronic Sensor

Eleonora Macchia,[1] Kyriaki Manoli,[1] Brigitte Holzer,[1] Cinzia Di Franco,[2] Matteo Ghittorelli,[3] Fabrizio Torricelli,[3] Domenico Alberga,[4] Giuseppe Felice Mangiatordi,[4] Gerardo Palazzo,[1,6] Gaetano Scamarcio,[2,5] and Luisa Torsi[1,6,,7]

[1]*Dipartimento di Chimica - Università degli Studi di Bari "Aldo Moro" - Bari (I)*
[2]*CNR - Istituto di Fotonica e Nanotecnologie, Sede di Bari (I)*
[3]*Dipartimento Ingegneria dell'Informazione - Università degli Studi di Brescia - Brescia (I)*
[4]*Dipartimento di Farmacia - Scienze del Farmaco - Università degli Studi di Bari "Aldo Moro" - Bari (I)*
[5]*Dipartimento di Fisica "M. Merlin" - Università degli Studi di Bari – "Aldo Moro" - Bari (I)*
[6]*CSGI (Centre for Colloid and Surface Science) – Bari (I)*
[7]*The Faculty of Science and Engineering - Åbo Akademi University – Turku (FI)*

Label-free single-molecule detection has been achieved so far by funnelling a large number of ligands into a sequence of single-binding events with few recognition elements host on nanometric transducers. Such approaches are inherently unable to sense a cue in a bulk milieu. Conceptualizing cells' ability to sense at the physical limit by means of highly-packed recognition elements, a millimetric sized field-effect-transistor is used to detect a single molecule. To this end, the gate is bio-functionalized with a self-assembled-monolayer of trillions of capturing anti-Immunoglobulin-G and is endowed with a hydrogen-bonding network enabling cooperative-interactions. The selective and label-free single-molecule IgG detection is strikingly demonstrated in diluted saliva while 15 IgGs are assayed in whole serum. The suggested sensing mechanism triggered by the affinity binding event, involves a work-function change that is assumed to propagate in the gating-field through the electrostatic hydrogen-bonding network. The proposed immunoassay platform is general and can revolutionize the current approach to protein detection.

E. Macchia, K. Manoli, B. Holzer, C. Di Franco, M. Ghittorelli, F. Torricelli, D. Alberga, G.F. Mangiatordi, G. Palazzo, G. Scamarcio and L. Torsi, *Nature Communications,* **volume 9**, Article number: 3223 (2018).
Highlighted in Nature: https://www.nature.com/articles/d41586-018-05950-z

# Materials' Variability enabling Neuromorphic Pattern Recognition in Organic Electrochemical Transistors Networks

Sébastien Pecqueur,[a] David Guérin,[a] Dominique Vuillaume,[a] Fabien Alibart[a,b]

*[a]Institut d'Électronique, Micro-électronique et Nanotechnologie, CNRS/Uni. Lille1, Villeneuve d'Ascq, France*
*[b]LN2-CNRS, Sherbrooke, Canada*
*Email: sebastien.pecqueur@iemn.univ-lille1.fr*

Neuromorphic computing proposes to process information inspiring from the brain mechanisms to aim computationally cost-effective and intuitive manners to process complex data. While neural network algorithms have proven their real potential in diverse pattern classification applications, their replication into hardware remains technologically challenging. An interesting solution for such hardware implementation is based on organic electrochemical transistors (OECTs) that have shown promises in emulating synaptic plasticity at the device level,[1] and coherent communication from one device to another.[2] We demonstrate (i) the bottom-up fabrication of OECT micro-arrays and (ii) the pattern classification task using this technology.[3] We achieved the electro-polymerization of a new p-type accumulation-mode conducting polymer, iteratively on top of 12 micrometric OECT devices in a honeycomb array (Fig. 1). We characterized the rich material's morphology of the bottom-up grown organic semiconductor structures and assessed their functionality as synaptic transistor devices. The exploitation of the array for the recognition of pulse-frequency-modulated gate-voltage patterns through an aqueous electrolyte showed that the pattern recognition can cope with the rich variability of device performances, but also that the recognition benefits from the large dispersion in device property of each individual OECTs.

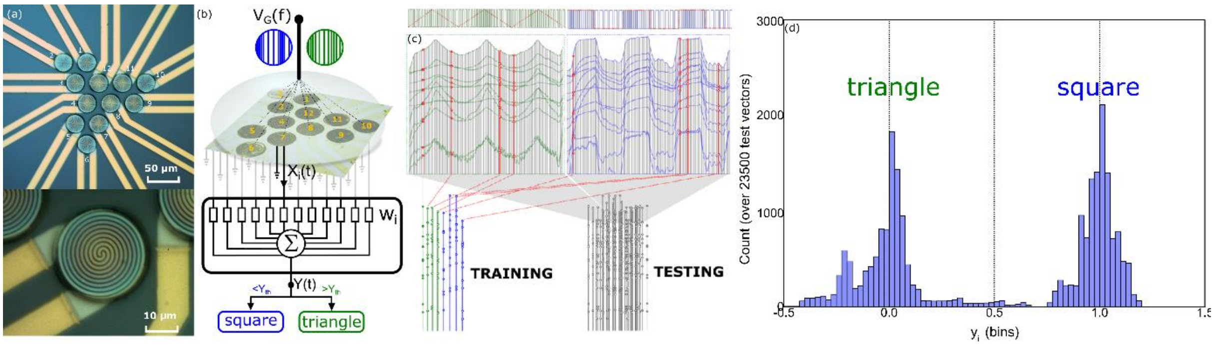

***Figure 1.*** *Optical images of the 12 OECTs network. Scheme of the pattern recognition with a reservoir computing made of the OECTs network in a common electrolyte. Distribution of the pattern recognition outputs after learning (<1% error)*

These results announce a new game-change for organic and molecular electronics. It shows that the chemical and morphological richness of these electronic materials, for which their disorder induces large property distributions, are actually enabling information processing in a neuromorphic computing context: at the image of our brain which exploits in a powerful way the natural morphological and chemical variability of its dendritic and synaptic network.

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# Self-Assembling Proteins for Bio-Inspired NanoElectronics

Saravanan Rengaraj[a,b], Lucie Altamura[a], Chantal Gondran[b], Patrice Rannou[c],
Alan Le Goff[b], Michael Holzinger[b], Vincent Forge*[a]

[a] *Univ. Grenoble Alpes, CEA, CNRS, BIG-LCBM, 38000 Grenoble, France. *Email: vincent.forge@cea.fr*
[b] *Univ. Grenoble Alpes, CNRS, DCM UMR 5250, F-38000 Grenoble, France*
[c] *Univ. Grenoble Alpes, CNRS, CEA, INAC, SyMMES, F-38000 Grenoble, France*

## Abstract:

The recent discovery of conduction in bacterial nanowires[1-2] connected to electrodes makes it possible to envision the development of a protein-based electronics[3]. Learning from these sophisticated architectures, we have recently developed a bio-inspired conductive nanowire (*See the top right part of the Figure*) consisting solely of proteins**[4]**. It consists in the fusion of a prion domain (*not involved in a disease*) capable of self-assembling into amyloid fibers with a redox center (*here rubredoxin*) whose function is to allow for transport of electrons. In this communication, we will discuss how the programmed self-assembly of the prion domain leads to high aspect ratio (length/diameter > 4000. Diameter of *ca.* 5nm) microfiber surface-decorated with rubredoxin units sufficiently close to one another (*i.e.* < *ca.* 1 nm) for authorizing efficient electron transport by hoping between redox centers. Going a step further in the implementation of our bio-inspired design, we will further demonstrate and exemplify how our protein nanowires authorize long-range electronic transport in between an electrode and an enzyme (*See the top left part of the Figure: illustration with an Hydrogenase*) over a few microns**[4-5]**, paving the way for the advent of next generation biosensors or biofuel cells; to name a few possible devices linked to the blossoming fields of bio-compatible/degradable electronics

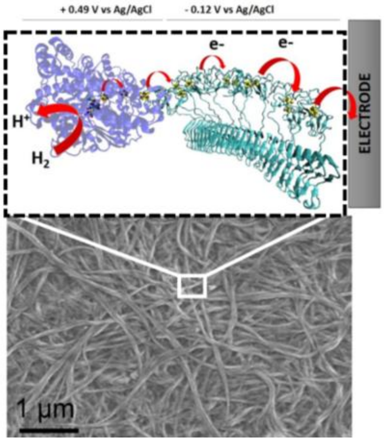

*Figure caption:* (***Top***) Schematic representation of the mediated electron transfer between Hydrogenases and electrode via bio-inspired conductive nanowires. (***Bottom***) Scanning electron microscopy of the electrode functionalized with conductive nanowires and Hydrogenases.

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# Imaging Defects and Electronic Disorder in Organic Semiconductors

C. Daniel Frisbie[1]

[1] *Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN (USA)*

Email: frisbie@umn.edu

The central thesis of this talk is that many structural defects in crystalline organic semiconductors have surface potential signatures that can be recorded and imaged by scanning Kelvin probe microscopy (SKPM) with sub-100 nm resolution.[1-5] This allows straightforward visualization of defects that are difficult to detect by other methods. Additionally, we argue that surface potential fluctuations are a direct measure of static electronic disorder, namely band edge variations, that will impact electron and hole transport. Thus, surface potential imaging not only reveals defects in crystalline organic semiconductors but importantly provides a direct link to electronic disorder (e.g., traps, scattering centers) that degrade transport performance. This talk will focus on three illustrative examples based on thin films and single crystals of benchmark organic semiconductors,[2,4,5] including one case where we can make a thorough connection between structure, surface potential, and field effect transport.[5] We propose that in many cases the surface potential contrast associated with a given defect arises due to inhomogeneous strain around the defect. To support this, we further describe the first direct measurements of the strain-surface potential relationship for macroscopic single crystals of rubrene.[3] Overall, we suggest that surface potential measurements are a powerful approach to understanding correlated structural and electronic disorder in soft organic semiconductors.

We acknowledge funding by the US National Science Foundation.

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# Multilevel charge storage in Flexible Organic Nano-Floating gate Memory

Shuo Li, Bilel Hafsi, David Guérin, Kamal Lmimouni

*Institut d'Electronique de Micro-électronique et de Nanotechnologie (IEMN), CNRS, Université de Lille-Faculté des Sciences et Technologies, avenue Poincaré, BP 60069, 59652, Villeneuve d'Ascq cedex, France*
*Email:kamal.lmimouni@iemn.univ-lille1.fr*

Abstract:

Due to the merits of organic materials such as mechanical flexibility, solution processability, and light weight characteristics, organic semiconductors and organic dielectrics are essentially expected to meet emerging technological demands that realizing flexible and wearable organic field-effect transistor (OFET) devices. In this work, we first report the pentacene based OFET that fabricated on ultra-flexible 2 µm parylene C (PC) substrate. The insulator hybrid polymers of PMMA and PC were selected to be dielectrics. In addition, the transistor was transferred on silicon, glass and kapton flexible substrates and the characteristics were compared. Furthermore, the flexible OFET worked stable and obtained high mobility of 0.15 $cm^2V^{-1}S^{-1}$ and current on/off ratio of $1.5\times10^5$ under bending condition. Then, the flexible nano-floating memory (NFGM) devices by using gold nanoparticles (Au NPs) and PC electrets as the charge store were realized, and the memory performances were demonstrated. In particular, the multi-level data storage were achieved from our flexible NFGM by using pentacene as channel material and polymers of PMMA, Hydrogen Silsesquioxane (HSQ) as dielectric layers, respectively, which could be explained the deeper level trapping behavior of NPs under the increase in gate bias and these energy levels of trapped sites in PC polymer electrets. The large memory window of 23 V were obtained by application of $V_{GS}$ pulse of ± 40 V. In further, the bending stability/mechanical stability test with stable retention property more than $10^5$ s, and reliable cycling endurance over 500 cycles were obtained. It confirms that our NFGM memory based on Au NPs floating gate and with all organic layers is suitable for flexible electronic memories. The results highlight the utility of combing the charge store medium in flexible NFGM devices.

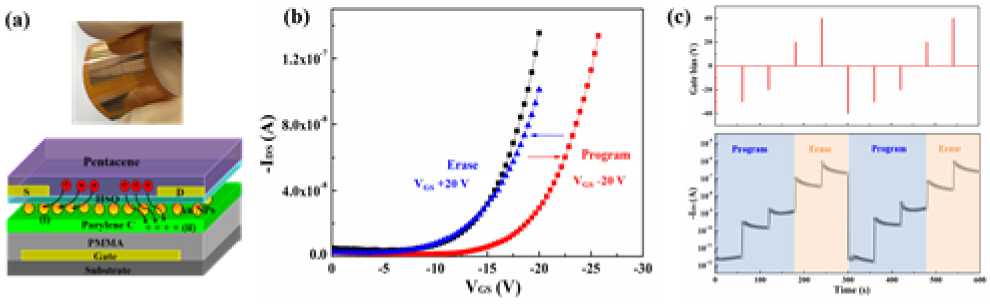

*Figure 1 (a) optical image of the flexible NFGM and scheme of charge trapping based on (i) Au NPs and (ii) polymer electrets layers; (b) The typical transfer curves of NFGM; (c)The dynamic behavior of the NFGM with corresponding current levels under application of various $V_{GS}$ pulse.*

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# Electrical and optical properties during doping relaxation process in light-emitting electrochemical cells studied by extended displacement current measurement

Yutaka Noguchi,[a] Tetsuya Higeta,[a] Fumihiro Yonekawa, [b]

*[a]School of Science & Technology, Meiji University, Kawasaki 214-8571, Japan. Email: noguchi@meiji.ac.jp*
*[b]Nippon Chemical Industrial Co., Ltd., Tokyo 136-8515, Japan.*

## Abstract:

We performed an extended displacement current measurement (DCM) to analyze the operation mechanisms of a poly(phenylenevynylene) derivative (Super Yellow)-based light-emitting electrochemical cell (LEC) [Fig. 1(a), (b)].4) We simultaneously measured the characteristics of the actual current ($i_{act}$), displacement current ($i_{dis}$), and electroluminescence (EL) intensity ($V_{APD}$) during the relaxation processes of electrochemical doping. The transient characteristics indicate correlations between the conductance ($di_{act}/dV$), capacitance ($\propto i_{dis}$), and EL efficiency ($\eta = V_{APD}/i_{act}$). The conductance and capacitance decrease with proceeding doping relaxation, whereas the EL efficiency increases [Fig. 1(c), (d)]. The EL efficiency is dominated by the electrochemical doping state, rather than the actual current density. Moreover, the EL efficiency deteriorates with increasing DC voltage applied for electrochemical doping ($V_{dc}$). Since the DCM revealed that the electrical properties of the device obey the trap charge limited current regime in the intrinsic region and are almost independent of $V_{dc}$, efficiency deterioration is not responsible for the intrinsic region but for the doped region. The results suggest that self-absorption in the doped region causes efficiency loss, otherwise the emitting zone is formed close to the doped region. The extended DCM enables us to comprehensively analyze the operation mechanisms of LECs on the basis of the simultaneous observations of electrical and luminous characteristics, including their transient changes.

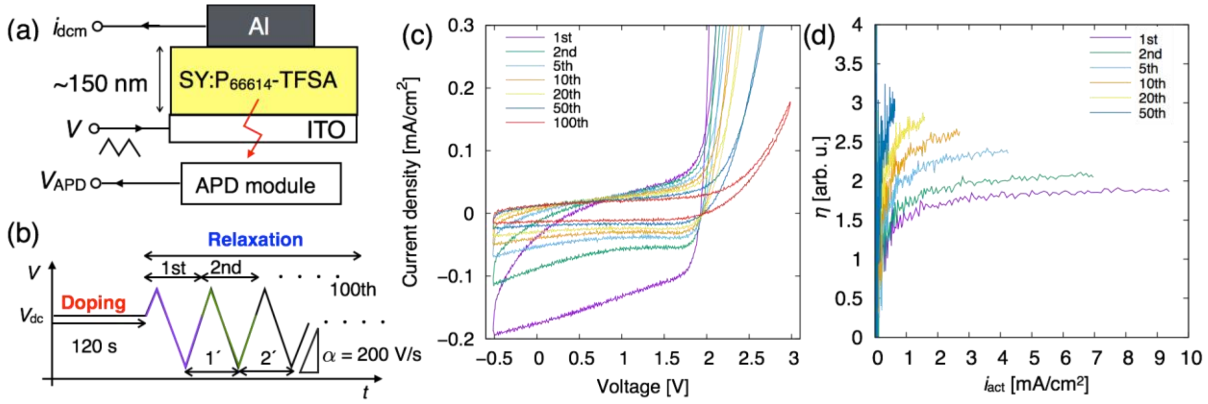

*Figure 1 (a)Device structure and experimental setup for extended DCM. (b)A typical waveform of the applied voltage for DCM. (c) Typical DCM curves of the SY-LEC during electrochemical doping relaxation ($V_{dc}$ = 2.8 V). (d) The luminous efficiency vs. actual current curves ($V_{dc}$=2.8 V). The efficiency increases with proceeding sweep cycles (relaxation of electrochemical doping), though the roll-off behavior is not observed.*

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# Large-area, Photosensitive, Molecular Devices with Tunable Electronic Behaviour Achieved through a Multilayered Architecture

Scott R. Smith,[a] and Richard L. McCreery,[a]

[a]*Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta, Canada.*
*Email: srsmith1@ualberta.ca*

## Abstract:

Molecular electronics research has involved studying the electrical behaviour through organic substituents that vary in structure and orbital energies between two electrode contacts. With careful consideration of the design, the electronic properties of a device can be easily varied within the organic molecular layers to achieve properties or applications unique from traditional electronics.[1–2] For example, by employing symmetric $sp^2$ carbon based contacts, extremely robust organic multilayers with non-linear electronic behaviour can be synthesized with relative ease and uniformity using an electrochemical diazonium "click" technique as a nanometric building block approach to bottom-up device fabrication. Here, an electron donating layer of bis-thienylbenzene that is subsequently overlaid with an electron accepting layer of anthraquinone between carbon contacts allows the electronic response to be varied from symmetric to asymmetric rectifying behaviour. Furthermore, optoelectronic properties like large photocurrents and photovoltages can be achieved for these bilayered molecular devices by employing photosensitive molecules.[1] Finally, incorporation of a third layer of lithium benzoate introduces a source of mobile $Li^+$ ions directly within the junction layer, thereby significantly altering the electronic behaviour. Mobile ions facilitate a means to switch between a symmetric and an asymmetric electrical response with further possibilities in non-volatile memory and on-chip energy storage applications.[2] Understanding the complex relationship between the structure, orbital energies, and electronic behaviour of a multilayered molecular junction is fundamentally paramount to engineering better molecular electronics. Therefore, electrochemical and spectroscopic characterization of these multicomponent, photo-active molecular devices (up to ~15 nm total thickness) is critical for future development and will be discussed in terms of their fabrication, structure, and intended applications.

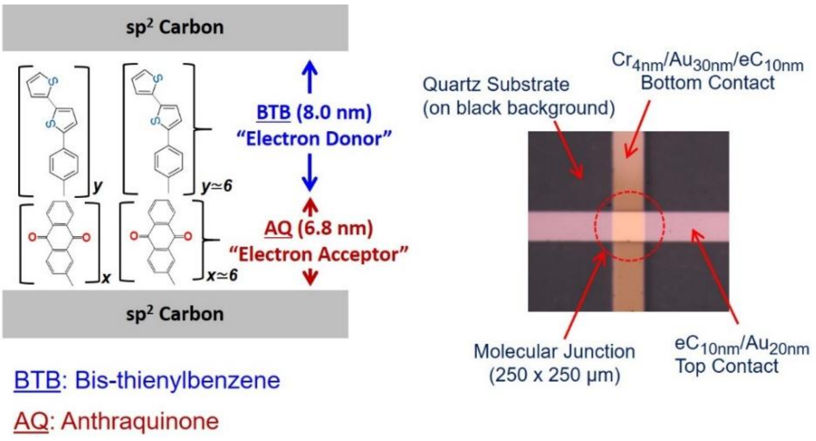

*Figure 1: Typical large-area, bilayered molecular device with a donor-acceptor pair example.*

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# Robust ultra-thin electrografted molecular layers for high yield vertical metal-molecules-metal junctions

Lebon F.[1], Lin T.-P.[1], Casademont H.[1], Cornut R.[1], Derycke V.[1], Jousselme B.[1]

[a]*LICSEN, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France. Email : florian.lebon@cea.fr*

## Abstract:

Despite the recognized potential of organic molecules for electronics, only very few types of devices (like OLEDs) incorporating thin molecular layers as active elements, have reached the level of industrial applications. Two major issues slowdown such integration: *(i)* the way of incorporating molecules in electronic systems is usually incompatible with device miniaturization, and *(ii)* thin molecular layers suffer from a limited robustness notably toward back-end process steps.

The properties of molecular layers are commonly studied using either self-assembled monolayers (SAMs) or thick non-patterned layers prepared by spin- or dip-coating. Electrografting by reduction of diazonium salts, provides an efficient alternative to these methods. It leads to robust covalent organic thin films of adjustable thickness (typically in the 5 to 50 nm range) and rich functionality. We notably showed recently that they can be used a nanodielectrics in transistors,[1] or as active material in organic memory-based circuits.[2] These films can be assembled on all conducting or semi-conducting electrodes, are compatible with lithography and allows the selective grafting of different electrodes of the same chip with different molecules.

However, the integration of such versatile organic thin films in functional devices requires a deep understanding and thorough control of their growth mode. In this presentation we will first present the formation of molecular thin films of controlled thickness based on two kind of diazonium salts (an insulating and an electroactive one) and then show how they can be combined in controlled double-layers for improved performances. The three different types of molecular layers were notably integrated in leakage-free large-area (>100 µm$^2$) vertical metal-molecules-metal junctions and their electronic performances were evaluated.

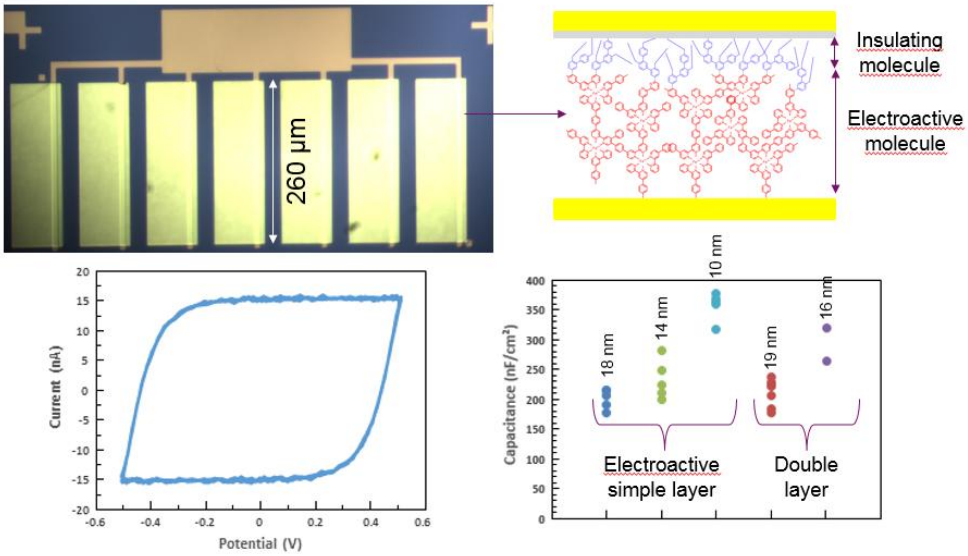

*Figure 1. Final sample obtained for electrical measurements (top). Electrical measurement at 1500 Hz for one electrode (bottom left). Capacitance results for various layers (bottom right).*

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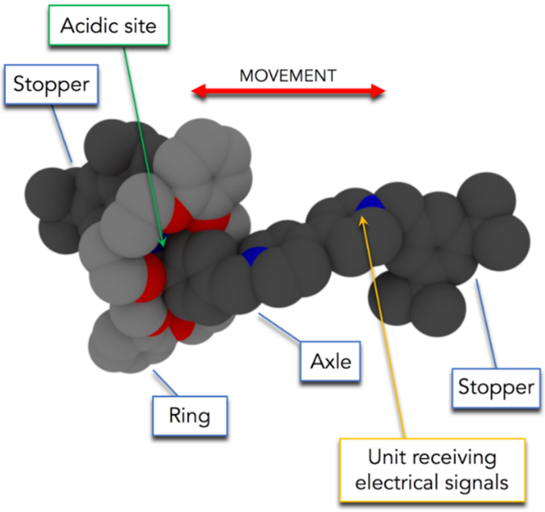
# Processing signals with (supra)molecular devices and machines

Alberto Credi
*Dipartimento di Scienze e Tecnologie Agroalimentari, Università di Bologna, viale Fanin 50, 40127 Bologna, Italy, and Center for Light Activated Nanostructures (CLAN), Istituto ISOF-CNR, via Gobetti 101, 40129 Bologna, Italy.* E-mail: *alberto.credi@unibo.it*; Web: *centri.unibo.it/clan*

The harvesting, transformation and storage of chemical, electrical or photonic signals by molecular systems constitute key phenomena for the operation of living organisms, and are at the basis of several technological applications. In appropriately designed molecular or supramolecular species, chemical and/or physical stimulation can trigger the occurrence of processes which, ultimately, may result in the ability to carry out useful tasks [1]. The use of light stimulation has several advantages in the present context, primarily because photons can be used to supply energy to the system (i.e., write) as well as to gain information about its state (i.e., read) [2].

Research in the past three decades has shown that molecular-scale devices capable of performing a function in response to external stimulation can be developed by following bottom-up strategies that rely on supramolecular chemistry. Molecular machines are a particular class of molecular devices wherein the function is related to non-trivial, controlled movements of the component parts [1,3]. Indeed, the realization of devices and machines at molecular scale that can harness energy to perform predetermined (and potentially useful) functions in a controllable manner continues to be a most stimulating challenge in nanoscience.



A rotaxane in whith the p$K_a$ of an acidic site can be modulated by electrochemical switching at a remote site. The possibility of the ring to shuttle between the two sites allows them to communicate.

In this talk I will discuss some fundamental concepts of (supra)molecular devices and machines, and present recent results of our research on these topics. Specifically, by inducing and monitoring large-amplitude molecular movements in rotaxane-type systems, we have developed prototypes of molecular pumps [4], transporters [5] and modulators [6] (see figure) that operate in solution. Photoswitchable solid materials for optoelectronic and gas storage applications [7], single molecular tetrapods on surfaces [8] and nanocrystal-chromophore conjugates with engineered long-lived emission [9] will also be discussed.

I am grateful to the European Research Council (AdG n. 692981 “Leaps”) and Ministero dell’Istruzione, Università e Ricerca (FARE Grant n. R16S9XXKX3 “Ampli”) for support.

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# The challenge of unidirectional motion in molecular machines

Jean-Pierre Launay

*CEMES-CNRS, 29 rue Jeanne Marvig, 31055 Toulouse, France. Email: launay@cemes.fr*

## Abstract:

A number of cleverly designed molecules potentially able to function as molecular machines is now available. The challenge is however to make them do what we want, in particular achieving a unidirectional motion, either in rotation (case of molecular motors) or in translation (case of molecular vehicles, nanocars, etc…). The symmetry of the molecule, including its environment, is a crucial parameter to orient the motion, but this is not enough, and one has to be careful when making comparisons with the macroscopic world. This communication is built as a tutorial.

A first kind of experiments involves molecules in solution. Starting from the triptycene-helicene molecule (Kelly, 1997), we move by rational construction to the Feringa photochemical motor based on a chiral overcrowded alkene (*ca* 2000). Unidirectional rotation is achieved by a sequence of photochemical and thermal steps conveniently skewed by chirality.

In a second kind of experiments, molecules are deposited on a surface and activated by the tip of a scanning tunneling microscope at low temperature and Ultra-High Vacuum conditions. This gives access to the behavior of individual objects. A tantalizing goal is to achieve unidirectional motion, exemplified by the “Nanocar race” (Toulouse, April 2017). In this event, the preferred propulsion mode was inelastic tunneling, a process in which a tiny fraction of the energy crossing the molecule is transformed into a mechanical motion in a direction perpendicular to the electron flux.

An interesting paradigm in this case is the Prost-Astumian mechanism involving the evolution of the system between two asymmetric potential energy curves. It can lead to unidirectional motion if the system is asymmetric (broken spatial symmetry) and if the perturbation has a suitable time structure (non-zero autocorrelation noise function).

Some of the molecules involved in the nanocar race will be reviewed, as well as the four-wheel vehicle of Kudernac, Feringa *et al* (2011) with four asymmetric centers. However, at the present time, it is not always easy to ascertain the role of inelastic tunneling with respect to other processes such as electric field gradient influence. The nanocar and nanocar race challenges are powerful incentives to increase our knowledge on controlled molecular motions at this scale.

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- Nanocar race on CNRS and YouTube sites: http://nanocar-race.cnrs.fr/

https://www.youtube.com/channel/UCkQixqt0xegeVEmo9y9gMXQ

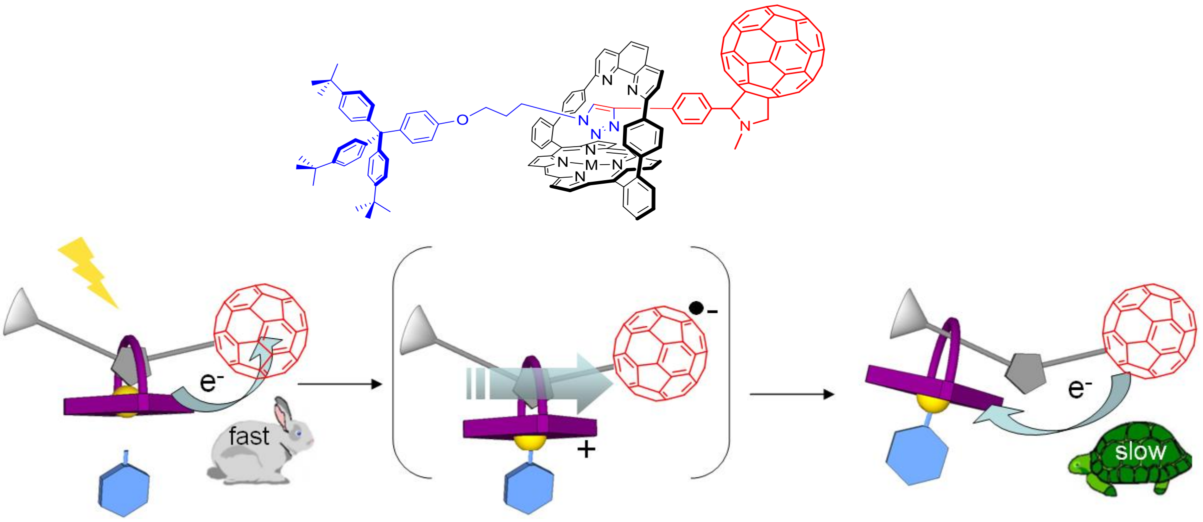
# Light Triggers Molecular Shuttling in Rotaxanes: Control over Proximity and Charge Recombination

M. Wolf,[1] A. Ogawa,[2,3] M. Bechtold,[1,5] M. Vonesch,[3] J. A. Wytko,[3] K. Oohora,[2] S. Campidelli,[4]
T. Hayashi,[2] D. M. Guldi,[1] **J. Weiss**[3,6]

[1] *Friedrich-Alexander-Universität Erlangen-Nürnberg, Department of Chemistry and Pharmacy, Egerlandstraße 3, 91058 Erlangen, Germany*
[2] *Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita 565-0871, Japan*
[3] *Institut de Chimie de Strasbourg, UMR 7177 CNRS-Université de Strasbourg, 4, rue Blaise Pascal, 67000 Strasbourg, France*
[4] *LICSEN, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France*
[5] *Institute of Inorganic Chemistry, KIT, Engesserstraße 15, D-76131 Karlsruhe, Germany*

## Abstract:

Taking advantage of the newly developed "tandem active metal template" synthesis of rotaxanes using a phenanthroline strapped porphyrin,[1] photochemical dyads and triads have been prepared with good yields. To this end, a fullerene-capped dumbbell-type axle containing a central triazole was threaded through strapped (metallo)porphyrins either a free-base or a zinc porphyrin. Depending on M (Zn or $H_2$) the positioning of the dumbbell in the rotaxane could be different, as well as the nature of photoinduced process.



Femtosecond-resolved transient absorption measurements revealed charge-separation between the porphyrin and fullerene upon light excitation. Solvent polarity and solvent coordination effects induced molecular motion of the rotaxanes upon charge separation and allowed, for the first time, the subtle control over the charge recombination by enabling and controlling the directionality of shuttling. The synthesis and morphology of the scaffolds will be presented and the photophysical data will be discussed.

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Miyazaki, Y., Kahlfuss, C., Ogawa, A., Matsumoto, T., Wytko, J.A., Oohora, K., Hayashi, T., and Weiss, J. (2017). CuAAC in a Distal Pocket: Metal Active-Template Synthesis of Strapped-Porphyrin [2]Rotaxanes. Chem. - A Eur. J. *23*, 13579–13582.

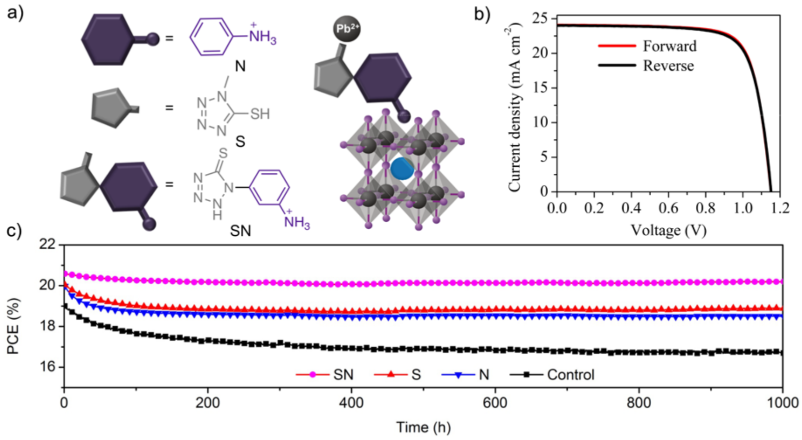
# Supramolecular Engineering and Molecular Modulation for Highly Efficient and Stable Perovskite Solar Cells

Jovana V. Milić,[a] D. J. Kubicki,[a,b] X. Li,[a] L. Emsley,[b] M. Graetzel[a]

[a]*Laboratory of Photonics and Interfaces, EPFL, Lausanne, Switzerland. Email: jovana.milic@epfl.ch*
[b]*Laboratory of Magnetic Resonance, EPFL, Lausanne, Switzerland.*

## Abstract:

The miniaturization of technology has reached the nanoscopic scale with the development of molecular machines that can act as elements of switches, sensors, actuators, memory devices, or elements in nanorobotics.[1–3] Such progress has relied on the concepts of molecular engineering and supramolecular chemistry, which exploits noncovalent interactions as essential tools in building complex molecular architectures. We employ the supramolecular approach beyond molecular nanotechnology in the development of novel materials for light harvesting, with a particular focus on the next generation of photovoltaic technologies featuring perovskite materials.[4–6] While perovskite solar cells exhibit high power conversion efficiencies, industrial applications are hampered by their limited stability against environmental factors, such as oxygen and moisture, as well as thermal and electrical stress.[4–6] These limitations could be overcome by treating the perovskite matrix with the electronically compatible and hermetically sealing hydrophobic materials, such as graphene composites.[4–5] Although this approach has provided consistently enhanced stabilities, this has mainly been achieved at the expense of the efficiency of the corresponding devices.[4] Our alternative strategy provides a unique stabilization without compromising efficiency by employing judiciously designed multifunctional molecular modulators that interact with the perovskite surface. As a result, we obtain durable and scalable perovskite solar cells with superior properties and high efficiencies exceeding 20%, accompanied by elevated tolerance to environmental factors.[6] This has been investigated using a combination of techniques, including scanning electron microscopy, X-ray diffraction, photoluminescence, as well as solid state NMR spectroscopy, to elucidate the mode of action and exemplify the advantages of supramolecular engineering in advancing perovskite solar cell research.



*(a) Schematic representation of the molecularly modulated perovskite structure with the (b) current-voltage characteristics and (c) evolution of efficiency over time of the corresponding perovskite solar cells.*[6]

## References:

[1] I. Pochorovski, **J. Milic**, F. Diederich, et al. *J. Am. Chem. Soc.* **2014**, *136*, 3852. [2] **J. Milic**, F. Diederich, et al. *J. Phys. Chem. Lett.* **2016**, *7*, 2470. [3] **J. Milic**, F. Diederich, et al. *Chem. Eur. J.* **2018**, *24*, 1431. [4] **J. V. Milic**, M. Graetzel, et al. *Adv. Mater. Interfaces* **2018**, doi:10.1002/admi.201800416. [5] H. Zhang et al. *Energy Environ. Sci*. **2018**. doi:10.1039/c8ee00580j. [6] X. Li, D. Bi, **J. V. Milic***, M. Graetzel*, et al. *Nat. Commun.* **2018**, accepted.

# WEDNESDAY 19TH

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| **Session 5** | |
| 8.30-9.10 | **Cyrille BARRETEAU (Keynote lecture)**<br>Concepts and modelling tools in molecular spintronics |
| 9.30-9.30 | **Ganna GRYN'OVA**<br>Conceptual Framework of Molecular Electronics |
| 9.30-9.45 | **Yannick DAPPE**<br>Graphene as a promising electrode for molecular electronics |
| 9.45-10.00 | **Marie-Laure BOCQUET**<br>Sigmatropic reaction to induce spin in a close-shell organic molecule on a metal |
| | 10.00-11.00 POSTER SESSION & COFFEE BREAK |
| 11.00-11.40 | **Magnus BERGGREN (Keynote lecture)**<br>Organic Bioelectronics – Nature Connected |
| 11.40-12.00 | **Alan Le GOFF**<br>Interfacing metalloproteins and models with nanomaterials for enzymatic and bioinspired electrocatalysis in fuel cells |
| 12.00-12.20 | **Nicola COPPEDE**<br>Textile biosensor based on conductive polymer for sweat analysis |
| 12.20-12.30 | **Sponsors presentation** |
| | 12.30-14.00 LUNCH |
| **Session 6** | |
| 14.00-14.40 | **Johannes BARTH (Keynote lecture)**<br>Probing vibrational excitations and switching at the molecular level |
| 14.40-15.00 | **Thierry MELIN**<br>High resolution imaging of molecular assemblies on Si(111):B by non-contact AFM at low temperature |
| 15.00-15.20 | **André Jean ATTIAS**<br>Beyond decorative 2D supramolecular self-assembly: strategies towards functional surfaces for nanotechnology |
| 15.20-15.35 | **Fabien SILLY**<br>Local Characterisation of On-Surface Synthesis of 2D Porous Organic Covalent-Nanoarchitectures |
| 15.35-15.50 | **Christian TEICHERT**<br>Polarized-light assisted charge spreading in 1D organic semiconductor nanocrystals on 2D materials |
| | 15.50-16.10 ………COFFEE BREAK |
| 16.50-17.30 | **Stefano SANVITO (keynote lecture)**<br>Constrained density functional theory: a versatile tool for studying charge dynamics in organic materials |
| 17.30-17.50 | **Vincent HUC**<br>Calixarenes-templated Zig-Zag-type single walled carbon nanotubes short segments |
| 17.50-18.10 | **Emmanuel ORGIU**<br>Hybrid van der Waals Heterostructures |
| 18.10-18.30 | **Laurent NONY**<br>Micrometer-long covalent organic fibres by photo-initiated radical polymerization on an alkali-halide surface |

# Concepts and modelling tools in molecular spintronics

Cyrille Barreteau

*CEA Saclay, IRAMIS SPEC*

Molecular spintronics is an emergent field combining the flexibility of molecular electronics and molecular magnetism with the advantages of spintronics. Its main goal is the manipulation of the eectron spin by a wise combination of *ad-hoc* molecules (magnetic or not) and inorganic substrate. Besides the rich magnetic behavior resulting from the interaction between a magnetic molecule and a metal surface, or vice versa, additional functions such as switchability by external parameters (light, voltage) can be integrated. Due to an almost infinite range of possible material combination, an extensive experimental investigation can evidently not be carried out. Therefore modelling approaches combined with driving physical concepts are necessary. In particular I will show that notions such as spinterface [1] and orbital engineering between the molecule and its substrate can efficiently be used to analyze and hopefully serve to devise strategies for the design of new materials or devices.

The presentation will be illustrated by a careful analysis of various relevant systems and their magnetotransport properties. I will first consider the case of nonmagnetic molecules in contact with a magnetic substrate. I will show how magnetic anisotropy can be tuned at a ferromagnetic/molecule interface [2], or how the adsorption geometry of a molecule affects its tunneling magnetoresistance [3] and based on orbital-symmetry arguments I will present molecular junctions that show perfect spin filtering [4]. Finally I will show recent results obtained with spin-crossover molecules forming well organized lattices on a gold surface while keeping their switching ability [5].

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[3] S. L. Kawahara, et al, Nano Lett. 12, 4558-4563 (2012) - D. Li et al. Phys. Rev. B **93**, 085425 (2016).
[4] A. Smogunov and Y. Dappe, Nano Lett. **15**, 3552 (2015) – D. Li, Y.J. Dappe and A. Smogunov, Phys. Rev. B **93**, 201403(R) (2016).
[5] K. Bairagi et al, Nature Communication **7**, 12212 (2016).

# Conceptual Framework of Molecular Electronics

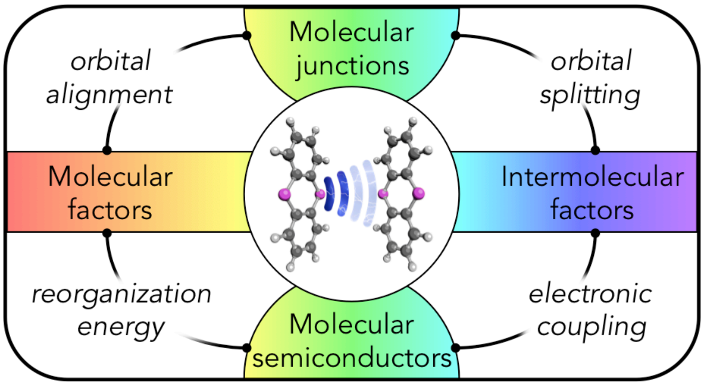
Ganna Gryn'ova,[a] Clémence Corminboeuf[a]

*[a]École polytechnique fédérale de Lausanne, CH-1015 Lausanne, Switzerland.*
*Email: clemence.corminboeuf@epfl.ch*

## Abstract:

Non-covalent interactions are important across a range of organic electronic materials, from molecular semiconductors (e.g., the crystalline organic semiconductors) to molecular junctions (such as dimer bridges in scanning tunnelling microscope experiments). These intermolecular interactions depend on the nature of molecular cores and define not only the stability of their non-covalent assembly, but also its charge transport properties.[1]

In the present contribution, we draw a parallel between the transport in the nanogap between metallic electrodes and charge carrier mobility in the bulk of an organic semiconductor.[2] We show that, within the model approximations, the same systems are consistently among the best and the worst performers, with similar principles guiding their performance in the two types of materials. More generally, we establish a conceptual framework for various non-covalent molecular electronic architectures that connects intrinsic properties of molecular cores with the properties of their non-covalent assemblies (see Figure). These results demonstrate the unifying footprint of the fundamental electronic structure of molecular cores on the diverse charge transport properties and offer the design strategies for more conductive organic electronic devices.



*Molecular and intermolecular factors, determining the transport properties of various non-covalent molecular electronic architectures.*

## References:

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[2] Gryn'ova, G.; Corminboeuf, C. *J. Phys. Chem. Lett.* **2018**, *9*, 2298.

# Graphene as a promising electrode for molecular electronics: role of the symmetry breaking on the attenuation factor

Yannick J. Dappe

*Service de Physique de l'Etat Condensé (UMR 3680 CNRS-CEA Saclay). Email: yannick.dappe@cea.fr*

## Abstract:

Single molecular junctions constitute elementary units in Molecular Electronics. In that respect, understanding electronic transport phenomena in those systems remains an important challenge. Electronic transport properties in molecular junctions are related to many factors such as molecular length, contact binding properties, and electronic level alignment between molecule and electrodes. In this frame, the use of graphene electrodes to form new type of asymmetric junctions sheds new light on the electronic transport properties in these systems, in particular with respect to the attenuation of the electric current in molecules.

In this presentation, after a brief introduction on electronic transport in molecular junctions, I will present some of my recent works on the study of attenuation factors in hybrid metal - organic molecule - graphene junctions, by discussing in particular some aspects of symmetry breaking induced by the use of a graphene electrode. Hence, I will show that this effect is related to the asymmetry of the coupling between the two extremities of the junction, namely covalent or van der Waals bonding. As a result, a lower electric attenuation is observed with respect to standard molecular junction based on metallic electrodes.

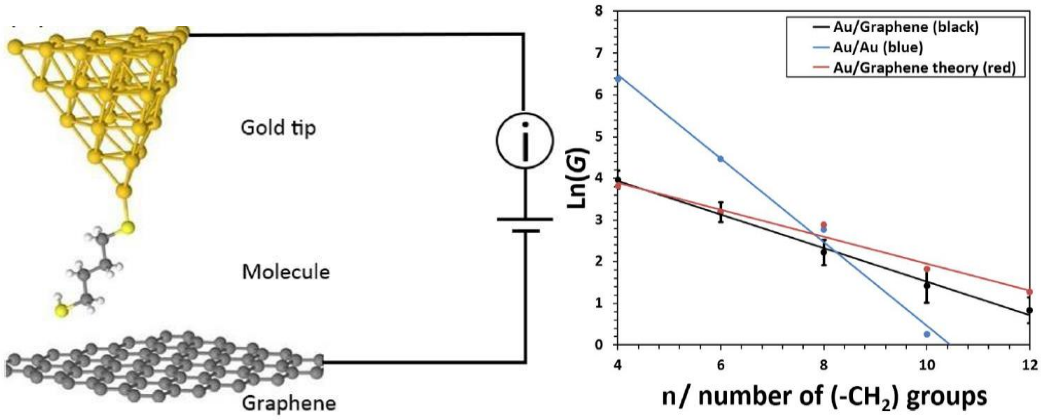

*Fig. 1: (left) schematic representation of a hybrid metal - organic molecule - graphene and (right) evolution of the electronic conductance as a function of the molecular length for different types of electrodes*.

References:

[1] Q. Zhang, S. Tao, R. Yi, C. He, C. Z. Zhao, W. Su, A. Smogunov, Y. J. Dappe, R. J. Nichols, and L. Yang, J. Phys. Chem. Lett. 8, 5987 (2017).

[2] Q. Zhang, L. Liu, S. Tao, C. Wang, C. Z. Zhao, C. González, Y. J. Dappe, R. J. Nichols, and L. Yang, Nano Letters 16, 6534 (2016).

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# Sigmatropic reaction to induce spin in a close-shell organic molecule on a metal

Marie-Laure Bocquet[1], Nicolas Lorente[2], Richard Berndt[3], Manuel Gruber[3]

*(1)PASTEUR, Département de chimie, École normale supérieure, PSL University, Sorbonne Université, CNRS, 75005 Paris, France*

*(2) Centro de Fısica de Materiales CFM/MPC (CSIC-UPV/EHU), Paseo Manuel de Lardizabal 5 and Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, 20018 Donostia-San Sebastian, Spain*

*(3) Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität, 24098 Kiel, Germany*

Abstract:

Metal surfaces are known to quench the spin of adsorbed organic radicals because of large electronic coupling. To preserve molecular spins, thin insulating layers have been used that provide a degree of electronic decoupling. Recently, retinoid molecules adsorbed on gold have been manipulated with a scanning tunneling microscope (STM) to exhibit a localized spin [1]. The mechanism of spin creation and stabilization is presently unknown. In this talk we propose the formation of a neutral radical that is spatially localized in a tilted and lifted cyclic end of the molecule. The spin is created in a two-step process: a [1,3] sigmatropic hydrogen shift yielding an allene motif and the abstraction of the moving hydrogen atom. The allene function provokes a perpendicular tilt of the cyclic end with respect to the rest of the conjugated chain and thus localizes the spin of the dehydrogenated allene in its lifted subpart. Our results of density functional theory (DFT) calculations and additional STM manipulations lend support to the proposed mechanism [2]. Our work indicates that the controlled generation of molecular spins directly on a metallic surface may be achieved with a range of molecule.

References:

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# Organic Bioelectronics – Nature Connected

Magnus Berggren

*Laboratory of Organic Electronics, ITN, Linköping University, 601 74 Norrköping, Sweden*

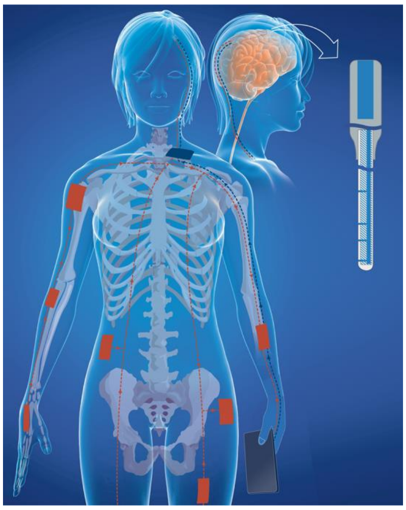
Abstract:

Organic electronic materials exhibit an array of desired characteristics making them excellent as the signal translator across the gap between biology and technology. These biocompatible materials, often complexed with polyelectrolytes and other functional materials, can be included in device structures, which are flexible, stretchable and even gelled, and can also process electronic, ionic and charged biomolecules in combination. This makes the organic electronic materials unique in several respects to record and regulate functions and physiology of biological systems.

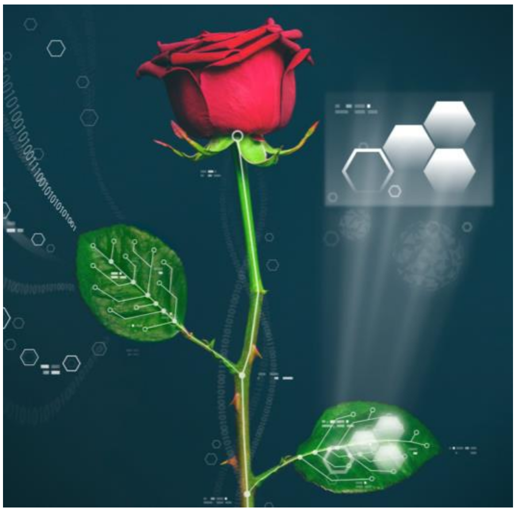
Here, a short review of some of the recent progresses from the Laboratory of Organic Electronics is given. In the BioComLab effort, a body area network is used to “connect” electronic skin patches with drug delivery components. This system provides a feedback system, also connected to the cloud for future healthcare. Sensors, converting biochemical signals into electric ones, are typically built up from organic electrochemical transistors and selectivity is typically provided from receptor mediation and oxidase approaches. Conversely, the organic electronic ion pump, converts an electronic addressing signal into the delivery of specific biomolecules, such as a neurotransmitter, to actuate and control functions of for instance the neuronal system. With the BioComLab technology the wide array of neuronal disorders and diseases are targeted, such as epilepsy, Parkinson’s disease and chronical pain.

In the e-Plant effort, the BioComLab technology is applied to the plant kingdom to record and impact the signaling pathways of phytohormones, thus allowing us to regulate the growth and expression of specific components of flowers and trees. Further, organic electronic materials can also be applied from aqueous solution directly into the biological system, thus enabling a unique approach to manufacture devices and electrodes *in vivo*. We are currently exploring this *in vivo*-manufacturing concept in several settings to define devices and circuits in various plants, to generate a seamless interface between Organic Bioelectronics and biological systems, in general.

BioComLab



Electronic Plants



# Interfacing metalloproteins and models with nanomaterials for enzymatic and bioinspired electrocatalysis in fuel cells

Alan Le Goff

[a]Univ. Grenoble Alpes, CNRS, DCM, 38000 Grenoble, France. Email: alan.le-goff@univ-grenoble-alpes.fr

## Abstract:

Conventional proton-exchange-membrane hydrogen/air fuel cell relies on platinum nanoparticles to harvest electrical energy from the $H_2$ oxidation and $O_2$ reduction reactions. In Nature, metalloenzymes use iron, nickel and copper-based active sites to oxidize $H_2$ or reduce $O_2$ with intrinsic performances closed to platinum. The electrical wiring of enzymes on electrode implies the optimization of catalyst loadings and electron transfers between the surface of the electrode and the enzyme active site. We have especially investigated the biomimetic wiring of nickel-iron hydrogenases and multicopper oxidases at nanostructured electrodes for their integration in fuel cell systems.[1–4] In parallel, we have developed the synthesis and immobilization of copper- and nickel-based molecular catalysts and their grafting on nanostructured electrodes.[5,6] These catalysts have to be designed by taking into account the important features of metalloenzymes which are responsible for their exceptional catalytic activity. This presentation will show our recent advances in the molecular engineering of the electrode surface for the immobilization of metalloenzymes or their synthetic models for their integration in fuel cells.

## References:

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2 L. Altamura, C. Horvath, S. Rengaraj, A. Rongier, K. Elouarzaki, C. Gondran, A. L. B. Maçon, C. Vendrely, V. Bouchiat, M. Fontecave, D. Mariolle, P. Rannou, A. Le Goff, N. Duraffourg, M. Holzinger and V. Forge, *Nat. Chem.*, 2017, **9**, 157–163.

3 S. Rengaraj, R. Haddad, E. Lojou, N. Duraffourg, M. Holzinger, A. Le Goff and V. Forge, *Angew. Chem. Int. Ed.*, 2017, **56**, 7774–7778.

4 S. Gentil, S. M. Che Mansor, H. Jamet, S. Cosnier, C. Cavazza and A. Le Goff, *ACS Catal.*, 2018, 3957–3964.

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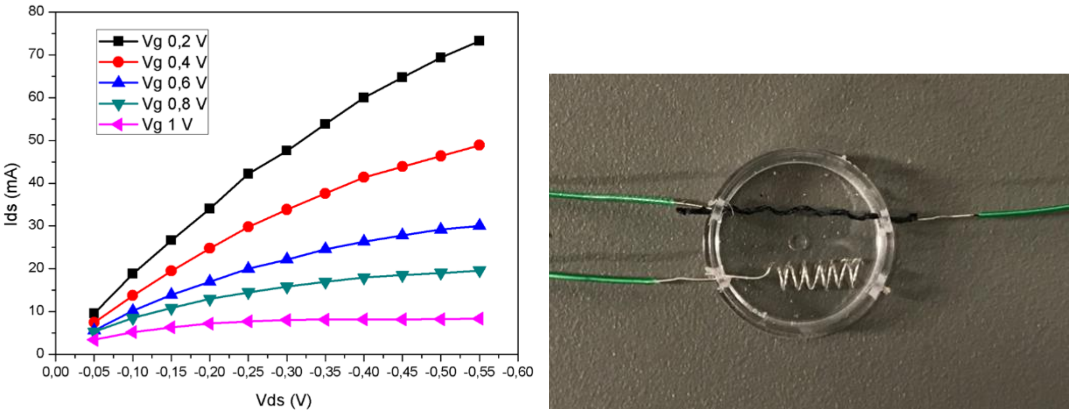
# Textile biosensor based on conductive polymer for sweat analysis

Nicola Coppedè,[a] Francesco Gentile [b], Andrea Zappettini,[a]

[a]IMEM-CNR Parco Area delle Scienze 37/A - 43124 Parma, Italy. Email: nicola.coppede@imem.cnr.it
[bc]Department of Electrical Engineering and Information Technology, University Federico II, Naples, Italy.

## Abstract:

Wearable devices are gaining much interest for the application in biomedical and athletic performance monitoring. Many devices are able to realize physical measurements, like heart beat or accelerometer monitoring. More difficult and more challenging is the realization of chemical and biochemical sensor that perform efficient measurements in wearable devices. A great challenge is to use wearable devices to monitor human sweat and control important physiological parameters in noninvasive way. In literature solutions have been tested with plastic patches, that use microfluidic to collect the sample and a printed device on plastic to monitor parameters. The limits of these technologies are represented by a difficult to collect the sample from the skin and the non-comfortable condition of having a plastic patch on the skin. To answer to these limitations IMEM CNR develop textile biosensors, based on conductive polymer PEDOT:PSS that are able to work completely embedded in textile materials[1,2]. Moreover, the textile devices are able to collect spontaneously the sweat and analyze it in the fibers. The polymers have been used in an Organic Electrochemical Transistors architecture. The devices could monitor saline concentration in human sweat, in a wearable setup, continuously and in noninvasive way. The biosensors could be used to monitor hydration of athletes and patients, giving crucial information on their physiological conditions. In this work we have tested different textile fibers, and we have characterized the device for different conductive polymer, for different substrate and optimized the response of the device. The textile sweat analysis biosensors are efficient candidates as wearable devices for monitoring human physiological conditions.



*Textile OETC characteristic and design*

## References:

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3 N. Coppedè et al.A single cotton fiber organic electrochemical transistor for liquid electrolyte saline sensing Journal of Materials Chemistry 22 (45), 23830-23834).

# Probing assembly, vibrational excitations and switching at the molecular level

***Johannes Barth***, *jvb@tum.de*
*Physik-Department E20, TUM, Garching, Bavaria, Germany*

The control and organization of molecular species is key to advance molecular science, organic electronics and the development of novel functional materials. We notably explore interfacial bonding, assembly and dynamic behaviour at well-defined homogenous surfaces, textured templates and sp2-sheet layers using scanning probe microscopy and complementary techniques. The developed bottom-up fabrication protocols employ biological and *de novo* synthesized building blocks, and implement error-corrective supramolecular bonding schemes as well as covalent chemistry. We thus advance the interfacial control of single molecular units and the design of nanoarchitectures with special structural features, intricate dynamics and tailored properties. Moreover, chemically-sensitive techniques for single-molecule electronics are described, notably addressing the fundamental challenge to quantitatively determine charge-vibrational coupling in well-defined single-molecule junctions. We thus explore current-carrying tethered molecules by combined vibrational and metal-molecule-metal junction current-voltage spectroscopy and the conformational response of a two-state molecular switch.

Recent key publications: Acc. Chem. Res. 51, 365 (2018); JACS 140, 4835 (2018); Nat. Chem. 10, 296 (2018); Nat. Chem. 9 33 (2017); Nat. Chem. 8, 657 (2016); Nature Chem. 7, 105 (2015); Nat. Comm. 7, 10700 (2016); Nano Lett. 15, 2242–2248 (2015); Acc. Chem. Res. 48, 2140 (2015); Nature Nanotech. 7, 41 & 673 (2012).

# High resolution imaging of molecular assemblies on Si(111):B by non-contact AFM at low temperature

Natalia Turek[a], Dominique Deresmes[a], Judicaël Jeannoutot[b],
Younes Makoudi[b], Frank Palmino[b], Frédéric Chérioux[b], Sylvie Godey[a], Thierry Mélin[a]
[a] *Institut d'Electronique, Microélectronique et Nanotechnologie, IEMN-CNRS UMR 8520, Av. Poincaré, CS 60069, 59652 Villeneuve d'Ascq Cedex, France.*
[b] *Institut FEMTO-ST, CNRS, Université Bourgogne Franche-Comté, 15B Avenue des Montboucons, 25030 Besançon Cedex, France*

Abstract:

We studied by non-contact AFM (nc-AFM) the formation of molecular self-assemblies on the passivated surface of boron doped silicon B-Si(111)-($\sqrt{3}$x$\sqrt{3}$) R30°. The investigated molecule (1-(4'cyanophenyl)-2,5-bis(decyloxy)-4-(4'-iodophenyl)benzene) possesses two aliphatic chains attached to a triphenyl core ended with two different terminations (either iodine or cyano group). The use of a passivated semiconductor substrate enables creating regular and extended structures without significant change in electronic properties of molecules [1, 2]. Scanning tunneling microscopy and nc-AFM imaging have been performed using a low-temperature (AFM/STM (JT AFM/STM, SPECS) operated at T=4K with high stiffness Kolibri sensors (k=540 kN/m, $f_0$=1 MHz). The growth of a periodic molecular network is observed, formed by parallel lines made by molecule aromatic cores and interdigitated aliphatic chains placed between adjacent rows (see Figure 1). We obtain submolecular resolution in the constant height $\Delta$f images without intentional tip functionalization [3], but only by conditioning the tip on the silicon surface [4]. We will discuss the high-resolution AFM imaging, as well as the conformation of the molecules in the observed assemblies (e.g. changes in the interdigitated aliphatic chains ordering), and in particular the role of the molecule dipoles.

References: [1] Makoudi Y,Beyer M, Lamare S, Jeannoutot J, Palmino F, Chérioux F, Nanoscale 2016, 8, 12347; [2] Makoudi Y, Jeannoutot J, Palmino F, Chérioux F, Copie G, Krzeminski C, Cleri F, Grandidier B, Surf Sci Rep. 2016, 72, 316; [3] Sweetman A, Jarvis S, Rahe P, Champness N, Kantorovich L, Phys. Rev. B 2014, 90, 165425; [4] Berger J, Spadafora EJ, Mutombo P, Jelínek P, Švec M, Small, 2015, 113686-3693.

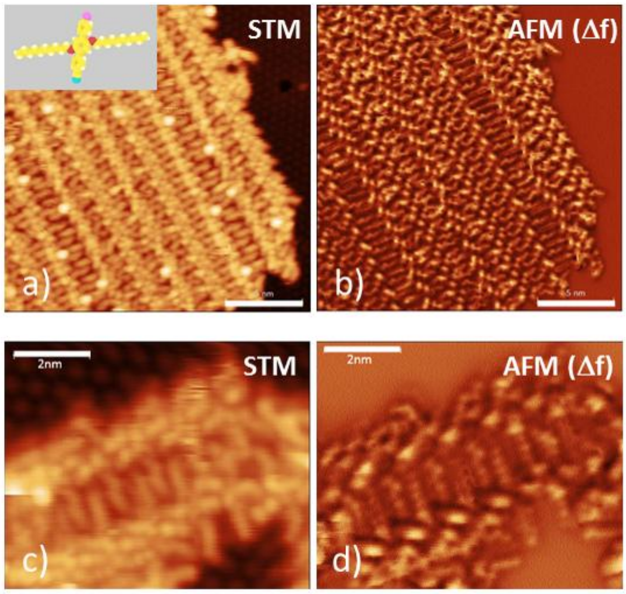

*Figure 1 : a) STM image (scale bar 5 nm) of a molecular assembly, $V_s$=-1.8 V, $I_t$=5 pA (the molecule is represented in the inset); b) constant height non-contact AFM image of the same zone; c) STM image (scale bar 2 nm) of a small organized domain taken at $V_s$=-1.9 V, $I_t$=5 pA; d) corresponding AFM image revealing submolecular contrast. All images have been recorded with a tip oscillation A=50pm.*

# Beyond "decorative" 2D supramolecular self-assembly: strategies towards functional surfaces for nanotechnology

Romain Brisse,[a,b] Imad Arfaoui,[a] Christophe Petit,[a] Ping Du,[b] David Kreher,[b] Fabrice Mathevet,[b] Lydia Sosa-Vargas,[b] Eunkyoung Kim,[c] Sylvain Le Liepvre,[d] Céline Fiorini-Debuisschert,[d] Fabrice Charra,[d] André-Jean Attias,[b,e]

[a]*MONARIS, CNRS-Sorbonne Université, France.*
[b]*IPCM, CNRS-Sorbonne Université, France. Email: andre-jean.attias@sorbonne-universite.fr*
[c]*Department of Chemical and Biomolecular Engineering, Yonsei University, Korea.*
[d]*SPEC, CEA, France.*
[e]*2B-FUEL, CNRS-Sorbonne Université-Yonsei University, Korea.*

## Abstract:

2D supramolecular self-assembly has emerged as a powerful tool in nanoscience for bottom-up fabrication of well-defined and long-range ordered two-dimensional (2D) molecular nanostructures at surfaces. The next step recently developed to go beyond decorative supramolecular self-assembly at surfaces is to provide a functionality to the whole 'substrate–organic adlayer' hybrid system.[1]

Here, we present two examples of strategies we have recently developed.

In the first example, we have developed a new method to trap a functional 3D functional building block (3D Zn-Phthalocyanine complex) into a large 2D nanoporous template on Highly Oriented Pyrolytic Graphite (HOPG).[2] This facile process combines the surface-confined host–guest chemistry and drop-casting method. We describe an unusual approach relying on the large-scale observation of the functionalized surface allowing the use of several experimental techniques such as scanning tunneling microscopy (STM) at the air/solid interface, resonance Raman spectroscopy, and contact angle measurements. By overlapping the different results, it is possible to reliably prove the controlled immobilization of the building block molecules at a long range.

In the second example, graphene and an emitting 3D building block are combined to obtain a light emitting graphene-based hybrid 2D system. We report the first fluorescent molecular self-assembly on graphene.[3] The quenching of the fluorescence of the adsorbed dye by the adjacent graphene is hindered at the molecular scale based on a spacer approach, through a specifically designed dual-functionalized self-assembling building block. This 3D tecton presents two faces, one forming a noncovalent graphene-binding pedestal and the other carrying a dye group linked by a spacer to the pedestal. The spontaneous ordering of the adsorbed layer is investigated by STM at liquid-solid interface, whereas the resulting optical properties of the whole graphene−dye hybrid system are characterized by absorption and fluorescence spectroscopies.

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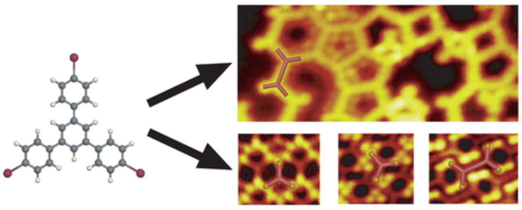
# Local Characterisation of On-Surface Synthesis of 2D Porous Organic Covalent-Nanoarchitectures

Fabien Silly,[a] David Peyrot,[a]

[a]TITANS, SPEC, CEA, CNRS, Université Paris-Saclay, 91191 Gif sur Yvette, France. Email: Fabien.silly@cea.fr

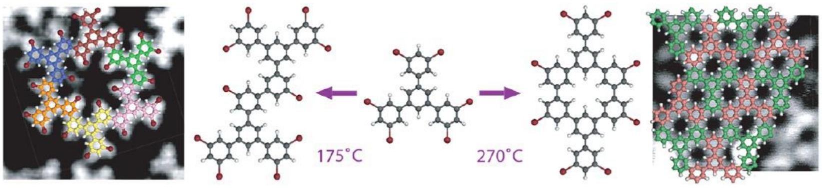
## Abstract:

We investigate on-surface bottom-up synthesis to create patterned graphene nanoarchitectures via Ullmann coupling. Star-shaped 1,3,5-Tris(4-iodophenyl)benzene molecules (Fig.2) self-assemble into halogen-bonded structures on graphite [1]. In contrast, our STM measurements reveal that on-surface synthesis of covalent nanoarchitectures is competing with the growth of self-assembled halogen-bonded structures when this molecule is deposited on Au(111) in vacuum [2], Fig.1. We show that the molecules form covalent polygonal nanoarchitectures at the gold surface step edges and at the elbows of the gold reconstruction at low coverage. With coverage increasing two-dimensional halogen-bonded structures appear and grow on the surface terraces. At high coverage the competitive growth between the covalent and halogen-bonded nanoarchitectures leads to formation of a two-layer film above one monolayer deposition.



*Hierarchical formation of porous structure using iodine-compounds on Au(111) [2]*

We then investigated the on-surface synthesis of covalent nanoarchitectures of star-shaped 1,3,5-tris(3,5-dibromophenyl)-benzene molecules on Au(111). This molecule has two bromine atoms at the extremity of each arm. At room temperature, the molecules self-assemble into a porous halogen-bonded network [3]. One-covalent-bond dimers appear on the surface after annealing at 145 °C. One-covalent-bond chains are created after annealing at 170 °C. One-covalent-bond hexagons (Fig.2, left) as well as two-covalent-bond dimers are appearing on the surface after annealing at 175 °C. Annealing at 275 °C leads to the formation of a porous 2D hexagonal two-covalent-bond nanoarchitecture (Fig.2, right). STM images show that the number of intermolecular covalent bonds increases as the temperature rises.



*Hierarchical formation of porous structure using bromine-compounds on Au(111) [4]*

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# Polarized-light assisted charge spreading in 1D organic semiconductor nanocrystals on 2D materials

Christian Teichert,[a] Aleksandar Matković, [a] Markus Kratzer, [a] Jakob Genser,[a] Bernd Kollmann,[b] Daniel Lüftner, [b] Peter Puschnig, [b] Zhongrui Chen,[c] Olivier Siri,[c] Conrad Becker [c]

*[a]Institute of Physics, Montanuniversität Leoben, Franz Josef Strasse 18, 8700 Leoben Austria.*
*Email:teichert@unileoben.ac.at*
*[b]Institute of Physics, University of Graz, NAWI-Graz, Universitätsplatz 5, 8010 Graz, Austria.*
*[c]Aix Marseille Université, CNRS, CINaM UMR 7325, 13288 Marseille, France.*

## Abstract:

Crystalline films of small conjugated molecules offer attractive potential for fabricating organic solar cells, organic light emitting diodes (LEDs), and organic field effect transistors (OFETs) on flexible substrates. Here, the novel two-dimensional (2D) van der Waals materials like conducting graphene (Gr), insulating ultrathin hexagonal boron nitride (hBN), or semiconducting transition metal dichalcogenides come into play. Gr for instance offers potential application as a transparent conductive electrode in organic solar cells and LEDs replacing indium tin oxide, whereas hBN can be used as an ultrathin flexible dielectric in OFETs. Recently, we reported on the self-assembly of crystalline nanowires (NWs) composed of rod-like oligophenylene molecules on exfoliated, wrinkle-free Gr [1-2] and hBN [3], both transferred onto SiO2. The NWs are several 10 nm wide and a few nm high, they can extend to several 10 µm in length. The discrete NW directions with respect to armchair and zigzag directions of the substrates were determined by atomic-force microscopy (AFM) in conjunction with density functional theory calculations.

Here, we study the growth of an oligoazaacene derivate dihydrotetraazaheptacene (DHTA7), which - due to nitrogen containing groups - forms crystals through H-bonding and dipolar interactions between neighboring molecules. Crystalline NWs of DHTA7 were grown by hot wall epitaxy on insulating hBN flakes. Using conductive AFM (C-AFM) and photo-assisted electrostatic force microscopy (EFM), we demonstrate charge trapping and light-assisted charge spreading within the networks of DHTA7 NWs. We found that the NWs are not conductive in the dark, while visible light - linearly polarized parallel to the long axis of the molecules, i.e. perpendicular to the nanowires' long axes - allows spreading of the charges across the network for tens of micrometers. The results indicate that - due to light excitation - charges that were trapped in the localized defects can spread through the bands of the organic semiconductor. The charge transport can be described by a simple diffusion model, considering the individual NWs as RC-transmission lines.

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# Constrained density functional theory: a versatile tool for studying charge dynamics in organic materials

Stefano Sanvito
School of Physics and CRANN, Trinity College, Dublin 2, Ireland

Constructing a materials-specific theory of charge dynamics in organic single materials is a complex problem, where the computation of accurate structural and vibrational properties needs to be coupled to ways of determining the charge mobility characteristics. In particular one needs an accurate method for describing excitations, which is also scalable to reasonably large systems. Here I will discussed how different flavours of constrained density functional theory (CDFT) can achieve such goal.

Firstly I will consider the most conventional form of CDFT, which allows one to calculate the energy of systems with displaced electron densities (e.g. in a charge transfer process). Such scheme can be used to extract a number of quantities important for charge dynamics. Here I will make examples of the calculation of 1) the charge transfer energies of molecules on surfaces, so to derive accurate level alignments[1,2]; 2) the quasi-particle gap renormalisation in molecular crystals[3]; 3) the reorganisation energy of molecules in the gas phase and on surfaces[4].

Then I will move to show a recently implemented scheme, which uses CDFT to compute elementary excitations in molecules[5]. This method, which we have named excitonic DFT (XDFT), calculates the M-particle excited state of an N-electron system, by optimizing a constraining potential to confine $N - M$ electrons within the ground-state Kohn-Sham valence subspace. The efficacy of XDFT will be demonstrated by calculating the lowest single-particle singlet and triplet excitation energies of the well-known Thiel molecular test set, with results which are in excellent agreement with time-dependent density functional theory (TDDFT).

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# Calixarenes-templated Zig-Zag-type single walled carbon nanotubes short segments

Ali Ben Saida, Ibrahim Abdellah, Cyril Martini, Vincent Huc

*Institute for Molecular Chemistry and Materials in Orsay (ICMMO)-Université de Paris-Sud.*
*15 rue Georges Clémenceau 91405 Orsay-France.*
*E-mail: Vincent.huc@u-psud.fr*

The synthesis of conjugated carbon nanorings is now a hot topic actively developed by several groups all over the world, since the pioneering work from Jasti and Bertozzi in 2008 [1].These molecules are of particular importance, as they can be considered as Single Walled Carbon NanoTubes (SWCNT) short segments, opening the way towards the total synthesis of "armchair-type" nanotubes. Recently, our group reported a very simple synthesis of another family of SWCNT short segments (of the so-called "zig-zag type"), using calixarenes as templates to preorganise small aromatic units (one example figure 1A) [2]. Very recently, we used the same synthetic strategy to introduce extra aromatic units on the previous segments, allowing for simple lengthening strategies to be envisioned (Two examples shown on Figures 1B and 1C) [2].

We also show that our approach offers the possibility to obtain new families of macrocyclic compounds, with interesting optic/electronic properties (figure 1C) [3].

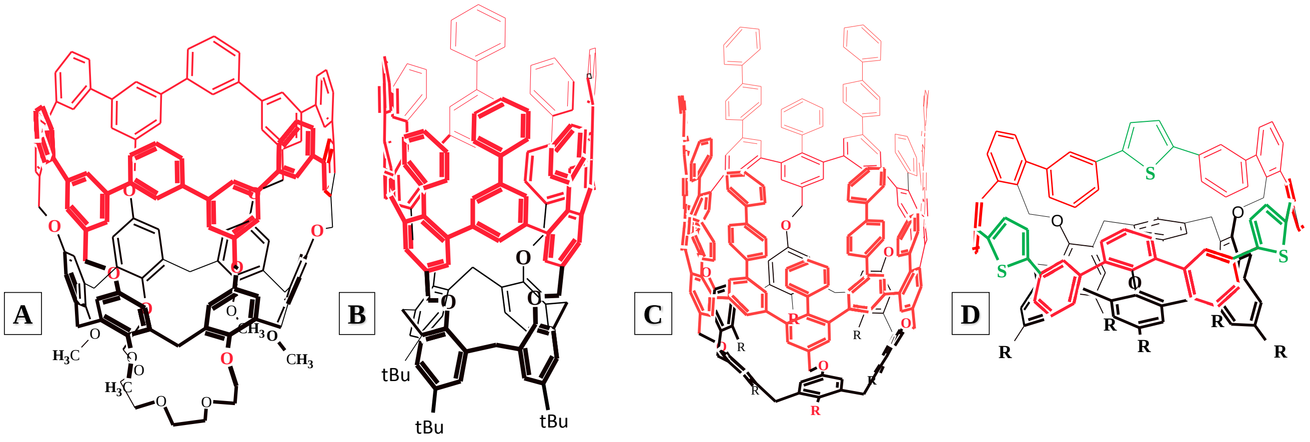

**Figure 1: some examples of calixarenes-templated SWCNTs short segments.**

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2- Ali Ben Saida, Vincent Huc et al, submitted
3- Cyril Martini, Vincent Huc et al, submitted

# Hybrid van der Waals Heterostructures

Marco Gobbi,[a] Chaoying Fu,[b,c] Dimitri F. Perepichka,[c] Paolo Samori, [a] Emanuele Orgiu [a,b]

*[a] University of Strasbourg, CNRS, ISIS UMR 7006, 8 allée Gaspard Monge, F-67000 Strasbourg, France.*
*[b] INRS, Énergie Matériaux Télécommunications Centre, 1650 boulevard Lionel-Boulet, Varennes (Québec) J3X 1S2, Canada.*
*Email: emanuele.orgiu@emt.inrs.ca*
*[c] Department of Chemistry, McGill University, 801 Sherbrooke Street W., Montreal (Québec) H3A 0B8, Canada.*

## Abstract:

The rise of graphene and related 2D materials makes it possible to form heterostructures held together by weak interplanar van der Waals (vdW) interactions. The incorporation of organic molecules within these systems holds an immense potential. Whilst nature offers a finite number of 2D materials, an almost unlimited variety of molecules can be designed and synthesized with predictable functionalities [1]. The possibilities offered by systems in which continuous molecular layers are interfaced with inorganic 2D materials to form hybrid organic/inorganic van der Waals heterostructures are emphasized. Similar to their inorganic counterpart, the hybrid structures have been exploited to put forward novel device architectures. Moreover, specific molecular groups can be employed to modify intrinsic properties and confer new capabilities to 2D materials. In particular, it is highlighted how molecular self-assembly at the surface of 2D materials can be mastered to achieve precise control over position and density of (molecular) functional groups, paving the way for a new class of hybrid functional materials. In particular, within such vdW heterostructures, currently assembled by mechanical superposition of different layers, periodic potentials naturally occur at the interface between the 2D materials. These potentials significantly modify the electronic structure of the individual 2D components within the stack and their alignment, thus offering the possibility to build up hybrid and novel materials with unique properties. In our work, we took a different approach by showing that pre-programmable periodic potentials arise in bi-layered structures formed by supramolecular lattices (SLs) over graphene, making them the hybrid equivalent of fully-inorganic vdW heterostructures. In particular, we work with molecules whose single domains extend over areas exceeding 1 µm$^2$, therefore on a relevant scale for device probing, and stable at ambient conditions. Such a novel approach for tailoring the periodic potential is easily applicable to other 2D materials, highlighting the rich prospects that molecular design offers to create *ad hoc* heterostructures [2].

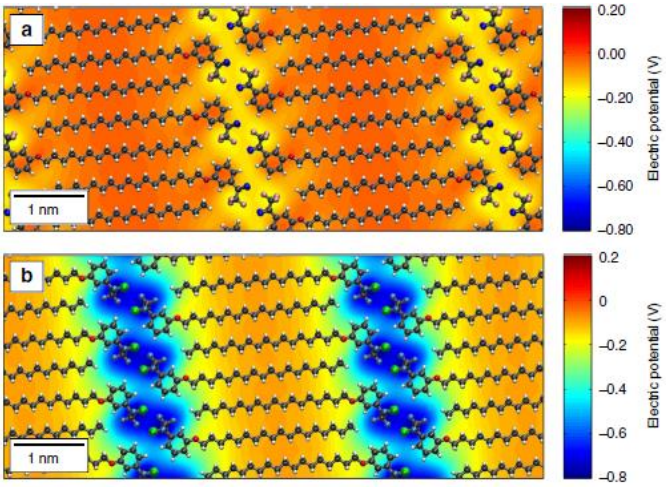

***Fig. 1***. *Periodic potentials introduced by the supramolecular lattices. Calculated differential electrical potential induced by two different supramolecular lattices on graphene. The supramolecular lattice is superimposed for clarity. The electrical potential is periodically modulated, with negative values in the region below the molecular heads.*

## References:

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# Micrometer-long covalent organic fibres by photo-initiated radical polymerization on an alkali-halide surface

Franck Para[1], Franck Bocquet[1], Laurent Nony[1], and Christian Loppacher[1*];
Michel Féron[2] and Fréderic Cherioux[2];
David Z. Gao[3], Filippo Federici Canova[3], and Matthew B. Watkins[4].

[1] Aix-Marseille Université, CNRS, IM2NP UMR 7334, 13397 Marseille, France;
[2] Institut FEMTO-ST, Univ. Bourgogne Franche-Comté, CNRS, F-25030 Besançon, France;
[3] Nanolayers Research Computing LTD, 15 Southgrove Road, Sheffield, UK, S10 2NP;
[4] School of Mathematics and Physics, University of Lincoln, UK.

## Abstract:

We present the fabrication of up to 1 µm long polymer fibres on insulating alkali-halide substrates by radical chain polymerisation [1]. The novelty of our approach is that first, the chosen dimaleimide molecules (fig.1a) perform a chain-like (and not a step-like) growth via a radical polymerization, second, that the polymerization is initiated from a two-dimensional gas phase rather than from an intermediate self-assembled structure, and third, that the cations of the chosen alkali-halide substrate interact with the molecule's oxygen atoms and facilitate a defect-free propagation of the polymer fibres along a preferred axis of the substrate.

We discuss the different initiation mechanisms of the polymer reaction at room-temperature that can either be spontaneous (fig.1b), or induced by UV-light (fig.1c). Once initiated, the chain-like polymerization proceeds easily and is only stopped by either defects on the surface or exhaustion of the precursor molecules. The propagation of this reaction on the surface, the involved reaction barriers as well as the structure and stability of the formed 1D polymer fibres (fig.1d) are discussed by means of Density Functional Theory calculations, Climbing Image Nudged Elastic Band Calculations, and noncontact Atomic Force Microscopy imaging and manipulation at room temperature.

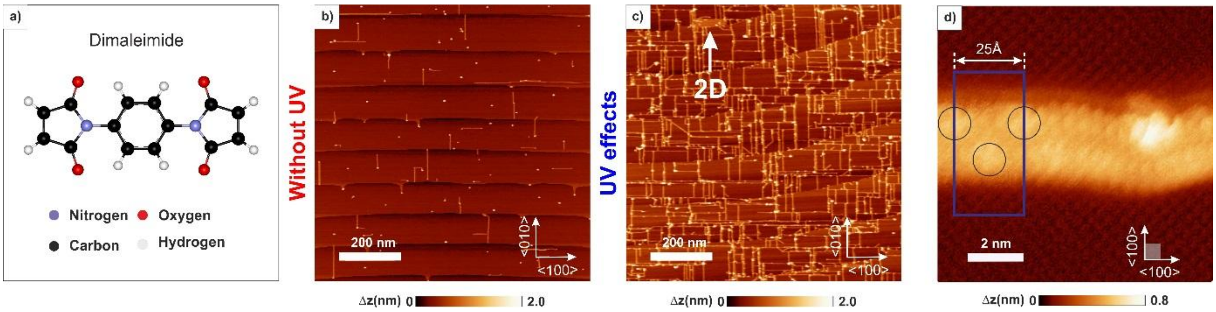

**Figure 1:** *a) Chemical structure of N,N'-(1,4-Phenylene) dimaleimide; ncAFM image of polymer fibres on a KCl substrate formed spontaneously (b) and assisted by UV-light (c); d) ncAFM image showing the KCl substrate as well as individual molecules within the polymer chain.*

## References:

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# THURSDAY 20ST

## Session 7

| | |
|---|---|
| 8.30-9.10 | **Yohan CORAUX (Keynote lecture)**<br>Hybrid (spin)interface between a 2D material and a metal |
| 9.30-9.30 | **Stefan BLIEN**<br>Coupling a suspended, ultraclean carbon nanotube quantum dot to a coplanar microwave resonator |
| 9.30-9.45 | **Stefano TOFFANIN**<br>Epitaxially ordered alkanes on 2D black phosphorous as passivating dielectric multilayers |
| 9.45-10.00 | **Anna FARQUHAR**<br>Electrochemical Grafting of Graphene-like Nanoribbons on Carbon Substrates for High Performance Energy Storage |
| | 10.00-10.20 ………COFFEE BREAK |
| 10.20-11.00 | **Valentin DEDIU (Keynote lecture)**<br>Interface as key unit in molecular spintronic devices |
| 11.00-11.20 | **Benoit QUINARD**<br>Spin-dependent transport in self-assembled monolayers |
| 11.20-11.40 | **Tong YONGFENG**<br>Selective spin switch at the molecular scale in a two-dimensional dense array of spin-crossover molecules |
| 11.40-12.00 | **Simon TRICARD**<br>Chemical Tuning of Coulomb Blockade at Room-Temperature in Ultra-Small Platinum Nanoparticle Self-Assemblies |
| 12.00-12.10 | **Sponsors presentation** |
| | 12.10-13.40 LUNCH |

## Session 8

| | |
|---|---|
| 13.40-14.20 | **Steven De FEYTER (Keynote lecture)**<br>Functionalization of 2D materials: a molecular approach |
| 14.20-14.40 | **Andrew MAYNE**<br>STM studies of a self-assembled NiPc molecular lattice on graphene |
| 14.40-15.00 | **Jerome LAGOUTE**<br>Electronic interaction between organic molecules and nitrogen doped graphene |
| 15.00-15.15 | **Timothé McCORMAC**<br>Polyoxometalates; Redox properties, surface manipulation and molecular electronic applications |
| 15.15-15.30 | **Matteo MAURO**<br>Light-responsive metallo-supramolecular polymers for 2D and selfhealable 3D materials |
| | 15.30-15.50 ………COFFEE BREAK |
| 15.50-16.30 | **Anders HAGFELDT (Keynote lecture)**<br>The Versatility of Mesoscopic Solar Cells |
| 16.30-16.50 | **Ya-Ping SUN**<br>Carbon Quantum Dots and Their Polymeric Nanocomposites - Materials Development and Optoelectronic Applications |
| 16.50-17.10 | **Tetsuya AOYAMA**<br>Mechanical rubbing-induced edge-on to face-on reorientation and molecular alignment in thienoquinoid transistors |

# Hybrid (spin)interface between a 2D material and a metal

Johann Coraux

*[a]Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut NEEL, 38000 Grenoble, France. Email: johann.coraux@neel.cnrs.fr*

Abstract:

Interfaces between molecules and inorganic materials, *e.g.* metals, are at the heart of molecular electronics, optoelectronics or spintronics. They sometimes even dominate the behaviour of devices, and for this reason are fields of investigation in their own right — spinterface being a striking illustration. Seeing two-dimensional materials (graphene, boron nitride or transition metal dichalcogenides, etc) as molecules may seem far-fetched. I wish to discuss the idea that just like molecules they form hybrid interfaces with metals, though. And in fact these interfaces share interesting similitudes with molecule/metal interfaces, but come together with original features. Graphene, as the first studied two-dimensional material, has been scrutinised by us and others, to try to answer several key questions in this respect: What is the physico-chemistry, noteworthy the nature of bonding, at the graphene/metal interface? What is special with having a highly cohesive material instead of molecules in contact with the metal surface? How can we prepare and control interfaces with (functional) metals at will? Answering these questions opens opportunities: Graphene (or molecules) may serve as a building-block in magnetic multilayers to be used in carbon-inside spintronic devices; Highly transparent graphene-superconductor junctions may be created and superconductivity induced in graphene; Other two-dimensional materials may be used instead of graphene, to seek for more advanced interfacial phenomena in the future.

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S. Vlaic *et al.* Phys. Rev. Mater. 1, 053406 (2017)
S. Vlaic *et al.* J. Phys. Chem. Lett. 9, 2523 (2018)

# Coupling a suspended, ultraclean carbon nanotube quantum dot to a coplanar microwave resonator

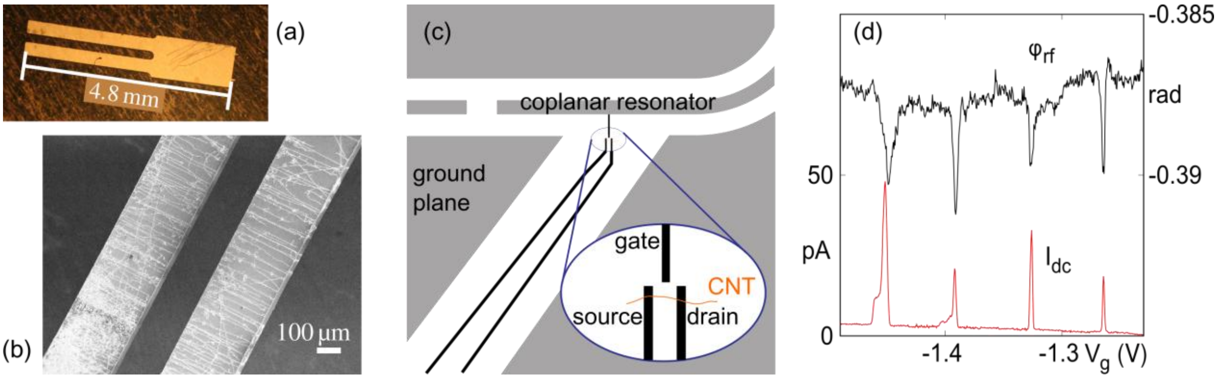
Stefan Blien,[a,*] Patrick Steger,[a] Niklas Hüttner,[a] Richard Graaf,[a] Andreas K. Hüttel[a]

[a] *Institute for Experimental and Applied Physics, University of Regensburg, 93040 Regensburg, Germany*
[*] *e-mail: stefan.blien@ur.de*

## Abstract:

A clean, suspended single wall carbon nanotube is the ultimate limit of a nanomechanical beam resonator [1], where the fundamental transversal vibration mode reaches resonance frequencies on the order of 100MHz and mechanical quality factors up to $10^6$ [2,3]. We have developed a transfer technique to insert such suspended nanotubes into coplanar superconducting circuitry [4], and present first measurement results on a combined device coupling the nanotube to a coplanar microwave resonator mode at millikelvin temperatures.

A GHz signal resonant to the microwave cavity probes the quantum capacitance of the attached nanotube [5,6], allowing us to characterize its charge response. In addition, however, the combination of nanotube vibration and microwave cavity forms an optomechanical system [7]; we propose that through the strong coupling of charge transport and vibration [8], Coulomb blockade and single electron tunneling lead to a rich physics of enhanced optomechanical coupling [9].



*(a) Commercial quartz tuning fork, with its metallization removed. (b) SEM image of long, aligned carbon nanotubes grown across the fork tines. (c) Schematic device, coupling a suspended carbon nanotube to a GHz coplanar waveguide resonator. (d) Coulomb oscillations detected in dc current and GHz transmission phase.*

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# Epitaxially ordered alkanes on 2D black phosphorous as passivating dielectric multilayers

Margherita Bolognesi[a], Marco Brucale[a], Salvatore Moschetto[a], Federico Prescimone[a], Vladimir Korolkov[b], Andrea Lorenzoni[a], Matteo Baldoni[a], Francesco Mercuri[a], E. Besley[b], Michele Muccini[a], Maurizio Peruzzini[c], Peter Beton[b] and Stefano Toffanin[*,a]

[a] *Italian National Council for Research - Institute for the Study of Nanostructured Materials, CNR-ISMN, Via Gobetti 101, 40129 Bologna, Italy.*
[b] *Univerisity of Nottingham, University Park Nottingham NG7 2RD, United Kingdom .*
[c] *Italian National Council for Research - Institute for the Chemistry of OrganoMetallic Compounds, CNR-ICCOM, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Florence, Italy*
*Email of the presenting author (*): s.toffanin@bo.ismn.cnr.it*

## Abstract:

Few- and single layer black phosphorous (2D BP) is among the most promising emerging semiconducting 2D material. 2D BP shares some structural similarities with other 2D materials, but it is generally more reactive than most of them. 2D BP is consequently more prone to degradation in air but also more suited to create atomically-controlled heterostructures for a wide range of applications.[1] Heterostructures based on 2D BP and other inorganic 2D materials have indeed shown a good stability and excellent functionalities.[2] Even epitaxial self-assembled monolayers (SAMs) of organic molecules on 2D BP have shown a good protecting ability, and can be formed more easily via solution or sublimation.[3]

In this framework, we studied a Van der Waals (VdW) epitaxial system composed of 2D BP coated with tetracosane (a n-alkane with 24 C atoms). High-resolution AFM of a SAM of tetracosane on a bulk BP crystal (used as a model system) showed the co-existence of both disordered and epitaxial domains. MD simulations and high-resolution AFM revealed that tetracosane chains are energetically favored to align along two principal crystalline axis of BP (at +35° and -35° with respect to the armchair direction). This epitaxial arrangement was also observed for tetracosane on exfoliated 2D BP. Here, ordered domains are able to inhibit the oxidation of 2D BP keeping the system unperturbed for around 1h (instead of a few minutes for pristine 2D BP), while amorphous/disordered domains are much less efficient. The protecting properties of the epitaxial domains were improved through a fine tuning of the deposition/processing conditions on the 2D BP flakes: tetracosane ordered multilayers showed a 18-fold enhanced protecting functionality with respect to monolayers.

Electrostatic force microscopy (EFM) was then employed as non-trivial technique to investigate on the functionality of the system, in detail on the dielectric properties of pristine and alkane-coated 2D BP. EFM supported the qualitative conclusion that (i) the oxidation process impacts on the electrical properties of BP, (ii) the multilayered tetracosane offers excellent protection against oxidation and (iii) is able to significantly depress BP polarization. Indeed tetracosane monolayers and multilayers responded to electrostatic stimuli as expected in the case of an electrical insulator. EFM results open to the implementation of the studied VdW epitaxial heterostructures based on 2D BP as stable components and devices with a metal-insulator-semiconductor architecture.[4]

*The European Research Council (ERC) is acknowledged for funding the work through the project PHOSFUN, an ERC Advanced Grant assigned to MP as PI (Grant Agreement No. 670173).*

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# Electrochemical Grafting of Graphene-like Nanoribbons on Carbon Substrates for High Performance Energy Storage

Anna K. Farquhar,[a] Mustafa Supur,[a] Scott R. Smith,[a] Colin Van Dyke,[b] Richard L. McCreery[a,b]

[a] *Department of Chemistry, University of Alberta, 11227 Saskatchewan Drive, Edmonton, Alberta, Canada. Email:farquhar@ualberta.ca*

[b] *Nanotechnology Research Centre, National Research Council Canada, 11421 Saskatchewan Drive, Edmonton, Alberta, Canada.*

## Abstract:

The world's growing demand for renewable energy has stimulated major research efforts in both battery and supercapacitor devices. Developing supercapacitors with increased energy density, while maintaining their high power density, fast charge and discharge time, low cost and high stability, is essential for utilizing supercapacitors in high performance energy storage.

This work employs diazonium chemistry of a diaminonapthalene precursor in a simple, solution-based process to grow a covalently grafted, hydrogen-terminated "brush" of graphene-like nanoribbons (GR) on carbon substrates.[1] These highly conjugated ribbon structures have layer thicknesses from 2-20 nm, depending on the grafting parameters. Initial work demonstrated a remarkably high conductance, which greatly exceeds that of other large area molecular electronic junctions.[2] Moving from solid state devices to an electrochemical cell with sulfuric acid electrolyte, a 20-100 times increase in the electrode capacitance could be realized after grafting the GR brush compared to the starting carbon substrate. This is due to both an increase in the electrode surface area, which provides an enhancement in the electrical double layer capacitance, as well as a distinct type of "pseudocapacitance" likely resulting from redox centers scattered throughout the ribbon structure. The electrodes showed outstanding stability, with minor changes in voltammetry after 10,000 charge-discharge cycles. Furthermore, this grafting process can be applied to a variety of carbon substrates. Current commercially available supercapacitors typically use high surface area activated carbon or carbon black electrodes. Modification of carbon black electrodes with GR brushes gave a capacitance of 950-1890 F/g. A capacitance of 1890 F/g projects to an energy density of 590 Wh/kg for devices operating over a 1.5 V range, which greatly exceeds the 10 Wh/kg for today's commercially available supercapacitors and approaches that of lithium ion batteries.

This presentation will focus on the preparation of graphene-like nanoribbons on both flat pyrolyzed photoresist films and high surface area carbon black electrodes. Subsequent characterization and electrochemical studies will also be described, to demonstrate the remarkable performance of these modified carbon surfaces.

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# Interface as key unit in molecular spintronic devices

Alek Dediu

*ISMN-CNR, Bologna, Italy*

Information and communication technology (ICT) is calling for solutions enabling lower power consumption, further miniaturization and multi-functionality requiring the development of new device concepts and new materials. A fertile approach to meet such demands is the introduction of the spin degree of freedom into electronics devices, an approach commonly known as spintronics. This already lead to a revolution in the information storage (GMR read heads) in the last decades. Nowadays, the challenge is to bring spintronics also into devices dedicated to logics, communications and storage within the same material technology [1].

Organic semiconductors emerged as an extraordinary spintronic material about ten years ago, when a few papers appeared with straightforward and encouraging claims on spintronics phenomena [2]. From then on Organic Spintronics has evolved into a prolific discipline populated by a large number of experimentalists and theoreticians.

Research in molecular spintronics began with the aim of using molecules as spin transport media, thanks to their intrinsically weak spin relaxation mechanisms. Initial experiments focused on reaching spin transport in molecular films and on replicating previous device concepts taken from inorganic spintronics, such as spin valves and magnetic tunnel junctions. However, it soon became apparent that molecules were playing another role beyond that of mere spin transport materials. For example, in experiments with vertical spin valves, many groups were reporting consistently negative magnetoresistance. These results were striking, as they contradicted the well-established spin polarization sign of the ferromagnetic electrodes and the present knowledge at that time regarding spin transport. A few years later, a coherent picture arose invoking the role of molecular layers in tuning the spin polarization of ferromagnetic materials at the interface, and 'spinterface' was officially born.

Along this line I will especially concentrate on interfaces, representing the most important and the most hidden part of any spintronic device. Revealing their secrets is scientifically hard and experimentally costly, requiring sophisticated spectroscopic methods and massive calculations. For an interface consisting of a hard metallic electrode touching a soft organic layer, the situation obviously becomes even more complicated. I will overview the main achievements of the community in the investigation of very complex and very rich interface properties [3] and will describe the possibilities to develop and fabricate multifunctional devices which operation is fully dominated by the interface.

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3) Activating the Molecular Spinterface, M Cinchetti, V.A Dediu, L Hueso, Nature Materials 16, 507 (2017)

# Spin-dependent transport in self-assembled monolayers

Benoît Quinard[1], Sophie Delprat[1], Marta Galbiati[2], Sergio Tatay[2], Aymeric Vecchiola[1], Florian Godel[1], Sophie Collin[1], Pierre Seneor[1], Richard Mattana[1] and Frédéric Petroff[1]

[1] *Unité Mixte de Physique CNRS-Thales, 1 Av. A Fresnel, 91767 Palaiseau, France, and Université Paris-Sud, 91405 Orsay, France. Email: benoit.quinard@cnrs-thales.fr*
[2] *Instituto de Ciencia Molecular (ICMol), Universitat de Valencia, 46980 Paterna, Spain*

## Abstract:

Molecular spintronics, an emerging research field at the frontier between organic chemistry and spintronics, has opened novel and exciting opportunities in terms of functionalities for spintronics devices. Among those devices, Magnetic Tunnel Junctions (MTJs) have attracted a growing interest over the years. MTJs are made of two ferromagnetic electrodes separated with an insulating layer. Depending on the applied field, the magnetization of the electrodes can be parallel or antiparallel, modifying the resistance of the device. Our group focuses on replacing the insulating spacer, usually made of an oxide, with an organic self-assembled monolayer (SAM).

Indeed, it was shown that spin dependent hybridization at the metal/molecule interface could lead to a radical tailoring of spintronics properties [1]. To achieve this, SAMs appear to be very promising candidates thanks to their impressive molecular scale crafting properties and easy-processing. Previous works were done with basic molecules such as linear alkanethiols [2]. We now focus on more complex molecules integrating aromatic moieties to study how the modification of the tunnel barrier impacts the magnetic and electronic behaviour of the devices.

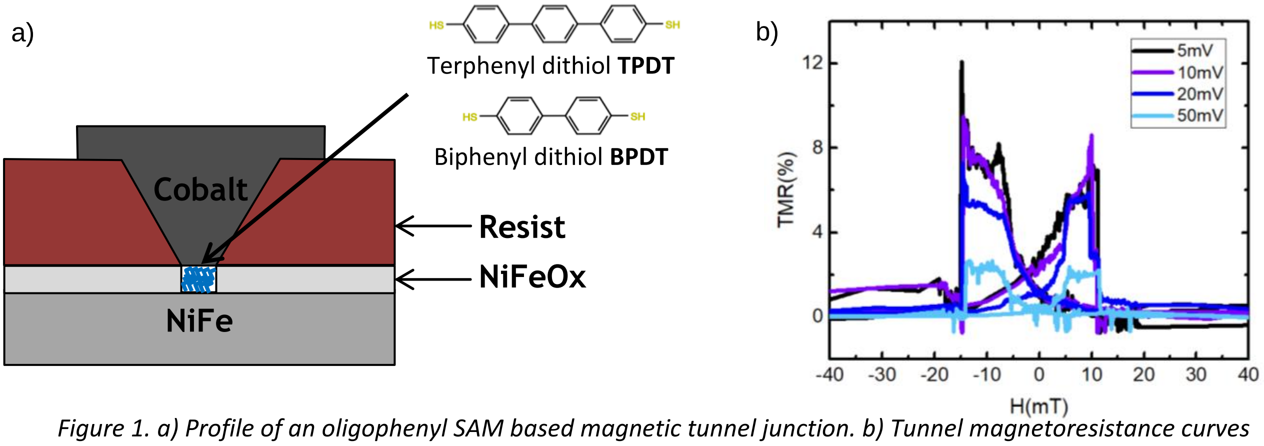

*Figure 1. a) Profile of an oligophenyl SAM based magnetic tunnel junction. b) Tunnel magnetoresistance curves obtained on a MTJ at 2K and different biases*

We will firstly present the fabrication procedure of our magnetic tunnel junctions, including a recently found method to recover the surface of an oxidized ferromagnet and graft a SAM ontop [3]. We will then present the transport experiments realized on our devices, including tunneling transport and tunnel magnetoresistance experiments. We will particularly try to underline the main similarities and differences between alkanethiols and oligophenyls MTJs.

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# Selective spin switch at the molecular scale in a two-dimensional dense array of spin-crossover molecules

Yongfeng Tong,[a] Amandine Bellec,[a] Jérome Lagoutea,[a] Cyril Chacona,[a] Yann Girard,[a] Sylvie Rousseta,[a] Marie-Laure Boillot,[b] Talal Mallah[b] & Vincent Repain[a]

*[a] Laboratoire Matériaux et Phénomènes Quantiques, Univ Paris Diderot, Sorbonne Paris Cité, CNRS, UMR 7162, 75013 Paris, France. Email: yongfeng.tong@univ-paris-diderot.fr*
*[b] Institut de Chimie Moléculaire et des Matériaux d'Orsay, Univ Paris Sud, Univ Paris Saclay, CNRS, UMR 8182, 91405 Orsay Cedex, France.*

Abstract:

Systems containing the spin crossover (SCO) complexes are attractive because the spin state can be controllably triggered by external stimuli. Herein we report a reversible spin state transition (SST) behaviour on a monolayer of $Fe^{II}$ spin crossover molecules ($Fe^{II}((3,5\text{-}(CH_3)_2Pz)_3BH)_2$, Pz for Pyrazolyl) that is vacuum sublimated onto a Cu(111) surface. Previous studies on arrays of those molecules on Au(111) have shown that it was possible to switch the spin state of a part of the molecules with blue light [1]. It was however not possible to switch molecules locally due to strong intermolecular interactions and the layer did not show any clear bistability (thermal hysteresis) [2]. Here, by using scanning tunnelling microscopy (STM), we show that on the Cu surface, we can switch single molecules one by one and independently in the array, a priori from the low spin to the high spin state by applying a local voltage pulse. Fig. 1 presents a typical image with the spin state of the molecules in the centre (square areas) selectively switched, giving a strong contrast to its surroundings. Moreover, we show that a visible light is able to erase those local writing. Surprisingly, the erased state is a disordered mixture of low spin and high spin molecules, what we inferred to an internal stress of the molecular layer induced by the substrate. Further studies should clarify the role of the substrate on the bistability of SCO layers and show if complete transitions are possible.

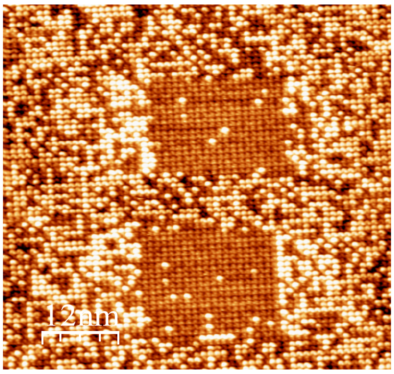

*Figure 1: 50 nm STM image showing the selective SST by voltage.*

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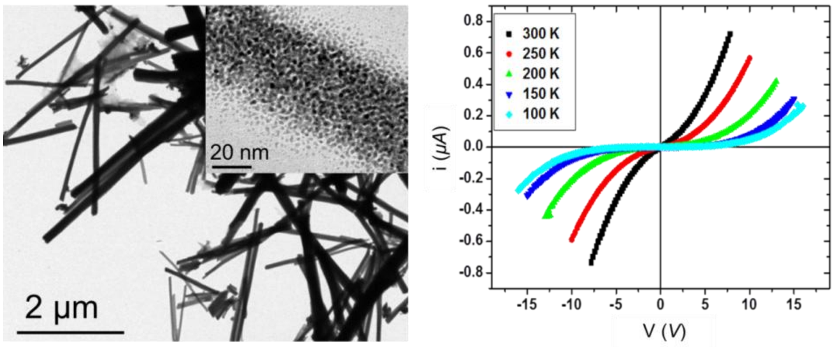
# Chemical Tuning of Coulomb Blockade at Room-Temperature in Ultra-Small Platinum Nanoparticle Self-Assemblies

Simon Tricard,[a] Olivier Saïd-Aïzpuru,[a] Donia Bouzouita,[a] Suhail Usmani,[a] Angélique Gillet,[a] Marine Tassé,[b] Romuald Poteau,[a] Guillaume Viau,[a] Phillipe Demont,[c] Julian Carrey,[a] and Bruno Chaudret[a]

[a] *LPCNO, INSA, CNRS, Université de Toulouse, Toulouse, France.* *Email: tricard@insa-toulouse.fr*
[b] *LCC, CNRS, Université de Toulouse, Toulouse, France*
[c] *CIRIMAT, CNRS, Université de Toulouse,Toulouse, France*

## Abstract:

Even if Coulomb blockade has been studied for over sixty years, and previously observed at room temperature, the new concept of our work is its fine modulation, which can only be achieved by a controlled organometallic chemistry approach, as a first step toward electronic devices. The goal is to tune Coulomb blockade in dense three-dimension self-assemblies of metallic nanoparticle with simple chemical tools. Synthesizing robust systems – stable in air for months – is a crucial condition; platinum nanoparticles stabilized by thiols, which form strong Pt-S bonds, are thus suitable systems. This presentation will describe the first system where the nanoparticle size, the ligand length and the ligand dielectric constant are independently varied to control the nanoparticle charging energy. Such a chemical approach allowed the determination of the most important parameters that influence Coulomb blockade, namely the dielectric constant of the ligands and the size of the nanoparticles. Elaborating such systems, stable in air for months, is a first step towards nanoelectronic systems, where the charging energy of the nanoparticles is tuned by the nature of the ligands.



*Platinum nano-particle assemblies in the presence of mercaptophenol: left: regular and zoomed (inset) TEM picture; right: charge transport measurements at temperatures ranging from 100 K to 300 K.*

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Tricard S.,* Saïd-Aïzpuru O., Bouzouita D., Usmani S., Gillet A., Tassé M., Poteau R., Viau G., Demont P., Carrey J., Chaudret B., *Chemical Tuning of Coulomb Blockade at Room-Temperature in Ultra-Small Platinum Nanoparticle Self-Assemblies,* Mater. Horiz. **2017**, 4, 487-492.

# Functionalization of 2D materials: a molecular approach

Steven De Feyter

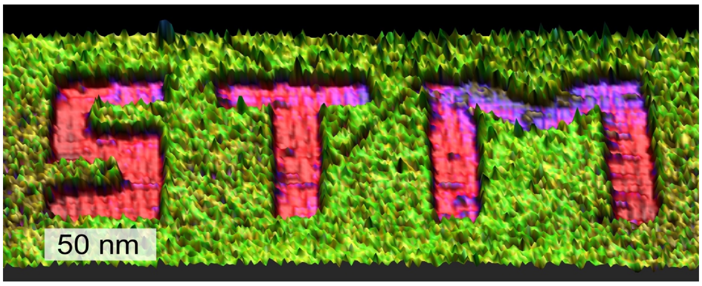
[a] KU Leuven, Department of Chemistry, Division of Molecular Imaging and Photonics, Celestijnenlaan 200F, B-3001 Leuven (Belgium)
Email: steven.defeyter@kuleuven.be

Abstract:

In this presentation, I will focus on the functionalization of graphite and graphene using two approaches. A first approach is based on molecular self-assembly at the interface between a liquid or air, and graphite or graphene. I will discuss concepts of nanostructuring emphasizing the effect of solvent, solute concentration and temperature, stimulus-driven self-assembly and self-assembly under nanoconfinement conditions. A second approach is based on grafting molecules on graphite or graphene via covalent chemistry. In addition to a discussion on the functionalization principles, it will be demonstrated how also nanolithography can be used to nanostructure such covalently modified surfaces.

Advanced interface specific methods such as scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) provide structural and other types of information at the nanoscopic level.

Various applications will be presented, including molecule modified graphene field effect transistors.



*Combined nanolithographic, covalent and non-covalent functionalization.*

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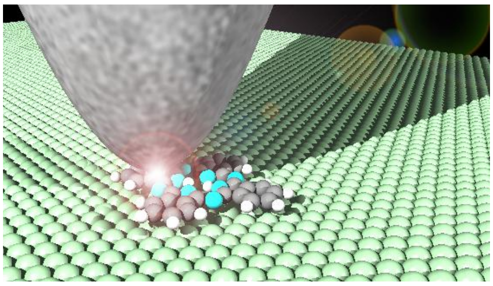
# STM studies of a self-assembled NiPc molecular lattice on graphene

Andrew J. Mayne,[a] Mali Zhao,[a] Gérald Dujardin,[a] Eric Duverger,[b] Philippe Sonnet,[c] Stéphane Campidelli,[d] Yannick Dappe,[d] Sophie Guéron,[e] Hélène Bouchiat[e]

*[a]Institut des Sciences Moléculaires d'Orsay, CNRS UMR 8214, Univ Paris-Saclay, 91405 Orsay, France.*
*Email: andrew.mayne@u-psud.fr*
*[b]Institut FEMTO-ST, Univ Franche-Comté, CNRS UMR 6174, 25030 Besançon, France.*
*[c]Institut de Sciences des Matériaux de Mulhouse, CNRS UMR 7361, Univ Haute Alsace, 68093 Mulhouse, France.*
*[d]Laboratoire d'Innovation en Chimie des Surfaces et Nanosciences, IRAMIS, NIMBE UMR 3685, CEA Saclay, 91191 Gif-sur-Yvette, France.*
*[e]Laboratoire de Physique des Solides, CNRS UMR 8502, Univ Paris Saclay, 91405 Orsay, France.*

## Abstract:

Graphene is a remarkable material for many electronic applications. Recent advances in devices involve the transport of electrons in molecular layers. A molecular layer on graphene containing transition metal atoms has been implemented in a prototype device for magnetic measurements.[1] I will discuss atomic-scale studies of the adsorption of Ni-phthalocyanine (NiPc) on monolayer graphene (MG) grown epitaxially on 6H-SiC(0001).[2] These molecular layers were studied using room-temperature scanning tunneling microscopy (STM). The molecules adsorb as self-assembled layers on the graphene with a square lattice, similar to perylene derivatives on graphene.[3] Tunneling spectroscopy with sub-molecular resolution at room-temperature reveals the localization of the NiPc molecular orbitals and their energies as a function of the sample bias. Density Functional Theory (DFT) calculations provide information on the charge transfer and charge localization. The results can be explained by the temporary charging of the NiPc molecules during the spectroscopy measurements. A brief comparison will made with the adsorption of PtTPP on graphene.[4] These studies provide a better understanding of the influence of metal-organic molecules on the electronic properties of graphene.



*Artistic view of STM tip imaging a Phthalocyanine molecule adsorbed on a hexagonal surface (G. Baffou).*

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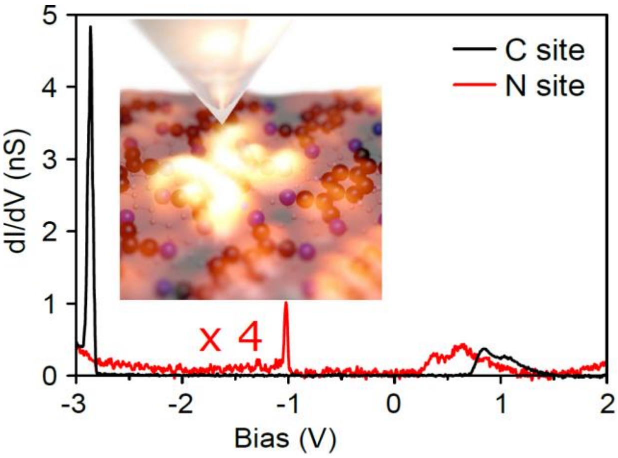
# Electronic interaction between organic molecules and nitrogen doped graphene

J. Lagoute[a], V. D. Pham[a], F. Joucken[b], R. Harsh[a], C. Chacon[a], Y. Girard[a], V. Repain[a], A. Bellec[a], S. Rousset[a]

*[a]Laboratoire Matériaux et Phénomènes Quantiques (MPQ), CNRS, Université Paris Diderot, Sorbonne Paris Cité, 75205 Paris Cedex 13, France. Email : jerome.lagoute@univ-paris-diderot.fr*
*[b]Laboratoire Physique de la matière et du rayonnement, Université de Namur, 61 Rue de Bruxelles, 5000 Namur, Belgium.*

## Abstract:

Tailoring the properties of graphene is of fundamental interest to uncover new functionalities and open new opportunities for graphene based applications. In this context, substitutional doping and molecular functionalization have focused tremendous efforts. Nitrogen doping obtained by replacing some carbon atoms by nitrogen atoms appears to be particularly interesting as it allows to perform n-doping with minor structural perturbations. This chemical doping can also modify the interaction of graphene with organic molecules that can be exploited for sensing or catalysis. To probe this effect at the molecular level, scanning tunneling microscopy and spectroscopy experiments have been performed on model systems with electron donor (porphyrin) [1,2] and electron acceptor (TCNQ) molecules [3] adsorbed on multilayer pristine and doped graphene on SiC(000-1). Local spectroscopy allows to measure resonances arising from the molecular states and to reveal the electronic coupling between molecules and graphene. On doped graphene, a local modification of the charge transfer between molecules and graphene occurs at the doping sites. Recent measurements on electron acceptor molecules show that the combination of this local charge transfer with an applied electric field allows for a selective control of the charge state in a molecular layer on graphene. This effect provides a route to tune the electronic interaction between molecules and graphene.



*Spectroscopy of TCNQ molecules on nitrogen doped graphene*

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# Polyoxometalates; Redox properties, surface manipulation and molecular electronic applications

Tim McCormac[a]

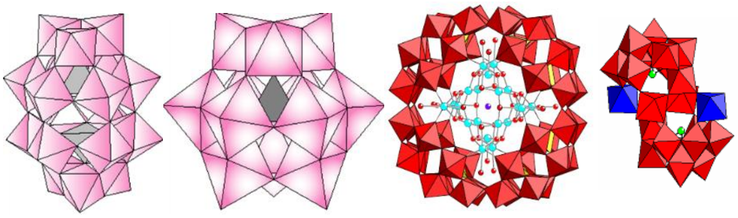
[a] *Electrochemistry Research Group, Dundalk Institute of Technology, Dundalk, Ireland. Email: tim.mccormac@dkit.ie*

Abstract: Polyoxometalates (POMs) are a significant class of inorganic metal – oxide cluster compounds that are of nanometer size and that are composed of a wide variety of types with varying anionic charge and shape[1]. They can be represented through the general formulae:

$[MmOx]p -$ Isopolyanions

$[XxMmOx]q -$ Heteroopolyanions

where M is typically $W^{6+}$ or $Mo^{6+}$. POMs have the ability to accept and donate varying numbers of multiple electrons in reversible steps without structural deterioration[2,3]. Due to this reversible redox activity, the ability to surface manipulate POMs onto an array of substrates (e.g. Au, ITO, Si, C, Pt, Graphene) through various methods (e.g. Electrodeposition, Layer by Layer, direct covalent attachment, polymeric deposition)[2,3], their nanometer size with discrete structures all make them ideal candidates for POM based molecular memory devices. Our group, in partnership with our collaborators, has been working on the design and surface manipulation of varying types of POMs onto varying substrates for the past number of years. This presentation will give an overview of some of our work paying particular attention to the current state of knowledge regarding POMs, their surface manipulation, redox switching abilities and their ability to be utilized within memory based devices.



(a) (b) (c) (d)

***Figure 1 :** Common POMs (a) Dawson type (b) Keggin Type (c) Crown Type (d)Krebs Type*

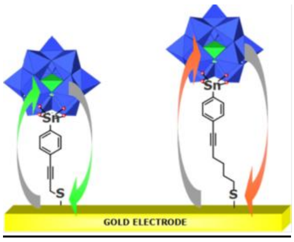


***Figure 2 :** Covalent attachment of POM onto a Au surface*[4]

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4. *Yaqub et al, Langmuir*, **2014**, 30 (15), pp 4509–4516

# Light-responsive metallo-supramolecular polymers for 2D and self-healable 3D materials

Matteo Mauro[a]

*Département des Matériaux Organiques (DMO), Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), University of Strasbourg & CNRS, 23, rue du Loess BP 43, F-67034 Strasbourg (France)*
*e-mail: mauro@unistra.fr*

## Abstract:

Smart functional materials that are able to translate an externally applied stimulus into a well defined, controllable, and reversible macroscopic response are one of the most fascinating materials nowadays. Soft and structurally dynamic functional materials are particularly attractive because of their intrinsic possibility to heal after damage. Amongst all possible triggers, light represents an interesting stimulus due to its advantageous features such as remote application with high spatiotemporal resolution.[1] During the talk, the straightforward molecular design of reversible and photo-switchable metallopolymers and their use as photo-responsive and autonomously healable gels will be presented (Fig. 1a). By simply mixing a proper metal salt and ligand(s) at the desired ratio, libraries of supramolecular metallopolymers have been straightforwardly prepared. In addition, judicious choice of the electronic properties of each building block allows to independently addressing luminescence and photo-isomerization by selection of the excitation wavelength. We found out that such materials can act as “supergelators” and either hydrogels or organogels have been obtained that display light-triggered reversible phase transition[2] and large photo-mechanical response (gel contraction),[3] respectively (Fig. 1b). Noteworthy, proper choice of the metal ion and its electronic excited-state features, *i.e.* Fe(II) *vs.* Co(II) and Zn(II), allowed control of the macroscopic photo-mechanical response in the gels state.[4] Finally, the monitoring of the reversible photo-triggered expansion/contraction processes at the sub-molecular level was achieved by means of scanning tunneling microscopy (STM)[5] on a highly oriented pyrolitic graphite (HOPG) surface (Fig. 1c).

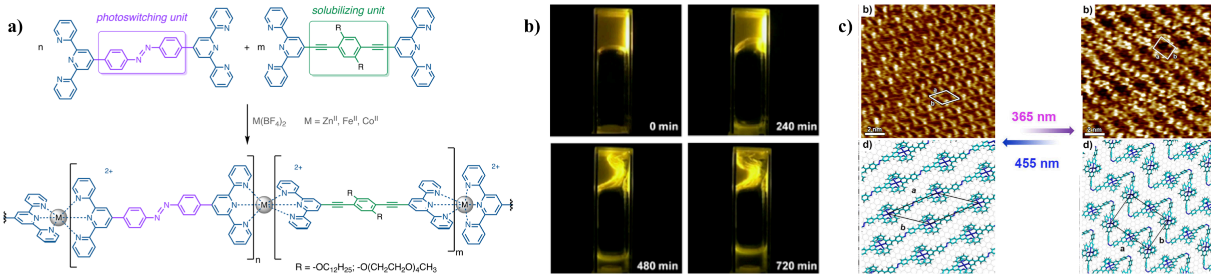

**Figure 1.** a) Molecular structure of the photo-responsive supramolecular metallopolymers and their schematic synthetic pathway; b) photo-mechanical response of the metallo-organogels under UV irradiation; c) reversible photo-induced expansion/contraction process under UV (365 nm) and visible (455 nm) irradiation monitored by STM.

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# The Versatility of Mesoscopic Solar Cells

Anders Hagfeldt

*Laboratory of Photomolecular Science, Swiss Federal Institute of Technology Lausanne (EPFL), CH-1015, Lausanne, Switzerland*

*Anders.hagfeldt@epfl.ch*

In our work on solid-state dye-sensitized solar cells (ssDSSC) we have recently shown that copper phenanthroline complexes can act as an efficient hole transporting material. We prepared ssDSCs with a novel organic dye WS-72 and $[Cu(tmby)_2]^{2+/+}$ as redox system and achieved record power conversion efficiencies for ssDSCs of 11.7% [1]. With this redox system DSSCs give also excellent performance under ambient light conditions [2]. Our best DSC efficiency of 13.1% for a liquid Cu-complex electrolyte is achieved by the discovery that the PEDOT based counter electrode can be directly contacted with the dye/$TiO_2$ photoelectrode [3]. Thus, there is no space between the two electrodes minimizing diffusion limitations and fill factors up to 0.8 is achieved.

In our work on perovskite solar cells (PSC) we have achieved efficiencies above 20% with a mixed composition of iodide/bromide and methyl ammonium/formamidinium [4]. With the use of $SnO_2$ compact underlayers as electron acceptor contacts we have constructed planar perovskite solar cells with a hysteresis free efficiency above 20% [5,6]. The strategy of cation mixing of the perovskite film was taken further by including the Cs in a so-called ‘triple cation’ composition, i.e. Cs/FA/Ma as well as Rb in a quadruple cation mixture [7,8]. Larger grains grown in a monolithic manner are observed and reproducibility and device stability are improved. For example, above 22% efficiency has been obtained with an outstanding open-circuit voltage of 1.24 V at a band gap of 1.63 eV entailing one of the smallest loss-in-potential of 0.39 V measured for any solar cell material. With regards to lifetime testing, we have shown a promising stability at 85 $^{o}$C for 500 h under full solar illumination and maximum power point tracking (95% of the initial performance was retained). Recently, we have also commented on the standardization of PSC aging tests [9].

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# Carbon “Quantum” Dots and Their Polymeric Nanocomposites - Materials Development and Optoelectronic Applications

Ya-Ping Sun

*Department of Chemistry and Laboratory for Emerging Materials and Technology*
*Clemson University*
*Clemson, South Carolina 29634-0973, USA*
*Email: syaping@clemson.edu*

## Abstract:

Carbon “quantum” dots or simply carbon dots (CDots),[1-3] exploring the unique attributes of small carbon nanoparticles that represent a distinctive zero-dimensional carbon allotrope, for optical and other properties rivaling or beyond those of the other more famous nanoscale carbon allotropes.[3-10] Even since their original finding,[1,2] CDots have emerged to become a rapidly advancing and expanding field for research and development. A wide variety of potential technological applications of CDots have been pursued and investigated extensively around the world. Among these applications, especially interesting are those in optoelectronics, including their uses in various devices in which presently fullerenes-derived materials are dominating, for improved performances and much lower costs. In this presentation, the fundamental and technological development of CDots will be highlighted with a status report, so will be their nanocomposite materials with electronic polymers such as poly(*N*-vinylcarbazole) (PVK) and polythiophenes. The emphasis will be on the photonic properties and photoinduced redox characteristics of CDots and their derived materials as relevant to applications in optoelectronics and photon-electron conversions in general.

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# Mechanical rubbing-induced edge-on to face-on reorientation and molecular alignment in thienoquinoid transistors

Tetsuya Aoyama,[a] Toshihiko Tanaka,[a,b] Benoît Heinrich,[c] Fabrice Mathevet,[d]
Toshinori Matsushima,[e] Kazuto Takaishi,[a] Shinya Matsumoto,[a,f] Masanobu Uchiyama,[a,g]
Chihaya Adachi,[e] Jean-Charles Ribierre[h]

*[a]RIKEN Cluster for Pioneering Research (CPR), Saitama 351-0198, Japan. Email:taoyama@riken.jp*
*[b]National Institute of Technology, Fukushima College, Fukushima 970-8034, Japan.*
*[c]Institut de Physique et Chimie des Matériaux de Strasbourg, UMR 7504, CNRS- Université de Strasbourg, 67034 Strasbourg, France.*
*[d]Sorbonne Universités, UPMC Univ Paris 06 CNRS Institut Parisien de Chimie Moléculaire, UMR 8232 Chimie des Polymères, Paris, France.*
*[e]Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, Fukuoka 819-0395, Japan.*
*[f]Graduate School of Environment and Information Sciences, Yokohama National University, Kanagawa 240-8501, Japan.*
*[g]Graduate School of Pharmaceutical Sciences, The University of Tokyo, Tokyo 113-0033, Japan.*
*[h]College of Optical Science and Engineering, Zhejiang University, Hangzhou 310027, China.*

## Abstract:

Control of molecular alignment is important to develop high performance organic optoelectronics devices. We obtained molecularly-oriented films of an ambipolar thienoquinoid derivative (QQT(CN)4) by a room-temperature mechanical rubbing technique.[1] Grazing incidence X-ray scattering (GIXS), polarized absorption spectroscopy and atomic force microscopy measurements showed that the rubbing technique converted molecule orientation from an edge-on to a face-on configuration and simultaneously aligned molecules parallel to the rubbing direction as shown in Figure 1. We also obtained high absorption dichroic ratio and anisotropy of transistor mobilities in rubbed QQT(CN)4 films (Table 1). Moreover, a solvent vapor treatment enhanced the dichroic ratio and the hole mobilities. Because no change of the molecular packing due to a cold isostatic pressure (CIP) technique was confirmed, the shear force by rubbing might play important role to convert the molecule orientation. This study would give new opportunities to investigate the structure–property relationship and to develop practical organic electronic devices.

## Acknowledgements:

T.A. would like to acknowledge funding from the Japan Society for the Promotion of Science via a JSPS KAKENHI grant (No. 22350084 and 18K04930). J.-C.R., T.M., and C.A. acknowledge the support by JST ERATO Grant No. JPMJER1305, Japan. 2D GIXS measurements were carried out at PLS-II 9A U-SAXS beamline of Pohang Accelerator Laboratory (PAL) in Korea.

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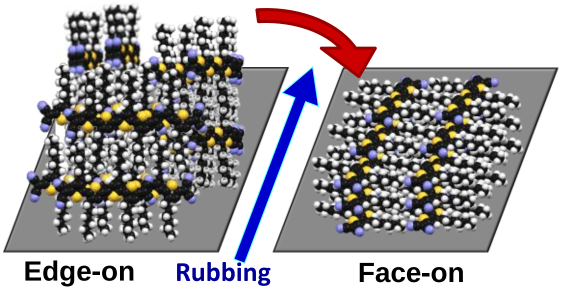

*Figure 1. Molecule orientation from an edge-on to a face-on configuration induced by room-temperature rubbing.*

*Table 1. Summary of the anisotropy of transistor mobilities in rubbed QQT(CN)4 films before and after a solvent vapor treatment (SVT).*

| | $\mu(//)$ / $cm^2(Vs)^{-1}$ | $\mu(\perp)$ / $cm^2(Vs)^{-1}$ | $\mu(//)$ / $\mu(\perp)$ |
|---|---|---|---|
| Before SVT | $1.1\times10^{-3}$ | $8.0\times10^{-6}$ | 131 |
| After SVT | $2.8\times10^{-2}$ | $2.5\times10^{-4}$ | 110 |

# Organic Hole Transporting Material for Perovskite Solar Cells: Effects of Doping and Design of New Molecules

Maria Ulfa,[a] Thierry Pauporté,[a] Thanh-Tuân Bui,[b] Fabrice Goubard,[b]

*[a] Chimie-ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris (IRCP), 11 rue P. et M. Curie, F-75005 Paris, France. *Email: thierry.pauporte@chimie-paristech.fr*
*[b] Laboratoire de Physicochimie des Polymères et des Interfaces, Université de Cergy-Pontoise, 5 mail Gay Lussac, 95000 Neuville-sur-Oise, France.*

## Abstract:

The hole transporting material (HTM) is a key component of many highly efficient optoelectronic devices, especially of perovskite solar cells (PSCs). The study and optimizing of the HTM remain a great challenge. The hole extraction/transport and the device stability are strongly dependent on the molecular structure and doping of the HTM. The use of organic HTM has allowed the PSC power conversion efficiency to steeply increase from 3.8% to 23.3% within only nine years. In a first step, we were interested in the comparison of molecular and polymeric HTMs. The electrical response of PSCs prepared with the benchmark molecular Spiro-OMeTAD HTM (Figure 1a) and the conducting polymer poly(3-hexylthiophene-2,5-diyl) (P3HT) (Figure 1b), selected as a low-cost and efficient polymer HTM, was compared. The device performance was improved in a much less extent by doping in the case of the polymeric HTM. The additives were shown to limit the charge recombination at the interface, to reduce the interfacial defects and to favor the hole transfer from the perovskite to the HTM layer. The conductivity increase was significant only in the case of the molecular HTM.

Developing new and cheap molecular HTMs is also an important topic. We have synthesized a new molecular dendritic core carbazole HTM, called B186, designed for PSC application (Figure 1c). Besides the photovoltaic efficiency and device stability, the role of doping agents in B186 PSCs was also investigated. We showed that B186 is a promising HTM characterized by good performance and better device stability compared to Spiro-OMeTAD. By deeply studying the electrical impedance response of the HTMs/perovskite interface, we could conclude that the doping agents improve dramatically the quality of the HTMs/perovskite interface and then the charge transfer leading to high efficiency PSCs.

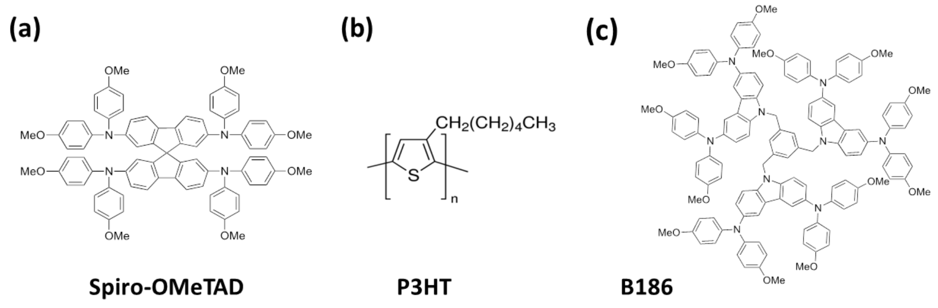

*Figure 1. Molecular structure of (a) Spiro-OMeTAD, (b) P3HT and (c) B186*

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# POSTERS SESSIONS

**Tuesday 18 December, 10:00 – 11:00**
**15:50 – 16:50**

# Electro-Optical and thermophysical characterization of composite materials based on polymers and liquid crystals

Zakia Hadjou Belaid[a], Derouiche Boroguiaa , Fatima Zohra Abdoune , Lahcen Mechernene

[a] *Laboratoire de Recherche sur les Macromolécules. Département de Physique, Faculté des Sciences, Université de Tlemcen, Rocade, Bp 119 Tlemcen 13000, Algérie.*
*Email: z_hadjou@yahoo.fr*

## Abstract:

This work examines the development and characterization of TPGDA / E7 mixtures of the PDLCs type. These systems are produced by UV irradiation photopolymerization (PIPS) of a mixture of monomers tripropylene glycol di-acrylate (TPGDA) and the liquid crystal E7, in the presence of the Lucirin TPO photoinitiator. An electro-optical, thermal and optical characterization is invested in order to understand the effect of CL concentration on the electro-optical and thermo-physical properties of these materials. Polarizing optical microscopy (POM) and differential scanning analysis (DSC) studies were performed so as to determine the transition temperatures of these materials in accordance with the composition of these systems. The findings show a slight variation of the nematic-isotropic transition temperature $T_{NI}$ of LC E7 and of the glass transition temperature $T_g$ of the TPGDA polymeric matrix, as a function of the mass percentage of CL E7. A very good electro-optical response for the composition 30/70 Wt.% In LC E7 was obtained.

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# Bidirectional Multiple Negative Differential Resistance (NDR) : An Interplay Between Interface Resistance and Redox Reaction

Parveen Dagar, Jayanta Bera, Giriraj Vyas, Satyajit Sahu*
*Indian Institute of Technology Jodhpur, Department of Physics, Jodhpur 342037, India, satyajit@iitj.ac.in*

## Abstract:

Multiple negative differential resistance (NDR) was observed on both the directions of the voltage window from a single 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) molecule when the device was studied by using density functional theory (DFT) in association with non-equilibrium Green's function (NEGF). The carrier transport in the device occurs mainly through the transmission channel corresponding to the highest occupied molecular orbital (HOMO) of the molecule and a commensurate change in the magnitude of transmission peak was observed at the peak and valley voltages. The reason for the NDR is proposed to be due to the two competing factors involved namely, the reduction of the molecule and the interface resistance between the molecule and the electrodes. The involvement of both the factors is validated from the molecular projected self-consistent Hamiltonian (MPSH) and the local device density of states (LDDOS) of the device at the corresponding peak and valley voltages.

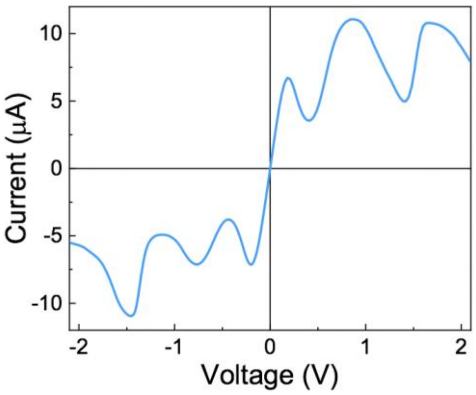

Figure-1

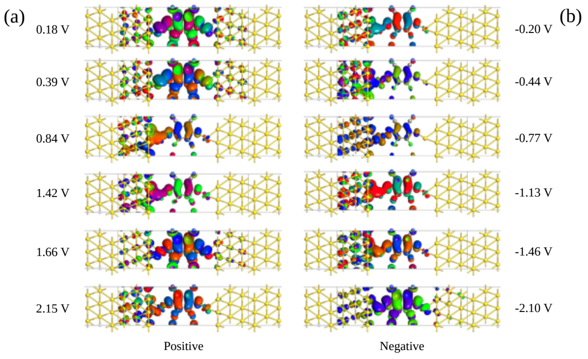

Figure-2

*Figure 1. The I-V characteristic curve for the device taken between -2.5 to 2.5 V, but here the range is shown from -2 to 2 V.*

*Figure 2. (a) and (b) represent the eigen states of MPSH for the positive and the negative peak and valley voltages. The peak and valley voltages in the positive side are 0.18 V, 0.84 V, 1.66 V and 0.39 V, 1.42 V, 2.15 V respectively. Similarly, for the negative side the peak and valley voltages are -0.2 V, -0.77 V, -1.46 V and -0.44 V, -0.13 V, -2.1 V respectively.*

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9th International Conference on Molecular Electronics
Paris, France
December, 17-20th 2018

T1 - 3

# Highly reproducible formation of polymer single-molecule junction for well-defined current signal

Takanori Harashima,[a] Tomoaki Nishino[a]

[a]*Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 W4-11 Ookayama, Meguro-ku, Tokyo 152-8551, Japan. Email: tnishino@chem.titech.ac.jp*

## Abstract:

Single-molecule devices attract much interest to develop nanoscale electronics. Although a variety of functional single molecule for single-molecule electronics have been developed, there still remain needs to implement sophisticated functionalization of the devices toward practical applications. Given its superior functionality encountered in macroscopic materials, polymer could be a useful building block in the single-molecule devices. Here, we created molecular junction composed of polymer. We found that the polymer junction exhibits the higher formation probability and the longer lifetime than its monomer counterpart, demonstrating that polymer provides unique opportunity to design both stable and highly functional molecular devices for nanoelectronics.

The tunneling current was measured by STM for an Au(111) surface modified by poly-vinyl-pyridine (PVP; Figure (a), bottom) or its monomer counterpart, tri-methylene-di-pyridine (TMDP; Figure (a), top). The spontaneous formation of the molecular junction was investigated using STM *I-t* measurement. In the *I-t* measurement, the tunneling current was recorded as a function of time at a fixed tip-substrate distance. The formation of the molecular junction was evident by the current increase and consecutive plateau (Figure (b)). We developed an automated algorithm for the precise detection of these current plateaus and evaluated the properties of individual molecular junctions.

The analysis revealed that the polymer junction exhibits the higher formation probability and the longer lifetime than its monomer counterpart (Figure (c,d)). Based on the XPS analysis, the higher formation probability of polymer junction was attributed to the presence of unbound pyridine linkers, which facilitate the formation of the molecular junction. The longer lifetime of PVP reflected the robustness of the polymer adsorption structure, originating from the multidentate effect. These results suggest that polymer provides useful perspectives to design both stable and highly functional single-molecule devices for nanoelectronics.

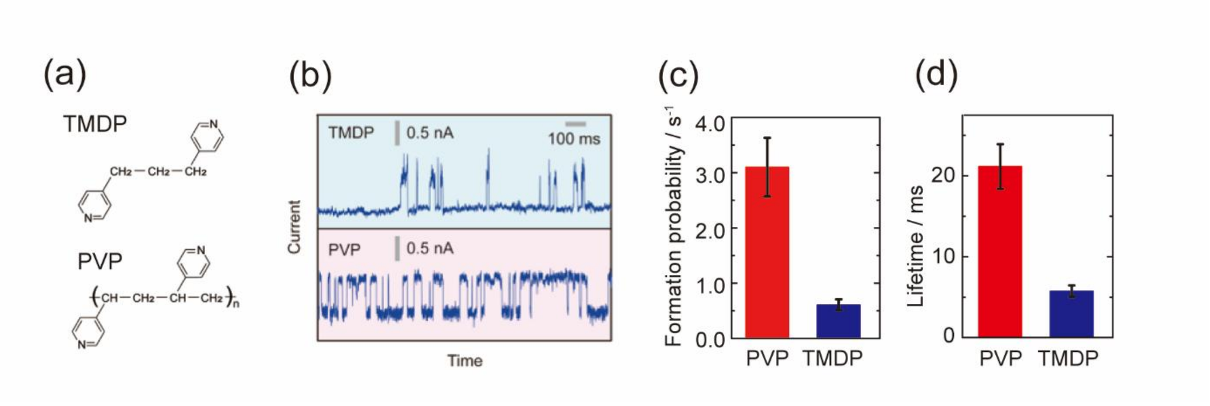

*Figure*
*(a) The chemical structures of TMDP and PVP. (b) Typical I–t traces measured with TMDP- and PVP-modified substrates. Bar graphs showing (c) formation probabilities and (d) lifetime of TMDP and PVP molecular junctions.*

# New way to rectify current thanks to Ferrocenyl Triazole derivatives

Damien Brunel,[a] Clément Reynaud,[b] David Duché,[b] Jean-Jacques Simon,[b] Ludovic Escoubas,[b] Chrystelle Lebouin,[c] Rose Marie Sauvage,[d] Didier Gigmes,[a] Frédéric Dumur[a]

*[a]Aix Marseille Univ, CNRS, Institut de Chimie Radicalaire, UMR 7273, F-13397 Marseille (France)*
*Email : damien.brunel@univ-amu.fr*
*[b]Aix Marseille Univ, CNRS, Institut Nanomatériaux Microélectronique Nanosciences de Provence, UMR 7334, F-13397 Marseille (France)*
*[c] Aix Marseille Univ, CNRS, Matériaux Divisés, Interfaces, Réactivité, Electrochimie UMR 7246, F-13397 Marseille (France)*
*[d] DGA/DS/MRIS, 75015 Paris (France)*

Abstract:

Rectification of current by molecules is a subject that attracts many attentions nowadays because it would permit to reduce the size of the electronic devices. Theorized by Aviram and Ratner, the rectification can be achieved by an asymmetric molecule, enabling the electrons to be transferred in a preferential direction through the molecule. The state of the art of the organic molecular rectifiers shows rectification ratios up to $10^5$. [1] Such rectification ratios were obtained with molecules composed of a ferrocene, which is the key of the rectification process, linked to an insulating alkyl chain. At present, few studies have been devoted to control the orientation of the molecular rectifiers, relative to the electrode. More precisely, the possibility to anchor the molecular rectifier to the two electrodes while controlling the orientation has only been scarcely investigated. In our case, such a control of the molecular orientation has been obtained by developing a two-step process based on Click Chemistry.

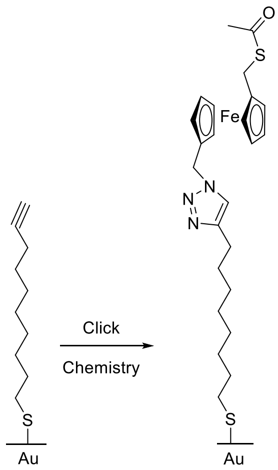

*Figure: Importance of position of ferrocene in the rectification*

Here, we present unprecedented works on the synthesis of new ferrocene derivatives designed as molecular rectifiers. Especially, a special effort is devoted: firstly, to allow the molecule to be covalently linked to an electrode and secondly to definitely control the orientation of the molecular rectifier relative to the electrode.

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# Random Telegraph Signal and Single Charge Trap Dynamics Investigated with Graphene Tunnel Junctions

Pawel Puczkarski,[a] Qingqing Wu,[b] Hatef Sadeghi,[b] Songjun Hou,[b] Amin Karimi,[a] Yuewen Sheng,[a] Jamie H. Warner,[a] Colin Lambert,[b] G. Andrew D. Briggs,[a] Jan A. Mol,[a]

*[a]Department of Materials, University of Oxford, United Kingdom.*
*[b]Department of Physics, Lancaster University, United Kingdom*
*Email:pawel.puczkarski@materials.ox.ac.uk*

## Abstract:

Graphene Tunnel Junctions (GTJs) have already been proven to be a facile experimental platform for measurements of electronic properties of single molecules. Such devices, formed by feedback-controlled electroburning, are advantageous because of the feasibility of controlling the inter-electrode distance with sub-nanometre precision[1], the possibility of the covalent and non-covalent functionalization of graphene with molecules, and their higher gate coupling compared to metal-based junctions[2,3]. In addition to single-molecule experiments, there is the prospect of exploiting GTJs for other applications, such as the investigation of thermoelectric effects or biosensing and in particular sequencing of DNA strands, protein chains and linear carbohydrates.

The performance of GTJs applied to molecular electronics and biosensing is strongly dependent on the noise characteristics of the devices. Here, we report on the first comprehensive study of the noise properties of GTJs.[4] The investigation of noise in GTJs at room temperatures reveals a flicker noise spectrum, typical to diverse electronic systems. The origin of this flicker noise spectrum can be attributed to the superposition of multiple two-level switching random telegraph signals (RTSs) with a distribution of characteristic dwell times.[5] We confirm this by the observation of RTSs and corresponding Lorentzian noise spectra in GTJs characterized at cryogenic temperatures. By means of electrostatic considerations and simple tight-binding model used to model transport through a GTJ we conclude that the observed switching behaviour can be attributed to the shift of a tunnel barrier induced by electrostatic field of a single electron, switching between two adjacent charge traps, present in the underlying silicon oxide substrate in the vicinity of the GTJ. Further statistical analysis of switching signals demonstrates that the devices can provide insight into trap interactions, showing effects related to the Coulombic intertrap repulsion.[6] This indicates high sensitivity of GTJs to their electrostatic environment, a feature that can be harnessed in GTJ biosensing protocols.

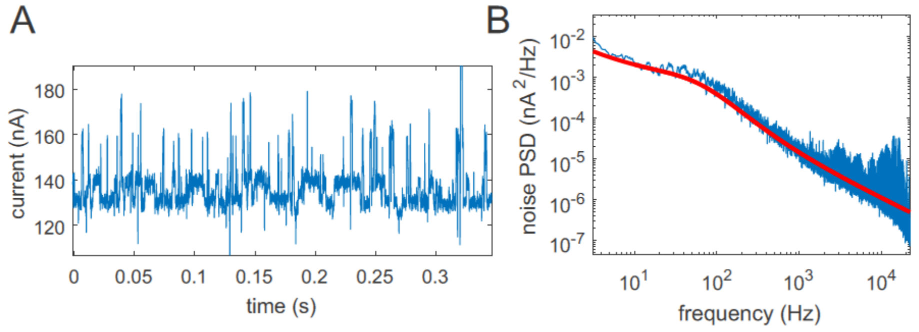

*Figure 1. Features of A) RTS and B) Lorentzian noise spectrum observed in tunnelling current measured in a GTJ at 77K.Red line in Figure B) shows fit to noise model consisting of a superposition of flicker, Lorentzian and white noise spectra.*

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# Understanding electronic transport trough porphyrin-based molecules

A Rates, [ab] D Stefani, [a] M El Abbassi, [a] P Zwick, [c] M Mayor, [c] D Dulić [b] and HSJ van der Zant [a]

*[a]Kavli Institute of Nanoscience, Delft University of Technology, The Netherlands. Email: d.stefani@tudelft.nl*
*[b]Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Chile.*
*[c]Department of Chemistry, University of Basel, Switzerland.*

## Abstract:

Porphyrin-based molecules have a great potential in molecular electronics as their electronic properties can be easily tuned by modifying their chemical structure [1]. Hereby, they offer an interesting platform to understand charge transport trough single molecule devices.

In this study, we have tested several Porphyrin-based molecules with different central elements and anchoring groups. The measurements were performed using the Mechanically Controllable Break-Junction (MCBJ) technique at room temperature. Using this technique, we acquire statistics of the conductance properties by recording thousands of traces.

To identify the different electronic configurations of the molecules and their conductance signature, we used a custom clustering method to sort the current-displacement traces. Several classes were identified and can be used in the future to gain more insight on the electronic pathways.

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# Ligand-field-modulated molecular rectifiers: on the junctions of acetylene-gold electrodes

Chih-Hsun Lin,[a] Er-Chien Horng,[a] Geng-Min Lin,[a] Wei-Chen Yen,[b] Tsai-Hui Wang,[b] Wei-Ling Hua,[b] Hsiu-Fu Hsu,[b]* Chun-hsien Chen[a]*

[a] *Department of Chemistry and Center for Emerging Material and Advanced Device, National Taiwan University, Taipei, Taiwan 10617. Email: chhchen@ntu.edu.tw*
[b] *Department of Chemistry, Tamkang University, New Taipei City, Taiwan 25137. Email: hhsu@mail.tku.edu.tw*

## Abstract:

The quest for a mechanism facilitating the rational design of molecular rectifiers is among the major challenges of molecular electronics. Demonstrated by acetylene-gold bonding in this presentation, we introduce the concept of ligand-field theory[1] to single-molecule junctions. With the formation of C–Au bond[2] at the under-coordinated gold atom of the electrode apex, the electrostatic field of –C≡C: drives the hybridized C–Au orbitals shifting towards $E_{\mathrm{Fermi}}$ and improve the degree of energy-level alignment at the molecular junction (left panel of Figure b). Transmission spectra (QuantumATK) of a series of apllied voltages (Figure a) show that the HOMO band is reached by the bias window at +1.2V but not at the opposite bias of –1.2V, indicative of the characteristics of rectification. The strength of ligand fileds is examined by ligands (*e.g.*, –C≡CN and $-S(CH_3)$) and electrode geometries (flat and pyramidal). The splitting magnitudes between the bonding and antibonding orbitals and the corresponding simulated $i$–$V_{\mathrm{bias}}$ curves will be reported. This work presents ligand-field theory-based molecular rectifiers and validates a new approach to design functional molecular devices.

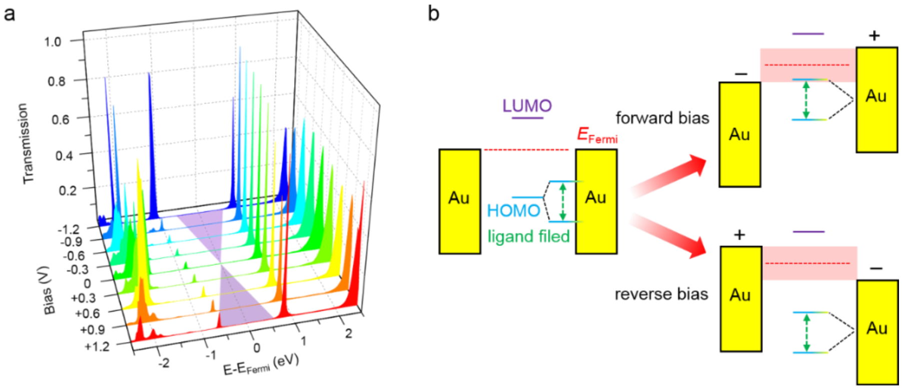

***Figure*** **a, $V_{\mathrm{bias}}$-dependent transmission spectra of Au-NC-$(C_6H_4)$-CC-$(C_6H_4)$-CC-$Au_{\mathrm{pyramidal}}$ junctions.** The purple triangles illustrate the windows of the applied bias voltages. Note that, upon the increase of $V_{\mathrm{bias}}$, the peak position of HOMO shifts toward $E_{\mathrm{Fermi}}$. **b, Illustration of the ligand-field theory-based rectification mechanism.** In the schemes, the acetylene-gold contact are made at the right electrode where the effect of orbital pinning takes place due to the strong –CC-Au coordination. Right panels dipict how orbital pinning leads to rectification. Apparently, a stronger ligand field effect would yeild a larger splitting and a smaller on-set voltage.

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# Designing of a "perfect" porphyrin molecule for the Mechanically Controllable Break Junction Experiments

Diana Dulić[a,b]

[a]*Address, Physics Department, Faculty of Physical and Mathematical Sciences, University of Chile, Santiago, Chile. Email: ddulic@ing.uchile.cl*
[b]*Address, Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands*

Abstract:

The biggest challenge of molecular electronics is to condense the functionality of an electronic device into a single molecule and to exploit the functional versatility offered by the chemical diversity of molecules for electronic device purposes.

Porphyrins and their related macrocycles are promising building blocks for the construction of bio-inspired molecular devices. Nature itself offers magnificent examples of porphyrin usefulness, such as activating and transporting molecular oxygen in mammals and harnessing sunlight in plant photosynthetic systems.

In spite of their potential, obtaining well defined single molecule conductance features is a difficult task. Due to $\pi$- stacking porphyrins can form a variety of junction configuration, leading to large spread in conductance values using the mechanically controllable break junctions (MCBJ) technique[1,2]. This limit the further progress in investigating the molecular functionalities on a single molecule level in porphyrin molecules.

In this presentation, I will show that by close interaction between synthetic chemists and physicists a "perfect" porphyrin molecular design for mechanically controllable break junctions[3,4] can be achieved, leading to well defined, highly conducting molecular junctions. This opens further prospects for "porphyronics" – porphyrin based molecular electronics.

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Acknowledgements: This work has been performed in collaboration with prof. van der Zant group at the TU Delft and has been supported by by the EU through a RISE(DAFNEOX) project, SEP 210165479 and FONDECYT Regular Grant 1140770. The author would like to acknowledge synthetic chemistry groups of Marcel Mayor (University of Basel), Jonathan P. Hill (NIMS, Tsukuba, Japan) and Rienk Eelkema (TU Delft) who provided molecules for these studies.

# Charge transport through graphene based molecular junctions

El Abbassi Maria,[abc] Mickael Lucien Perrin,[a] Herre Van der Zant [c], Michel Calame [ab]

[a] *Empa, Swiss Federal Laboratories for Materials Science and Technology, Transport at nanoscale interfaces Laboratory, CH-8600 Dübendorf, Switzerland*.,
m.elabbassi-1@tudelft.nl
[b] *Department of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland*
[c] *Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands*

## Abstract:

Understanding charge transport at the level of a single molecule is of great importance for both fundamental research and applications in electronic devices. Due to its electronic and mechanical properties, graphene offers a stable and gateable platform to study charge transport through molecules. However, to realize reliable graphene-based junctions, several issues still need to be addressed. First, graphene-based junctions have been reported to exhibit signatures similar to these of molecules, with gate-dependent resonance features [1,2]. Secondly, connecting molecules to the graphene remains challenging as achieving at the same time mechanical stability and electrical reproducibility is not straightforward. Both impose different requirements on the junction properties and finding the proper balance between electronic and mechanical stability is therefore challenging. Third, the silicon dioxide substrate has been reported to yield feature-rich charge-transport characteristics, primarily due to switching within the oxide [3].

In this study, we report on the realization of a mechanically and electronically robust graphene-based multi-molecule junction [4]. The mechanical stability is achieved by anchoring molecules directly to the substrate using silanization, rather than to graphene electrodes. The electronic stability, on the other hand, is due to a large overlap of the π-sytems of neighboring head groups. The nature of the stacking also renders it less sensitive to the electrode properties. The junctions are reproducible throughout several devices and operate up to room temperature. Our approach allows for the future integration of novel molecule based functions into stable and controllable nano-electronic devices.

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# Single-Molecular Conductance in the Junction of Electrodeposition-Modified Electrodes

Mong-Wen Gu,[a] Chun-hsien Chen[a]

[a]*Department of Chemistry, National Taiwan University, No.1, Sec.4, Roosevelt Rd., Taipei 10617, Taiwan.*
*Email: d02223141@ntu.edu.tw*

## Abstract:

The electrode-headgroup coupling plays an important role in the contact resistance/electrical performance of single-molecular devices.[1] Minimizing the contact resistance is one of major tasks to reduce the unwanted voltage loss across the molecular junction. To achieve superior electrode-headgroup contact, ideal anchoring groups are those exhibiting reasonable affinity to the electrode. For example, the sulphur-gold contact is popular but the carboxylate-gold contact is not, due to the difference in the strength of adsorption. Alternatively, carboxylate-terminated molecules are known to interact strongly with silver which, however, bears native oxides under ambient conditions and is prone to contamination. Such drawback associated with the oxide layer is circumvented by an electrochemical phenomenon termed underpotential deposition (UPD) that only a monolayer or sub-monolayer of foreign metal is deposited at a potential positive from the Nernst potential of the bulk reduction. Our previous XPS (x-ray photoelectron spectroscopy) study demonstrated that UPD-modified surface was oxide-free yet exhibited affinity toward carboxylate.[2] Herein, we employ Ag-UPD-modified Au electrodes to measure single-molecule conductance of carboxylate-terminated molecules. To conserve the Ag monolayer, a non-destructive methodology (atomic force microscope) developed by Chen etc. instead of conventional break-junction techniques was employed.[3] By keeping constant the force between the molecule and the AFM tip, the lifetime of the junctions can be maintained for longer than 150 sec. which enables (1) reducing the times of fusing together and breaking apart between two electrodes and (2) the measurements of i-V curves from the same junction. In this presentation, we will show that, with UPD-modified electrodes, the junctions of alkanedicarboxylic acids have the better electrical and mechanical properties than bulk Au electrodes. Furthermore, Au electrodes modified by other UPD metals such as copper and bismuth also exhibit enhanced coupling and contact conductance for carboxylic anchoring group.

## References:

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# Environment-Dependent Electron Transfer in Single-Porphyrin Transistors

James O. Thomas[ab], Bart Limburg[ab], Jakub K. Sowa[b], Kyle Willick[c], Jonathan Baugh[c], G. Andrew D. Briggs[b], Erik M. Gauger[d], Harry L. Anderson[a], Jan A. Mol[b]

[a] *Department of Chemistry, University of Oxford, Oxford, UK. Email: james.thomas@chem.ox.ac.uk*
[b] *Department of Materials, University of Oxford, Oxford, UK*
[c] *Institute for Quantum Computing, University of Waterloo, Waterloo, ON N2L 3G1, Canada*
[d] *SUPA, Institute of Photonics and Quantum Sciences, Heriot-Watt University, Edinburgh, UK*

## Abstract:

Electron-transfer is central to biological processes and emerging quantum technologies, and is at the core of chemical challenges related to energy conversion. In Nature, electron transfer takes place within well-defined environments, whereas fabricated systems usually feature an uncontrolled solvent shell, or substrate, surrounding the centre of electron transfer. There are gaps in fundamental descriptions of electron transfer at the single-molecule level, and this is reflected in the absence of a model that quantitatively reproduces current-voltage responses in molecular devices. We have studied electron transfer in a single-molecule transistor to test the role of the inner and outer sphere rearrangement of the nuclei. We find that at low temperature (4 K) electron-vibrational coupling leads to fine structure in the charge transport properties; this structure is washed out over 20 K. Our data display a simultaneous breakdown of quantum coherent Landauer and semi-classical Marcus theory at liquid nitrogen temperature. We find that quantum mechanical nuclear tunnelling enhances low-energy electron transfer rates, and our experimental results can be reproduced quantitatively using a quantum master equation model.[1] The combination of our experiment and theory shows that electron transfer at the quantum-classical boundary is extremely sensitive to the outer sphere reorganisation. The impact of the environment cannot be neglected in the development of single-molecule devices.

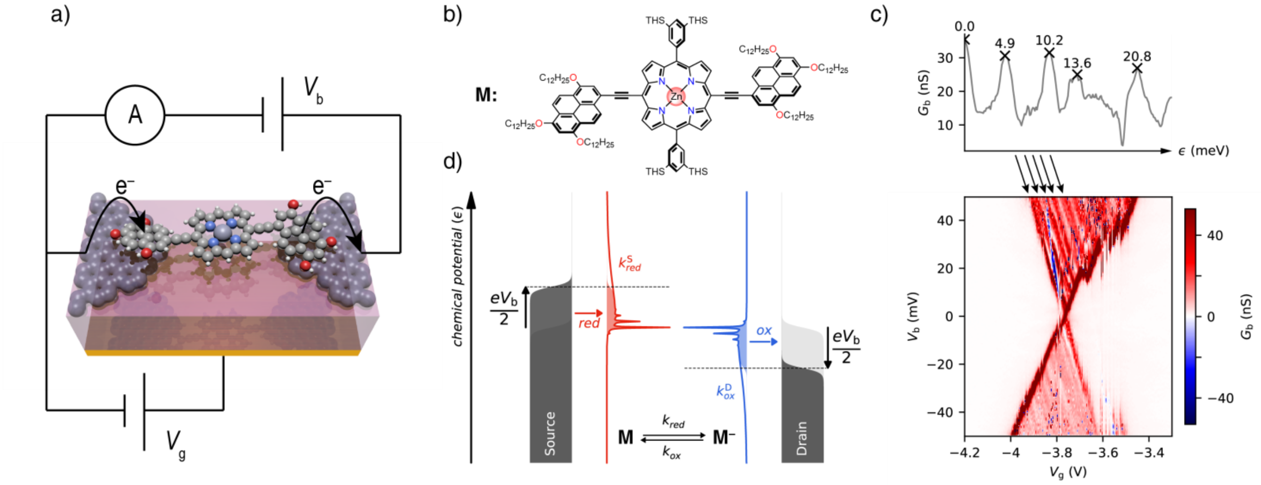

*Figure 1 : (a) Schematic of our device architecture[2]. Molecule M, shown in (b), spans nanometer-spaced graphene electrodes. (c) Charge stability diagram as a function of bias and gate voltages, lines running parallel to the edges of the resonant transport region indicate vibrational excitations accompanying electron transfer. (d) Schematic of current flow through our device at negative source-drain bias, the energy-dependent electron-transfer rates of reduction at the source and oxidation at the drain are shown in red and blue respectively.*

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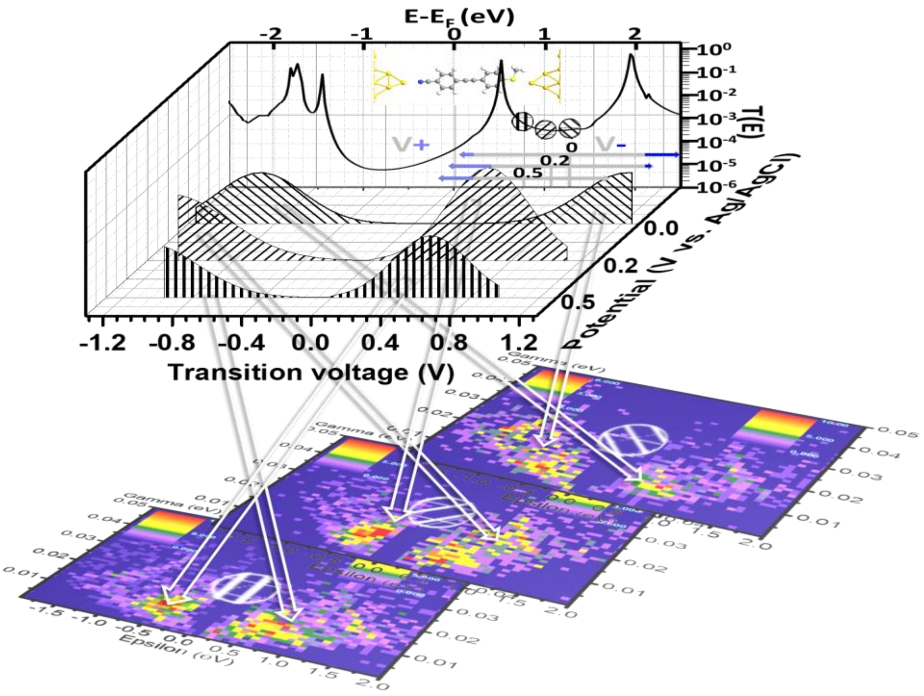
# Transmission Spectra of Single Molecule Junctions: Fitting of *i*-$V_{bias}$ curves acquired under electrochemical control

Hao Howard Peng,[a] Chih-Hsun Lin,[a] Tsai-Hui Wang,[b] Hsu-Fu Hsu,[b] and Chun-hsien Chen[a]

[a] *No. 1, Sec. 4, Roosevelt Rd., Taipei 10617, Taiwan (R.O.C.) Email: chhchen@ntu.edu.tw*
[b] *No. 151, Yingzhuan Rd., Tamsui Dist., New Taipei City 25137, Taiwan (R.O.C.)*

Abstract:

Transmission spectra simulate electron transport across electrode-molecule-electrode junctions and facilitate the prediction of the electric performance. To turn the conceptual spectra into measurable quantities receives much attention.[1] Herein, the molecular junctions were integrated in an electrochemical setup. The relative potential of the working electrode ($E_{wk}$) to those of the frontier orbital levels of the bridged molecule was driven electrochemically to change the degree of the energy-level alignment. *i*-$V_{bias}$ measurements which conferred transition voltage ($V_t$)[2] was conducted as a function of $E_{wk}$. Energy offsets (ε) between Fermi level of the electrode and that of frontier orbitals were derived from a single-level Landauer fitting.[3] Ambiguity may arise when correlating $V_t$ with ε due to possible contribution from additional resonance levels. Hence, we revisited and discussed the meaning of $V_t$ and the suitability of the single-level Landauer fitting.



*Histograms of transition voltages (upper, main) and simulated transmission spectrum (upper, inset). The lower three are 2 dimentional energy offset-coupling (2D ε-Γ) plots.*

References:

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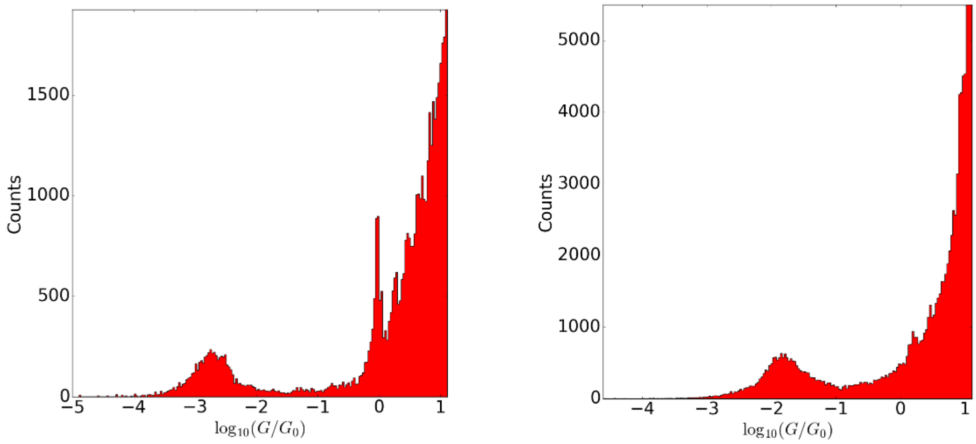
# Contact Metal Effects on the Conductance of Alkanedithiol Single-Molecule Junctions

Keisha Michael, Walther Schwarzacher

*HH Wills Physics Laboratory, Bristol, United Kingdom. km16964@bristol.ac.uk*

## Abstract:

The conductance of pentanedithiol (PDT) molecules was assessed using a mechanically controllable break junction (MCBJ) with notched wire samples of cobalt and gold wire. The current through PDT was measured by repeatedly forming break junctions between the two electrodes which had been exposed to a high concentration of PDT in ambient air for 48 hours. Measurements of Au-PDT-Au junctions show a molecular conductance of ~$10^{-3}G_0$, a value supported by the literature [1]. Preliminary measurements of the Co-PDT-Co junction indicate that molecular conductance is an order of magnitude higher than for gold ~$10^{-2}G_0$. This suggests a difference between the binding mode of the thiol at the metal surface. Such a distinction could arise from a significant role of the Co d band electrons in the thiol linking mechanism. In addition, the measurements of the Co-PDT-Co junction were carried out under ambient conditions without electrochemical control. Hence, it was anticipated that rapid oxidation of the cobalt surface would impede acquisition of high-quality results. The ability to collect good data without electrochemical control is an interesting result. It has previously been suggested that the amount of surface oxide on an oxidised cobalt substrate can be decreased if the exposure time to an alkanedithiol-rich environment is increased [2]. Alternatively, these results may indicate that on formation of a new junction, a cobalt-PDT interaction can occur more quickly than oxidation. Initial results collected using Nickel electrodes agree with the larger conductance value found using cobalt electrodes.



*Conductance histograms showing molecular peak measured during (left) Au-PDT-Au junction (130 traces) and (right) Co-PDT-Co junction (332 traces)*

References:

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# Electronic characteristics in single extended metal-atom chains

Yu-Chan Shih,[a] Gung-Ming Lin,[a] Ming-Chuan Cheng,[b] Shie-Ming Peng,[a,b] Chun-hsien Chen[a]

[a] *No. 1, Sec. 4, Roosevelt Rd., Taipei 10617, Taiwan (R.O.C.) Email: chhchen@ntu.edu.tw*
[b] *Institute of Chemistry, Academia Sinica, 128, Sec. 2, Academia Road, Taipei 11529, Taiwan (R.O.C.)*

## Abstract:

Prototypical EMACs (Extended Metal-Atom Chains) are one-dimensional metal atoms helically coordinated by nitrogen atoms of four α-pyridylamine ligands (Figure1). The conductance of EMACs can be adjusted by ligand design, the selection of the element used for the metal centers, and the oxidation states of the metal centers. In this poster presentation, we show that $[Rh_3(dpa)_4(CN)_2]$ exhibits an interesting behavior of conductance switching, from a lower conductance level to a higher one when the molecule was subjected to stretching. This is opposite to the findings in most studies of single-molecule conductance where the molecular conductance decreases when the molecules are stretched. Experiments that repeatedly change the molecular lengths by mechanical modulation of the junction size and tune the oxidation states of $[Rh_3(dpa)_4(CN)_2]$ electrochemically suggest that the one-electron oxidized form, $[Rh_3(dpa)_4(CN)_2]^+$, adopts a shorter configuration and lower conductance than those of its neutral form, $[Rh_3(dpa)_4(CN)_2]^0$. Simulations are underway to correlate the relative energy-level alignment between the electrode Fermi level and the frontier molecular orbitals of the two oxidation states.

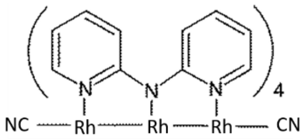

*Figure 1. The molecular structure of $[Rh_3(dpa)_4(CN)_2]$.*

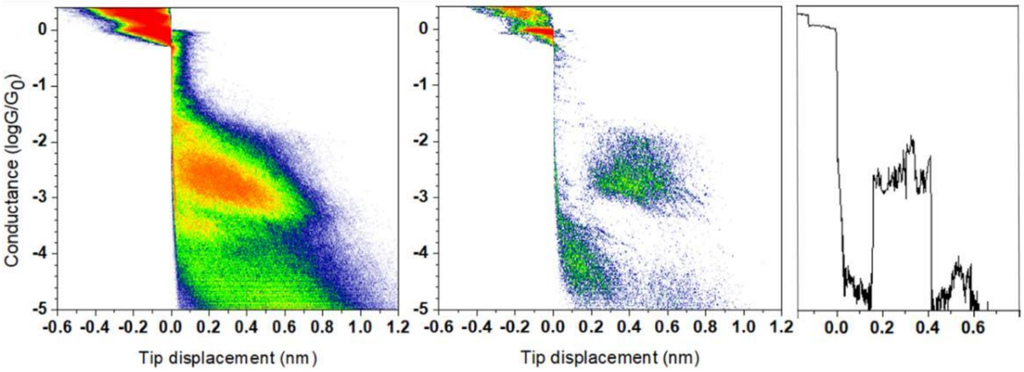

*Figure 2. (Left Panel) 2D conductance histogram of $[Rh_3(dpa)_4(CN)_2]$ junction in 1,2,4-trichlorobenzene under a bias of 50 mV. (Middle) 2D histogram exhibiting the behavior of conductance switching. (Right) A sample trace with conductance switching. The numbers of traces for the left and middle panels are 5846 and 311, respectively.*

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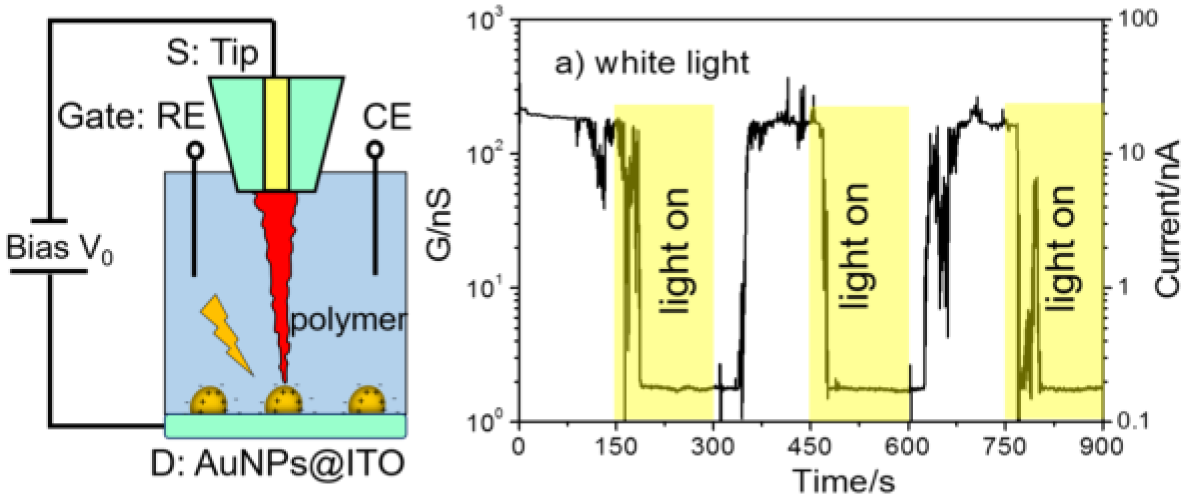
# Plasmon-Induced Conductance Switching of an Electroactive Conjugated Polymer Nanojunction.

*Yong Ai, Nguyen Van Quynh, Jalal Ghilane, Pierre-Camille Lacaze and Jean-Christophe Lacroix*

*Université Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS, 15 rue JeanAntoine De Baïf, 75205 Paris cedex 13, France*

A plasmonic molecular electronic device, consisting of poly(3,4-ethylenedioxythiophene) (PEDOT) nanowires bridging an ultramicroelectrode and an indium tin oxide (ITO) substrate covered by gold nanoparticles (Au NPs), has been developed. Light irradiation of this device has a dramatic impact on its conductance. Polymer strands, maintained electrochemically in their oxidized, conducting state, reversibly switch to their insulating state upon irradiation by visible-wavelength light, resulting in a sharp de-crease in the conductance. The highconductance state is restored when the light is turned off. Switching depends on the wavelength and the intensity of the incident light. It is due to reversible reduction of the nanosized region of PEDOT nanowires in contact with a gold NP and is attributed to plasmoninduced hot-electron injection into the PEDOT. The high/low conductance ratio can be as great as 1000, and switching requires low light intensity (220 W/m$^2$). These results could open the way to the design of a new family of optoelectronic switches.



Ref: Ai, Y., Nguyen, V. Q., Ghilane, J., Lacaze, P. C., & Lacroix, J. C. ACS applied materials & interfaces, 2017, 9(33), 27817-27824.

# Control of Rectification in Molecular Junctions: Contact Effects and Molecular Signature

Quyen van Nguyen[a,d], Pascal Martin[a], Denis Frath[a], Maria Luisa Della Rocca[b], Frederic Lafolet[a], Clément Barraud[b], Philippe Lafarge[b], Vineetha Mukundan[c], David James[c], Richard L. McCreery[c] and Jean-Christophe Lacroix[a]

*a) Université Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS, 75205 Paris France.*

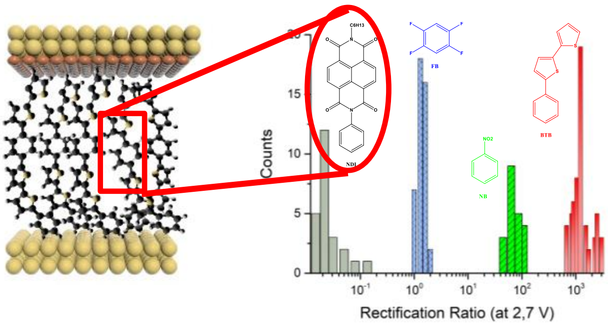
*b) Université Paris Diderot, Sorbonne Paris Cité, MPQ, UMR 7162, 75205 Paris, France.*

*c) University of Alberta, National Institute for Nanotechnology, AB T6G 2M9, Canada*

*d) Department of Advanced Materials Science and Nanotechnology, University of Science and Technology of Hanoi (USTH), Vietnam*

Molecular electronics started with the idea that a molecule sandwiched between electrodes may behave as a rectifying device. Since then, a number of studies have been reported that a molecule can rectify. Recently, C.A. Nijhuis et al has reported a SAMs molecular diode with high, robust, rectification ratios of 1.1 $10^3$. [1]

In this work thin layers of oligomers with thickness between 7 and 9 nm were deposited on flat gold electrode surfaces by electrochemical reduction of diazonium reagents, then a $Ti_{(2\ nm)}$/Au top contact was applied to complete a solid-state molecular junction. That makes it possible for the direct evaporation of various metals on the grafted organic layer in order to fabricate the top electrode through CMOS processes[2,3]. The influences of various molecules have been investigated. The molecular layers investigated included donor molecules with relatively high energy HOMO, molecules with high HOMO-LUMO gaps and acceptor molecules with low energy LUMO and terminal alkyl chain. Using an oligo(bisthienylbenzene) based layer, (HOMO energy level in vacuum is close to the Fermi level of the gold bottom electrode) the devices exhibit robust and highly reproducible rectification ratios above 1000 at low voltage (2.7 V). When the molecular layer is based on a molecule with a high HOMO-LUMO gap, i.e. tetrafluorobenzene, no rectification is observed while the direction of rectification is reversed if the molecular layer consists of naphtalene diimides having low LUMO energy level.



We demonstrate that rectification is induced by the asymmetric contact but is also directly affected by orbital energies of the molecular layer. A “molecular signature” on transport through layers with thicknesses above those used when direct tunneling dominates is thus clearly observed.

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# Quantum transport in magnetostrictive nanocontacts

Kannan Udayamohanan,[a] Suryanarayana Jammalamadaka,[a] Christoph Sürgers,[b]

[a] *Magnetic Materials and Device Physics Laboratory, Department of Physics, Indian Institute of Technology Hyderabad, Hyderabad 502 285, India. Email: surya@iith.ac.in*
[b] *Physikalisches Institut, Karlsruhe Institute of Technology, Wolfgang Gaede Str. 1, Karlsruhe 76131, Germany.*

## Abstract:

One of the main challenges in realising single molecular electronic devices is the control of electronic transport through these devices [1,2]. $Fe_{1-x}Ga_x$ (Galfenol) is a rare-earth free magnetostrictive alloy which has recently gained a lot of attention due to its large magnetostriction ($\lambda_{001}$>3x $10^{-4}$) and the ability to retain its magnetostriction value under high mechanical stress. Here, we demonstrate the conductance switching of a melt-spun magnetostrictive $Fe_{73}Ga_{27}$ (Galfenol) ribbon sample using a mechanically controlled break junction (MCBJ) [3] set up at 10K. Apart from the mechanically controlled conductance switching, we also utilised the magnetostrictive property of Galfenol to control the switching behaviour in such nanocontacts. Fig. 1(a) shows the variation of the conductance as a function of the piezo voltage while closing the contact from an initial open configuration. The observed quantized conductance steps are typical of a few-atom contact and reveal a change in the local atomic arrangement. The histogram in the inset of Fig. 1(a) exhibits a broad maximum at $G/G_0 \approx 0.8$ during contact opening and $G/G_0 << 1$ while contact closing. This may be attributed to the fact that the junction closing occurs much more gradually when the contacts are close together whereas opening of nanocontacts occurs abruptly. Figure 1(b) shows the tunnelling behaviour observed for G(V) and G(H) during closing of the nanocontacts. The linear behaviour of the semi-logarithmic plots for $G/G_0$ vs. piezo voltage and $G/G_0$ vs. magnetic field (Fig. 1(b)-inset) is evidence for electron tunnelling. The electrode distance Δx and piezo voltage (or magnetic field) can be related using the equation G ~ exp (-Δx/ξV), where ξV = 0.36 Å is the average work function of the electrode in helium (7.55 eV).

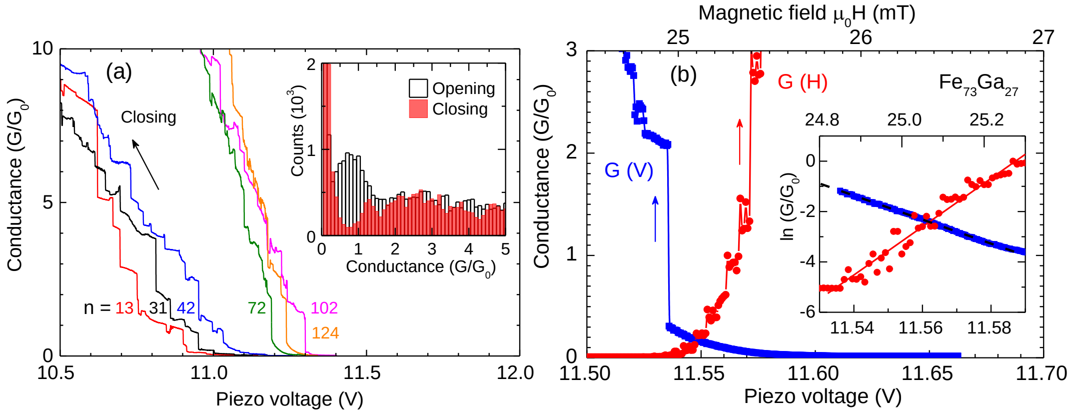

*Figure 1: (a) Variation of Conductance ($G/G_0$) with piezo voltage while closing the junction for various cycle numbers(n). Inset shows the conductance count distribution for opening and closing of the nanocontacts. (b) $G/G_0$ vs. piezo voltage (blue) and $G/G_0$ vs. magnetic field H (red) while closing a nanocontact which shows electron tunneling for $G/G_0$ <<1. Inset shows a straight line fit for the semi-logarithmic plots of the same data indicating a tunneling behavior in this regime*

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# Quantum Interference in Single-Molecule Anthraquinone Devices

John Cully,[a] Bart Limburg,[b] James Thomas,[b] Andrew Briggs,[a] Harry Anderson,[b] Jan Mol,[a]

[a] *Department of Materials, University of Oxford, UK. Email: john.cully@materials.ox.ac.uk*
[b] *Department of Chemistry, University of Oxford, UK.*

## Abstract:

Anthraquinone (AQ) offers an interesting model system for studying quantum interference (QI) effects in molecular transport. Reversibly reducible from a cross-conjugated form to the linearly-conjugated dihydroxyanthracene (HA), AQ presents an attractive single molecule redox switch[1]. Directly correlated to this change in conjugation behaviour is the destructive QI that has been observed in this system[2], resulting in order-of-magnitude differences in conductance between the two redox forms[3]. Through the application of an electrostatic gate, AQ-based molecular devices can be charged, lifting the destructive QI in the N state, and allowing for the transport physics to be probed across multiple charge states[4]. This system has also been predicted to exhibit Fano resonances, arising from the interaction between localised states on the pendant oxygen groups with the continuum of transport through the conjugated backbone[5]. The energetic position of Fano resonances can be tuned through chemical modification of side groups[6], and for AQ this resonance lies around the Fermi level of the electrodes. Due to the proximity of this anti-resonance to the Fermi level, AQ is predicted to display a greatly enhanced Seebeck coefficient making it a promising candidate for thermoelectric applications[7]. Recently, theoretical work has shown that the conjugation-based argument breaks down when the connectivity of AQ is changed from *para* to *meta*; the destructive QI in the N state is lifted for the *meta* connectivity and is instead shifted to the N+2 state, electronically equivalent to HA[8]. This work aims to verify this hypothesis, and to highlight whether the predicted Fano physics can be observed in this system. Here I will present initial results of charge transport measurements on individual AQ molecules contacted using electroburned graphene nanogaps.

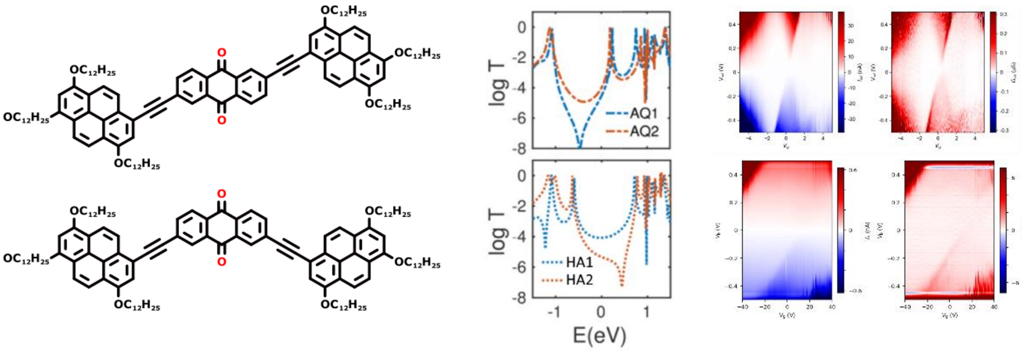

*Figure 1: a) 'para' and 'meta' coupled anthraquinone molecules with tri-alkoxy-pyrene anchor groups. b) Calculated transmission spectra for both para (blue) and meta (red) forms of anthraquinone (AQ) and the related species dihydroxyanthracene (HA) across graphene electrodes (reproduced from [8]). c) Example stability and differential conductance diagrams measured for para (top) and meta (bottom) molecular junctions.*

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# Synthesis of new OPE derivatives and a study of their electro-thermal properties in molecular junctions

Herve Dekkiche,[a] Andrea Gemma,[b] Nico Mosso,[b] Thomas Niehaus,[c] Samy Merabia,[c] Bernd Gotsmann[b] and Martin R. Bryce[a]

[a]*Department of chemistry, South Road, Durham DH1 3LE, UK. Email: herve.dekkiche@durham.ac.uk*
[b]*IBM Research – Zurich, Saeumerstrasse 4/Postfach, CH-8803 Rüschlikon , Switzerland.*
[c]*Institut Lumière Matière, Université Claude Bernard Lyon 1, 10 rue Ada Byro, 69622 Villeurbanne, France.*

## Abstract:

In the past few years, the development of new devices involving electronic technology have not ceased to increase both in demand and in complexity. With the miniaturization needed to build always smaller computers, smartphones and other tools that came along, new problems arose. Among them, the increase of the heating/power ratio represents one of the biggest issues.[1] The understanding of how electrons, photons and phonons interact together is not very well understood as yet. To tackle that problem, top-down and bottom-up approaches should be exploited. The work presented here is focused on investigating the phenomenon involved at the molecular level. We aim to study the single-molecule electro-thermal conductance of synthetically tailor-made chemical species anchored between the gold electrodes of a custom STM setup. The experimental results obtained will be supplemented with computer simulations which use DFT principles.

Our first targets were based on the oligophenylene-ethynylene (OPE) model. Although being generally less conductive than their vinyl-based homologs, namely the oligophenylene-vinylene (OPV), OPEs offer a good compromise between electron delocalization, chemical stability and synthetical feasibility. A few years ago, oligoynes having a dihydrobenzothiophene (DBT) anchoring group were developed in our group and have proven to be excellent candidates for the study at the gold-gold interface.[2] For that reason, the synthesis of a new series of OPE3s having DBT end groups has been investigated. First, the molecules have been prepared with various central units and presented single-molecule conductance values of approximately $4.10^{-4}$ $G/G_0$. This result can be corroborated with the electronic density of the first molecular energy levels of the molecules (DFT), which is fully delocalized over the whole molecule. More elaborated species, containing more than one OPE3 unit have also been studied and their conductance profiles showed very interesting features.

Acknowledgements : We acknowledge funding by the European Commission H2020-FETOPEN project 'EFINED', Grant Agreement no. 766853.

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# Si-Bridged Quinoidal Fused Oligosilole Derivative Single Molecular Transistor with H-ELGP Pt-based Nanogap Electrodes

SeungJoo Lee [a], Jaeyeon Kim [a], Tomohiro Tsuda [b], Ryo Takano [c],
Ryo Shintani [b], Kyoko Nozaki [c], and Yutaka Majima[a]

*Email: lee.s.as@m.titech.ac.jp, majima@msl.titech.ac.jp*
*[a]Laboratory for Materials and Structures, Tokyo Institute of Technology, Japan.*
*[b]Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Japan*
*[c]Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Japan*

## Abstract:

Nowadays, many researchers have proposed the next-generation transistors such as fin field-effect transistor (Fin-FET), tunneling field effect transistors (T-FETs), and magnetic field effect transistors (MFETs) toward 3nm technology node, since current logic transistors of Fin-FETs need to overcome the requirements of a reduction in leakage current. Here, we demonstrate molecular transistors based on Si-bridged quinoidal fused oligosilole derivative (Si-2). Quinoidal fused oligosilole derivative (Si-2) used in this study is a strong candidate of functional group for molecular devices due to good structural stability for change in the valence charge. Si-2 molecule which has a 20π-conjugated molecular structure with two silicon atoms in **Figure 1** was introduced between hemispheric electroless Au-plated (H-ELGP) Pt-based nanogap electrodes owing to two ethanethiol groups with strong S-Au chemical bond. **Figure 2** shows $I_d$-$V_d$ and $dI_d/dV_d$-$V_d$ characteristics with gate voltage dependence at 9K. Gate voltage dependence on $I_d$-$V_d$ characteristics are clearly observed, and on/off ratio ($I_{on}/I_{off}$) is as high as 80 under $V_d$ of 200 mV.

This study was partially supported by MEXT Elements Strategy Initiative to Form Core Research Center from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan; and the BK Plus program, Basic Science Research (NRF-2014R1A6A1030419).

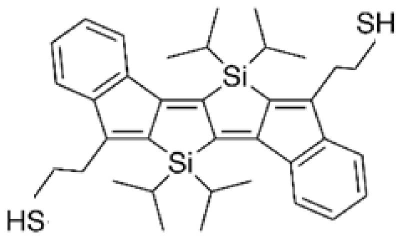

*Fig 1. Molecular structure of Si-2.*

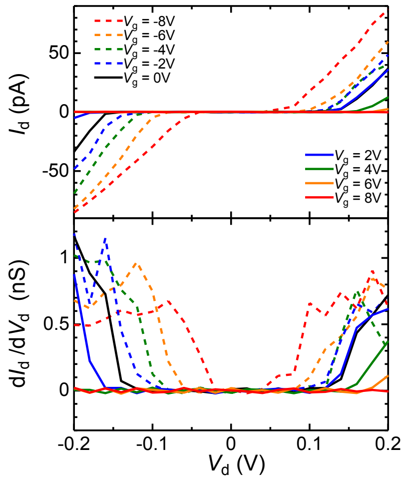

*Fig 2. $I_d$-$V_d$ and $dI_d/dV_d$-$V_d$ characteristics under gate voltages of -8, -6, -4, -2, 0, 2, 4, 6 and 8 V, respectively.*

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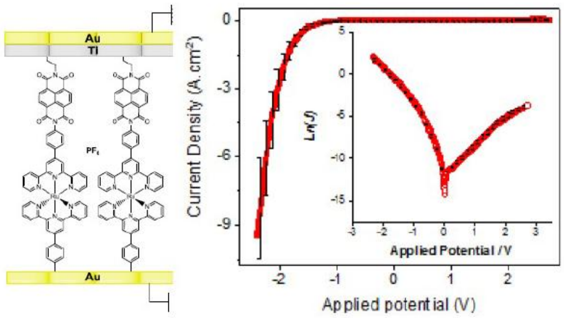
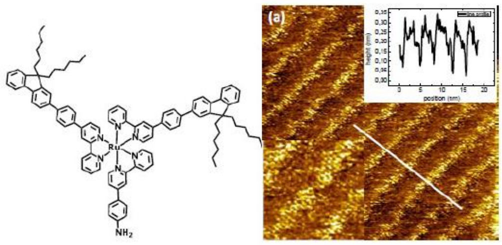
# Molecular junctions based on ruthenium complexes

Frédéric Lafolet, [a] Van Quyen Nguyen, [a] Denis Frath, [a] Xiaonan Sun, [a] Pascal Martin, [a] Jean-Christophe Lacroix[a]

*[a]Université Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS, Nano-Electro-Chemistry group, 15 rue Jean Antoine de Baif, 75013 Paris, France.*
*frederic.lafolet@univ-paris-diderot.fr*

The research efforts devoted to the design and the incorporation of ruthenium complexes onto ordered arrays systems are driven by their potential use as building blocks in molecular electronics, especially in the elaboration of photoactive surfaces. The long-lived excited state lifetimes of the 3MLCT excited state is especially of interest for a multitude application such in, e.g., heterogeneous catalysis, chemical and biological sensors, electrical and optical thin-film devices, and optics. Electrodeposition of aryl diazonium salts has been used as an alternative efficient method to functionalize surfaces with a strong covalent bond between the reagent and the electrode. Bulky substituted bi or ter-pyridine ligands have been designed to generate ruthenium complex monolayers.[1, 2] Robust molecular junctions using naphthalene diimine substituted terpyridine ligand and unexpected self-organized monolayer using novel fluorene substituted bipyridine ligand will be presented and fully characterized by AFM, XPS, electrochemistry and STM.
Bipolar light emission and charge transport in symmetric molecular junctions based on $[Ru(bpy)_3]^{2+}$ or $[Ru(bpy)_2ppy]^+$ oligomers will be also presented.[3-4]





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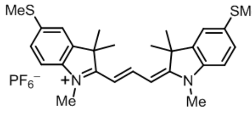
# Molecular Wires without Bond Length Alternation

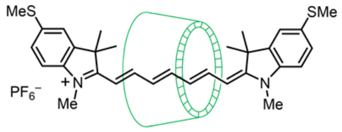
Wenjun Xu,[a] Lara Tejerina,[a] Harry L. Anderson[a]
Edmund Leary,[b] Richard J. Nichols[b] and Simon J. Higgins[b]
[a]*Department of Chemistry, University of Oxford, United Kingdom. Email:wenjun.xu@chem.ox.ac.uk*
[b]*Department of Chemistry, University of Liverpool, United Kingdom.*

## Abstract:

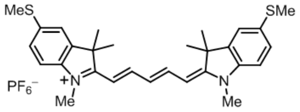
Molecular conductance normally decreases exponentially with increasing the length of a molecule. However, molecules with small bond-length-alternation (BLA) are predicted to have lower HOMO-LUMO gaps, which may compensate for molecular elongation.[1,2] We chose cyanine dyes and their rotaxane derivatives as our research topic. These are molecules bearing π-conjugated polymethine bridges without BLA and presenting lower HOMO-LUMO gap as their carbon chain length increases.[3,4] Using α-cyclodextrin to protect the cyanine dyes not only improves their stability,[5] but also prevents the molecules from aggregation, which may facilitate molecular conductance measurements. We are interested in exploring the relationship between molecular length, conductance and attenuation factor (β) within this family of dyes, and we are exploring the distance-dependent conducting properties and the ability to mediating long-range charge transport of the cyanine dye molecules. (Related work from another group was reported recently.[6])



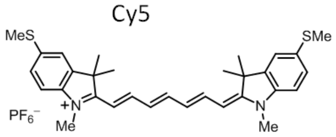
Cy3



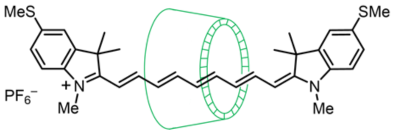
rotaxane Cy7



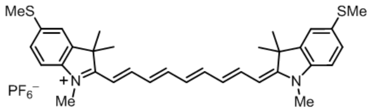
Cy5



Cy7



rotaxane Cy9



Cy9

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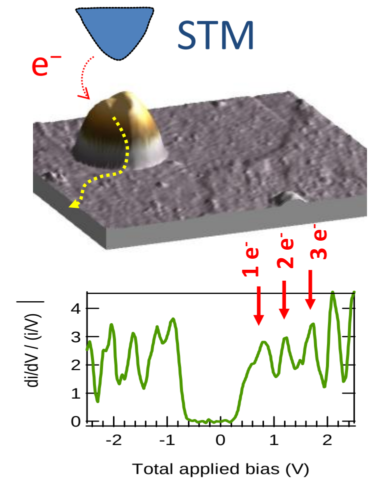
# Single charge electronics with gold nanoparticles, organic monolayers and semiconductor substrates

Olivier Pluchery[a], Léo Bossard Giannesini[a], Hervé Cruguel[a], Louis Caillard[a,b], Yves J. Chabal[b]

[a] *Institut des NanoSciences de Paris, Sorbonne Université, 4 place Jussieu, Paris, FRANCE.*
*Email: olivier.pluchery@insp.jussieu.fr*
[b] *University of Texas at Dallas, Lab. for Surf. & Nanostructure Modifications, Dallas, TX 75080,USA.*

Highly controlled organic layers offer flexible and tunable materials to control the electronic properties of ultrathin materials. For example such layers can be used for connecting nanosize electrodes such as metallic nanoparticles. Particles serve as the core element of assemblies where the electrical current is reduced to the smallest possible since electrons are controlled one by one by using the Coulomb blockade phenomenon. Here we describe how we combined ordered monolayers on silicon with nanoparticles to study fundamental properties of charge transport at the nanoscale.



*Investigation with the STM of the transport properties of gold nanoparticles chemically attached to an organic mononlayer on silicon. Coulomb blockade is detected with transfer of single electrons.*

We prepared colloidal gold nanoparticles of 6 nm and grafted them on a grafted organic monolayer (GOM) on silicon. GOM are highly ordered monolayers prepared by hydrosilylation of alkene molecules and subsequently modified with an amine group so that gold nanoparticles can be firmly immobilized on top of the layer. A wide range of characterization methods were used to assess the preparation: AFM, STM, Scanning Tunnel Spectroscopy (STS), High Resolution-TEM, XPS, FTIR and UV-visible spectroscopy [1, 2].

We will discuss several electrical properties at a single electron level. By placing an STM tip above a nanoparticle, Coulomb blockade allows controlling the number of electrons simultaneously injected in the nanoparticle [1, 3]. Using the conductive tip of KPFM, we were also able to reveal the spontaneous charging behavior of the gold nanoparticles [3]. This opens the way for new kinds of single electron memories or single electron transistors.

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# New architectural molecular junction

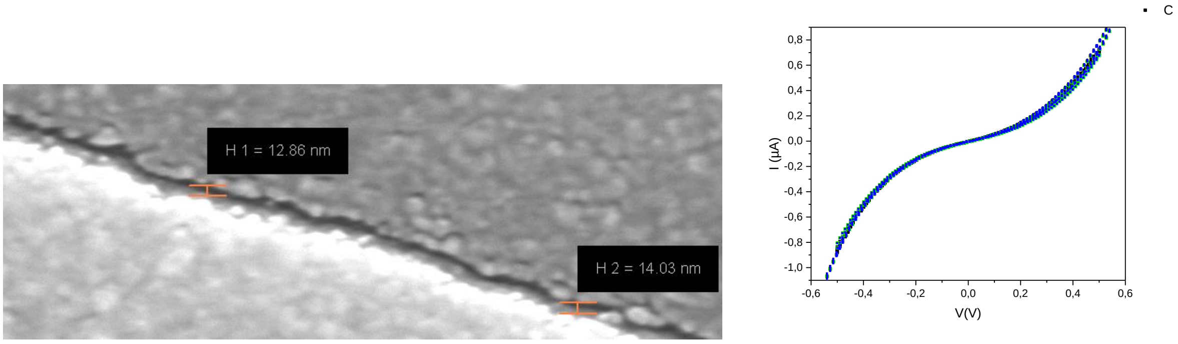
K.Dalla Francesca,[a] C.Salhani,[a] P.Martin,[b] J-C.Lacroix,[b] M-L.Della Rocca,[a] P.Lafarge,[a]

*[a] Université Paris Diderot, Sorbonne Paris,Laboratoire Materiaux et Phenomenes Quantiques (MPQ), 5rue Thomas Mann,75013 Paris, France*
*[b]Université Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS, 15 rue Jean-Antoine de Baïf, 75205 Paris Cedex 13, France.*

## Abstract:

A classical way to studies molecular junction is to work with a top and down electrode. The problem of this architecture is to have a largest surface and no control the characterizations with and without molecular. This work presents new architectural molecular junctions where we can studied before and after molecule grafting and an easy accessibility to the molecule.

Molecular junctions were fabricated with the combined use of electrochemistry and conventional CMOS tools. They consist of a 15 nm thick layer of anthraquinone between two gold electrodes. The layer was grafted between the two electrode using diazonium electroreduction, which yields a stable and robust gold−oligomer interface. The contact was obtained by the growth of the anthraquinone film between the two electrodes. Transport mechanisms across the layers were investigated by analysis of current−voltage (I−V) curves.



*SEM image of a nanogap around 15nm, and an I/V curves obtain for a molecular junction with antraquinone on this junction*

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# Quantum interference induced enhanced thermoelectricity in molecular junctions

Valentin Matton,[a] Oliver Braun,[b] Mickael Perrin,[c] Jianhui Liao,[d] Michel Calame,[e]

(a) *Empa – Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland, valentin.matton@empa.ch*

(b) *Empa – Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland, oliver.braun@empa.ch*

(c) *Empa – Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland, Mickael.perrin@empa.ch*

(d) *Key Laboratory for the Physics and chemistry of nanodevices, Departement of Electronics, Peking University, Bejing, China, 0006176243@pku.edu.cn*

(e) *Empa – Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland, Michel.calame@empa.ch*

Abstract:

Nanoscale junctions embedding designed molecules and taking advantages of quantum interferences are predicted to enhanced thermoelectricity. This would lead to a better recovery of heat-wasted energy and increase the energetic efficiency of many devices.

My Ph.D. just started in April and is focused on the growth of graphene by chemical vapor deposition and reactive ion etching. The next step is the fabrication of nanodevices on silicon chips using E-beam lithography and metallic evaporation. Electrical breakdown in a probe station is then performed on the graphene junctions to make nanogaps. The desired molecules, graphene nanoribbons (GNRs) or gold nanoparticles are then deposited in the junctions where they electrically connect the two graphene electrodes. Electronic measurements are performed before and after the deposition to observe the differences and measure thermoelectric properties.

In this poster, I will present the fabrication of the graphene and gold nanoparticles, the devices on the silicon chip. I will explain the electrical breakdown as well as the deposition of the molecules, GNRS and gold nanoparticles in the junctions. Finally, the already obtained results and the future objectives will be presented.

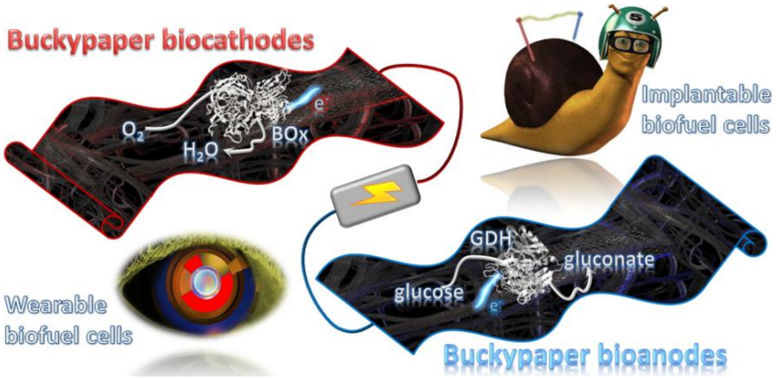
# Electrical wiring of dehydrogenases at flexible and redox-active carbon nanotube buckypaper electrodes towards body-integrated energy-harvesting

Andrew J. Gross[a], Luminita Fritea [b], Alan Le Goff[a], Rachel K. O'Reilly[c], Michael Holzinger[a], Serge Cosnier[a]

[a] *Département de Chimie Moléculaire, Univ. Grenoble Alpes, CNRS, 38000 Grenoble, France*
*Email: andrew.gross@univ-grenoble-alpes.fr*
[b] *Medicine and Pharmacy, Univ. of Oradea, 410073 Oradea, Romania*
[c] *School of Chemistry, University of Birmingham, Birmingham, B15 2TT, England*

## Abstract:

Buckypapers is a randomly oriented self-supporting film of carbon nanotubes, resembling an electronic paper, with excellent prospects for a plethora of applications ranging from aerospace materials to sensors, actuators and fuel cells. Over the last 5-7 years, buckypaper materials have emerged for the construction of bioelectronics devices, including implantable and wearable biofuel cells, owing to properties including high electrical conductivity and porosity, light weight and flexibility, and the possibility to electrically connect enzymes and microbes. This talk will describe the development of lab-made and commercial buckypaper electrodes and their functionalization with different organic and inorganic electro-active redox molecules, and polynorbornene polymers, for the electrical wiring of glucose dehydrogenases. Most enzymes do not exchange electrons with electrodes on which they are adsorbed but this talk will reveal several types of functionalized electrode which promote electron and substrate transfer for electro-enzymatic glucose oxidation. The ultimate goal of this work is to obtain compact, flexible and catalytically powerful electrodes for a new generation of body-integrated biofuel cells.



*Buckypaper electrodes for energy-harvesting biofuel cells with bilirubin oxidase & glucose dehydrogenase*

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**A. J. Gross**, X. Chen, F. Giroud, C. Abreu, A. Le Goff, M. Holzinger and S. Cosnier. A High Power Buckypaper Biofuel Cell: Exploiting 1,10-Phenanthroline-5,6-Dione with FAD-Dependent Dehydrogenase for Catalytically-Powerful Glucose Oxidation, *ACS Catalysis*, **2017**, 7, 4408

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# Magnetic field control of the Franck-Condon electron-vibron coupling in a carbon nanotube

Peter L. Stiller,[a] Daniel R. Schmid,[a] Alois Dirnaichner,[a] Andreas K. Hüttel[a,*]

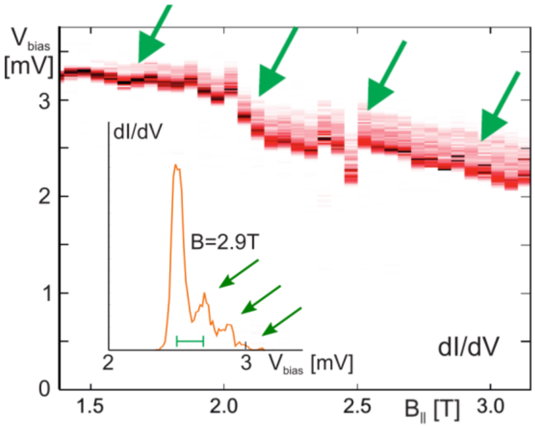
[a] *Institute for Exp. and Applied Physics, University of Regensburg, 93040 Regensburg, Germany*
[*] *e-mail: mail@akhuettel.de*

## Abstract:

Suspended carbon nanotubes display at cryogenic temperatures a distinct interaction between the quantized longitudinal vibration of the macromolecule and its embedded quantum dot. It becomes visible via Franck-Condon side bands in the single electron tunneling current, with clear quantized harmonic oscillator behaviour [1,2].

Here, we present first data on such Franck-Condon side bands in a clean, as-grown suspended carbon nanotube device [3], at known *absolute* number $N$=1 and $N$=2 of conduction band electrons and consequently well-defined electronic ground and excited states. The electronic system is localized at the center of the nanotube, far away from any metal contacts; the electronic transport spectrum indicates unperturbed one- and two-electron states.

The Franck-Condon side bands evolve only at a large magnetic field parallel to the carbon nanotube axis, and display a distinct magnetic field dependence of the Franck-Condon coupling parameter g. The coupling is different for different electronic base states, indicating a valley-dependent effect [4]. Tentative models are discussed.



*Differential conductance as function of magnetic field and bias voltage, displaying the evolution of harmonic side bands at the edge of the 2-electron ground state single electron tunneling region.*
*Inset: Trace cut, with the side bands highlighted.*

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# Transport properties of tungsten disulfide nanotubes

Simon Reinhardt,[a,*] Luka Pirker,[b] Christian Bäuml,[a] Maja Remškar,[b] and Andreas K. Hüttel[a]

[a] *Institute for Experimental and Applied Physics, University of Regensburg, 93053 Regensburg, Germany*
[b] *Solid State Physics Department, Institute Jožef Stefan, 1000 Ljubljana, Slovenia*
[*] *e-mail: simon.reinhardt@ur.de*

## Abstract:

Research on carbon nanotubes has led to a multitude of insights regarding low temperature transport spectroscopy. However, while synthesis procedures for tubular morphologies of layered materials other than graphene are well-known [1, 2, 3], their transport properties are largely unexplored [4]. Here, we introduce transition metal dichalcogenide (TMDC) nanotubes as a new material platform for transport spectroscopy. We present results on optimized nanotube synthesis, first device fabrication, and electrical characterization.

$WS_2$ and $MoS_2$ nanotubes are synthesized using a chemical transport reaction. Optimized growth parameters lead to thin nanotubes with diameters down to 10nm, lengths up to several millimeters, and an extremely low number of structural defects. Transferring tubes from the growth substrate yields individual macromolecules which are then localized and contacted using electron beam lithography. We observe both p-type and ambipolar behaviour, depending on the contact metal.

*SEM micrograph of an individual $WS_2$ nanotube*

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# Printed electrolyte gated field-effect transistors from graphene oxide formulations: electrochemical tuning of charge transport

Sandra Vasilijević,[a] Nicolas Battaglini,[a] Giorgio Mattana,[a] Guillaume Anquetin[a], Benoît Piro[a]

[a] *Université Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS,*
*15 rue Jean-Antoine de Baïf, 75205 Paris Cedex 13, France*
*Email: sandra.vasilijevic@univ-paris-diderot.fr*

Graphene-based materials have lately become a subject of many researches due to their extraordinary properties such as high intrinsic mobility, good electrical conductivity, and a wide range of potential applications such as biosensors.[1] In particular, graphene-based field-effect transistors (GFETs) offer interesting perspectives due to their high sensitivity. By applying the appropriate potential to the gate, it is possible to modulate the charge carriers' concentration in the graphene-based channel of the GFET.[2] Among the different fabrication techniques, inkjet-printing is particularly interesting as it permits fabricating this kind of devices outside the clean room, thus saving time and reducing costs.

In this work, the goal is to combine these two approaches. A home-made graphene oxide (GO) formulation is used as active material for the channel and is deposited by inkjet-printing. Among many ways to reduce GO[3,4], we developed an *in situ* electrochemical approach to obtain conductive reduced GO (rGO) directly on the device. The morphology (Fig. 1a) of the printed rGO layer as well as its electrical properties in electrolyte-gated configuration (Fig. 1b) are investigated. Our transfer curves show a strongly marked Dirac point (Fig. 1c) and ambipolar behavior as previously described.[2] Surprisingly, transfer curves exhibit a drastic evolution with the reduction degree of GO, which we will discuss. Our results pave the way to the electrochemical control of charge carrier transport in rGO-based materials.

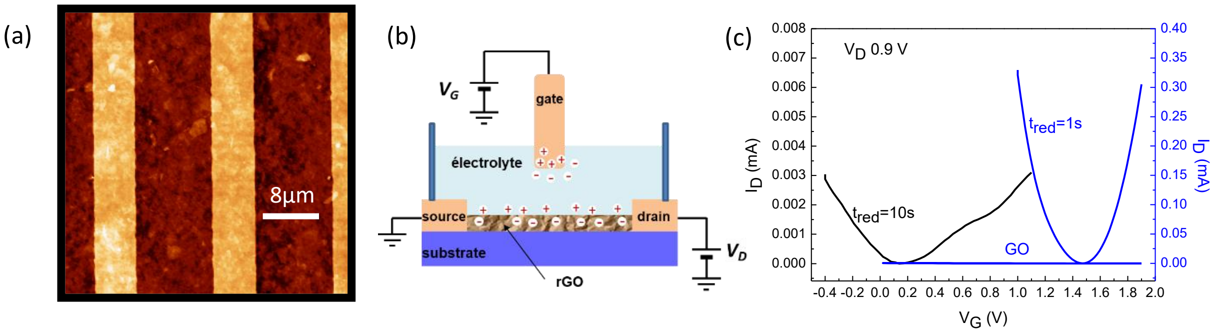

*Figure 1. (a) AFM image of inkjet-printed GO layer on interdigitated electrodes on silica substrate, (b) GFET setup in electrolyte gated configuration, (c) transfer curves of GO and rGO at different reduction times.*

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# Electrochemical gating for single-molecule electronics with graphene contacts

Shuhui Tao,[a,b] Yannick J. Dappe,[c] Li Yang,[a,b]

[a] *Department of Chemistry, Xi'an-Jiaotong Liverpool University, Suzhou, 215123, China.*
[b] *Department of Chemistry, University of Liverpool, Liverpool, L69 7ZD, UK.*
[c]*SPEC, CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif-sur-Yvette Cedex, France.*

## Abstract:

The single-molecular conductance of a redox active viologen molecular wire bridged between Au/graphene electrode has been studied in an electrochemical gating configuration in the 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMIOTf) ionic liquid environment. The scanning tunneling microscopy (STM) based *I*(*s*) (where *I*=current, *s*=distance) non-contact method[1] has been used to measure the conductance value as a function of the electrode potential, as shown in Figure a. An effective electrochemical gating of molecular junction has been achieved using an electrochemical STM with biopotentiostat control. Observed plateaus containing *I*(*s*) traces indicated the successful forming of molecular junctions as shown in the inset of Figure b. Here, A clear "off-on-off" conductance switching behavior was obtained through gating of the redox state when the electrode potential is swept from positive to negative potentials. Au/viologen/graphene junctions showed a single-molecule conductance maximum centered close to the equilibrium redox potential as shown in Figure b. We found that the conductance of Au/viologen/graphene junctions is significantly higher than the standard Au/viologen/Au junctions. Compared to Au/Au contacts, a more obvious gating effect was also observed for asymmetric Au/viologen/graphene junctions. Density Functional Theory (DFT) and electronic transport calculations support the measured data. These results highlight the important role of the contact material for molecular devices and show the potential application of graphene electrode material.

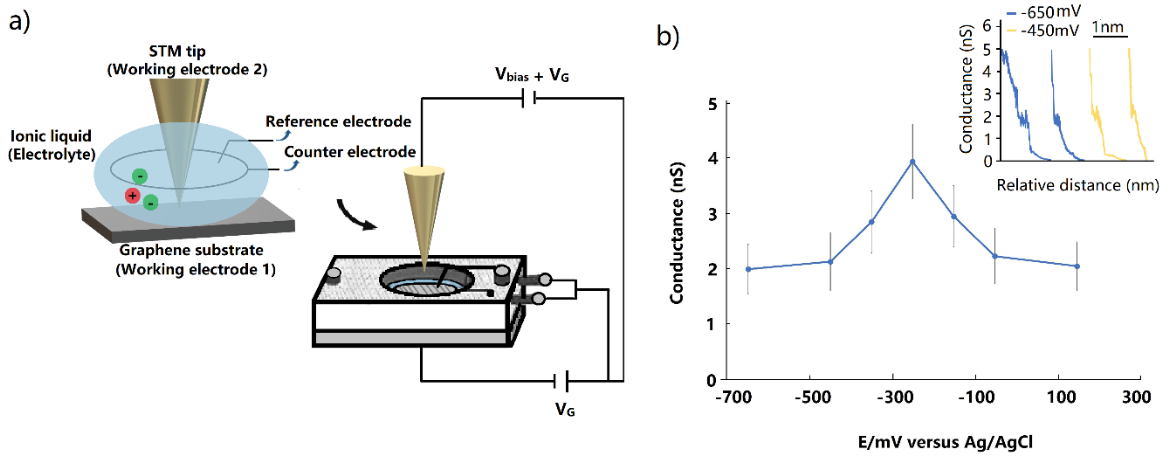

*Figure: a) Schematic diagram of the electrochemical STM-based I(s) technique, the inset shows the four electrodes systems with two working electrodes (STM tip and graphene substrate), Pt counter electrode and Pt reference electrode. The counter and reference electrode provide the gate electrode in this four-electrode bipotentiostat setup with independent electrochemical potential control. b) The conductance values measured for Au/6V6/graphene junctions in BMIM-OTf electrolyte are plotted as a function of substrate electrochemical potential. Inset: The plateau contained I(s) traces of Au/6V6/graphene.*

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# Control of Rectification in Molecular Junctions: Contact Effects and Molecular Signature

Pascal Martin[2], Clément Barraud[1], Quyen Van Nguyen[2], Roméo Bonnet[1], Charlotte Bessis[1], Jean-Christophe Lacroix[2], Maria Luisa Della Rocca[1] and Philippe Lafarge[1]

*1) Université Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS, 75205 Paris France.*

*2) Université Paris Diderot, Sorbonne Paris Cité, MPQ, UMR 7162, 75205 Paris, France.*

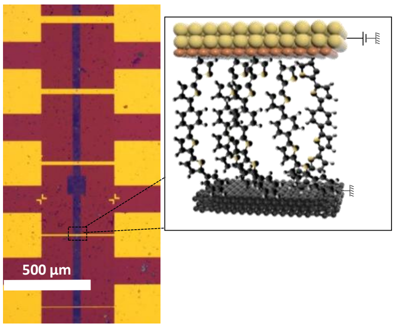
The quantum interaction between molecules and electrode's material at molecules/electrode interfaces is a major ingredient in the electronic transport properties of organic junctions. Driven by the coupling strength between the two materials, it results mainly in a broadening and an energy shift of the interacting molecular orbitals. Using new electrodes materials, such as the recent semi-conducting two-dimensional nanomaterials, has become a recent challenge in the field of molecular/organic electronics that opens new possibilities for controlling the interfacial electronic properties and thus the charge injection properties.[1]

It has been shown that to introduce asymmetry (rectification) in the electronic response of molecular and organic junctions, it is necessary to introduce an asymmetry along the transport direction[2,3]. This can be achieve either by using different contact electrodes (i.e. with different injection properties), and/or by using asymmetric anchoring moieties or molecular structures as originally proposed by Aviram and Ratner[4].

Recently, we have shown that based on diazonium approach oligo-BTB form high quality organic layer and lead to highly stable organic junctions.[5–7] Those organic diodes presented large rectification ratio RR of 1000 and we clearly demonstrated that the rectification behaviour in this configuration is an evidence of molecular signature even if the two metallic electrodes have different Fermi energies. Several molecules have been tested into junctions and the RR varied from $10^{-2}$ to $10^{3}$ with a very good reproducibility and same conditions.[8]

We report the use of atomically thin two-dimensional multilayer graphene films as base electrode in organic junctions with a vertical architecture. The interfacial electronic structure dominated by the covalent bonding between bis-thienyl benzene diazonium-based molecules and the multilayer graphene electrode were probed by ultraviolet photoelectron spectroscopy and the results compared with those obtained on junctions with standard Au electrodes. Room temperature injection properties of such interfaces were also explored by electronic transport measurements. We find that, despite strong variations of the density of states, the Fermi energy and the injection barriers, both organic junctions with Au base electrodes and multilayer graphene base electrodes show similar electronic responses. We explain this observation by the strong orbital coupling occurring at the bottom electrode/ bis-thienyl benzene molecules interface and by the pinning of the hybridized molecular orbitals.

**A**



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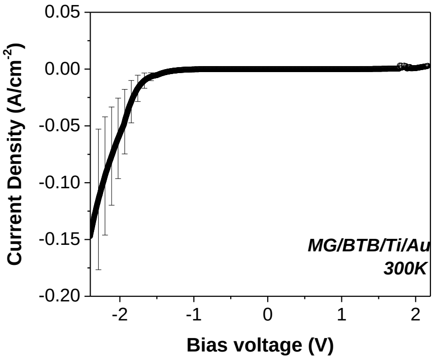

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# Adsorbate Induced Changes on the Metallicity of the Quasi-One-Dimensional Electron System of the Si(553)-Au Surface, Studied by Infrared Spectroscopy

Michael Tzschoppe,[a,*] Christian Huck,[a] Fabian Hötzel,[a] Benjamin Günther,[b] Zamin Mamiyev,[c] Andrey Butkevich,[a] Constantin Ulrich,[a] Lutz H. Gade,[b] and Annemarie Pucci[a]

[a] *Kirchhoff Institute for Physics, Heidelberg University, Heidelberg, Germany*
[b] *Institute of Inorganic Chemistry, Heidelberg University, Heidelberg, Germany*
[c] *Institut für Festkörperphysik, Leibniz Universität Hannover, Hannover, Germany*

[*] *michael.tzschoppe@kip.uni-heidelberg.de*

## Abstract:

Plasmonic signals of quasi-one-dimensional electron systems, for example, related to atomic gold wires on vicinal Si(553), are a direct measure of their metallic properties. Because of the finite length of the ordered atom chains on real surfaces, a localized plasmonic excitation can be measured with infrared (IR) spectroscopy. The measured IR signals are extremely sensitive to changes of the metallic behavior, for example, due to the exposure to hydrogen [1] or the deposition of additional gold atoms [2]. We also observed strong spectral changes for oxygen exposure which can be ascribed to a transition towards an insulating state, similar to the behavior under hydrogen exposure and with gold adatoms, respectively. For $C_{70}$ [3] and TAPP-Br (a core brominated TAPP derivate [4]) deposition, the plasmonic signal almost keeps its original strength up to the coverage of many monolayers. But, differently to $C_{70}$, TAPP-Br exposure results in a huge shift of the resonance position to higher frequencies and a strong increase of the electronic damping, indicating a stronger confinement of the free charge carriers in the quasi-one-dimensional channel due to the adsorbate coverage [5].

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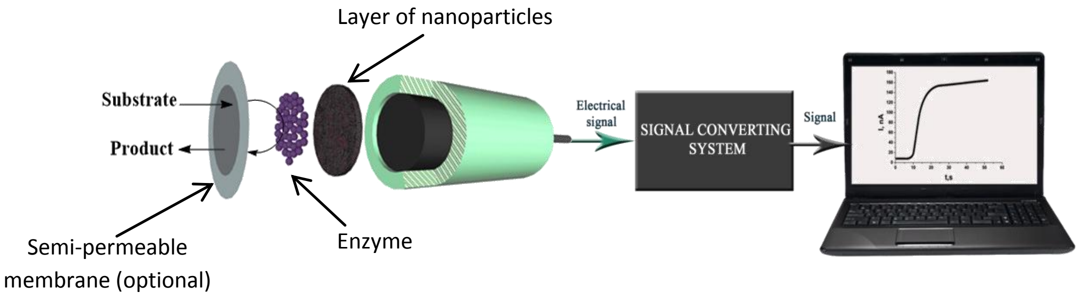
# Enzymes for electronics in analytical devices

Julija Razumiene,[a] Justina Gruzauskaite,[a] Vidute Gureviciene,[a] Lidija Tetianec,[a] Ieva Sakinyte,[a] Jurga Jasinskaite,[a] Marius Dagys[a]

[a] *Institute of Biochemistry, Life Sciences Center, Vilnius University, Saulėtekio av. 7*
*Vilnius LT-10257, Lithuania. Email: julija.razumiene@bchi.vu.lt*

## Abstract:

The current demands of sustainable green methodologies have increased the use of enzymatic technology in industrial processes. Employment of enzymes as biocatalysts offers the benefits of direct electron transfer (DET). DET-type bioelectrocatalysis of redox enzymes is an essential technique for constructing bioelectrochemical devices such as biosensors, bioreactors, and biofuel cells. Significant breakthrough has been achieved by using various conductive nanoparticles to promote the direct bioelectrocatalysis. Enzymes can be attached to nanoparticles in a "wired" configuration, i.e. one that provides a conducting path to facilitate mediatorless electron transfer between the protein redox center and the electrode or between the redox centers of two different proteins [1–6]. For this reason we synthesized a few types of graphite or magnetic nanoparticles using different protocols and tested as the matrix for the bioelectrocatalytic systems working with glucose dehydrogenases from *Acinetobacter calcoaceuticus*, *Ewingella americana*, urease from *Canavalia ensiformis* and laccase from *Didymocrea* sp. In the presence of the analyte – respective substrates of the enzymes – the electric current (response) is generated. Based on these approaches the urea analyzer for fertilizer analysis has been developed and the practical application of device has been demonstrated.



*Schematic diagram of bioelectrocatalytic system using immobilized enzyme and nanoparticles modified electrode.*

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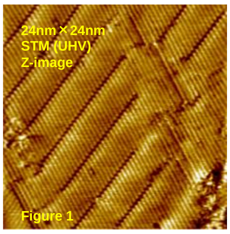
# Formation of nano-carbon sheets from two dimensional self-organized structures of organic molecules via on surface reaction

Shukichi Tanaka,[a] Yukihiro Tominari,[a] Hitoshi Suzuki,[b] Eiichi Kobayashi [c]

[a] *National Institute of Information and Communications Technology, Japan. Email:tanakas@nict.go.jp*
[b] *Graduate School of Advanced Sciences of Matter, Hiroshima University, japan.*
[c] *Kyushu Synchrotron Light Research Center, Japan.*

## Abstract:

Graphene composed of carbon atoms arranged in a two-dimensional hexagonal lattice is a promising for device application. With the progress of research in recent years, various fascinating properties has been confirmed, while the proto-typing of various electronic devices using graphene has been also tried. However, fundamental growth technique of graphene sheets is still under development. In many cases, the most widely used technique is a metal-catalysed CVD. By means of this method, it is possible to prepare large area graphene sheets at a practical growth rate, however, its quality must be much more improved towards device applications. Another promising technique is a thermal decomposition of SiC under ultra-high vacuum condition. In this method, all processes are carried out in a clean vacuum environment, so that graphene sheets with few defects and impurities can be obtained. On the other hand, since the materials is exposed to an extremely high temperature more than 1300°C, integration with other device components and processes are difficult. As a method combining the advantages of these two methods, we developed a local CVD reaction system under high vacuum condition. By means of this method, high-quality graphene sheets can be produced at a relatively low reaction temperature of about $T$=800°C in a clean vacuum environment. However, the growth speed of sheets is extremely slow, and improvement in order to obtain large area graphene sheets is still demanded. In this reaction, it has been found that, prior to the formation of graphene sheets, lamella-like structures in which molecular chains are densely packed and conjugated, are formed as preliminary structure of graphene. Since the formation and conformation of lamellar-like structures observed is similar to the self-organized structures of organic molecules on the surface, it seems reasonable that sheet formation process is improved by replicating these preliminary structures by self-organized structures of organic molecules. Figure 1 shows a molecular resolution STM image of triacontane molecules ($C_{30}H_{62}$) self-organized on Cu (111) surface under UHV condition. When this structure was gradually heated in a vacuum, uniformed self-organized structures deformed to small patches of several nano-meters around $T$=400°C and finally the image of molecules became structure-less around $T$=800°C as shown in Figure 2. By means of XPS obtained from the surface using synchrotron radiation indicates that both $sp^2$ hybrid orbital and $sp^3$ hybrid one of carbon atoms were simultaneously existed. This result suggests that reactions towards formation of graphene sheet are progressing on the substrate from self-organized structure by triacontane via on-surface reaction.



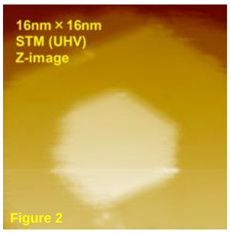


Figure 1 shows a molecular resolution STM image of triacontane self-organized on Cu (111) surface. Figure 2 shows a STM image of surfaces shown as figure 1 after heat treated in UHV.

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# Selective growth of Metallo-Tetraphenylporphyrin Nanowires by Post-Growth Processes

Luisa Raimondo, Silvia Trabattoni, Adele Sassella

*Department of Materials Science, University of Milano - Bicocca, Milan, Italy. Email: adele.sassella@unimib.it*

Abstract:

Controlling self-organization of small organic molecules in nanostructures with the desired shape and size is one of the main challenges in organic nanoelectronics. Here, a strategy for selectively growing uniaxially aligned nanowires of meso-tetraphenyl porphyrin-Zn(II) (ZnTPP, Fig. 1a) is presented, based on post-growth processes. ZnTPP is deposited by Organic Molecular Beam Epitaxy on potassium hydrogen phthalate (KAP), an organic salt easily giving cm-sized single crystals, demonstrated to be particularly suitable as substrate for organic epitaxy. The as-grown films typically display a rather rich surface morphology, characterized by the presence of nanowires and other nm-sized aggregates (see Fig. 1b). Properly tuned aging processes in vacuum and in air are demonstrated to be a tool for the selection of crystalline ZnTPP nanowires, with controlled crystal structure, shape and size, and with uniaxial orientation (see Fig. 1c), at the expenses of the other phases via quasi-Ostwald ripening. This phenomenon is driven by organic epitaxy between the matching crystal surfaces of ZnTPP and KAP. The ability of growing ZnTPP nanowires with a unique crystal structure and precise orientation gives the chance to study the intrinsic properties of the triclinic polymorph of ZnTPP, such as the role of intermolecular interactions in driving its optical response.

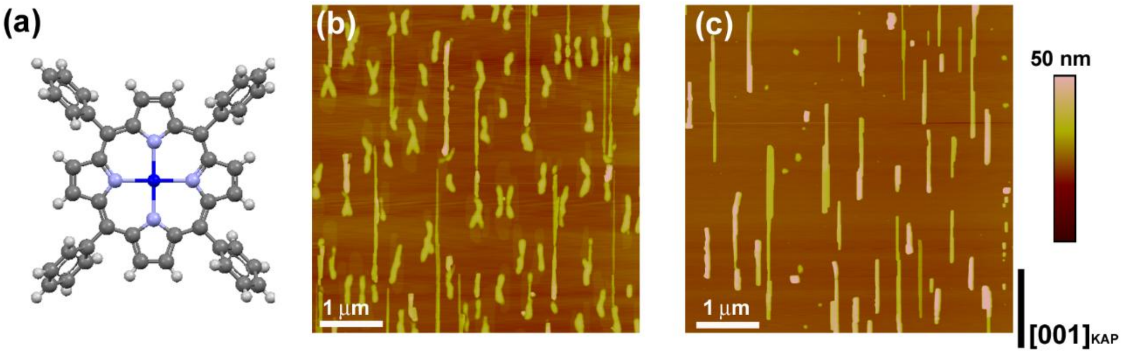

Figure 1
*a) Molecular structure of ZnTPP: H atoms in white, C atoms in grey, N atoms in light purple, Zn atom in blue; AFM height (5×5) µm$^2$ images of a ZnTPP sample grown on KAP, one (b) collected immediately after growth and the other one (c) collected after applying a proper post-growth aging protocol, aimed at selecting the nanowires. The color scale and the orientation of the [001] KAP axis on the right apply to both panels.*

# Quantifying the Impact of Covalent Functionalization on Surfaces using Diazonium Chemistry

Anton Brown,[a] Brandon Hirsch,[a] Peter Walke,[a] Stefan De Gendt,[b] Steven De Feyter [a]

*[a] Division of Molecular Imaging and Photonics, KU Leuven, Celestijnenlaan 200F,*
*3001 Leuven, Belgium. Email: anton.brown@kuleuven.be*
*[b] IMEC, Kapeldreef 75, 3001 Leuven, Belgium.*

## Abstract:

Covalent modification of surfaces is targeted to explore the fundamentals underpinning the manipulation of material properties. Model graphite surfaces as well as applied graphene materials have been characterized. Initially, surfaces are covalently modified using electrochemically activated aryl diazonium chemistry. [1]

We subsequently established quantitative links using scanning tunneling microscopy (STM), Raman spectroscopy, and photoelectron spectroscopies (Fig. 1). The degree of chemisorption on the graphite surface is altered by varying the diazonium concentration and the electrochemical activation parameters. Experimental connections between inter-defect distance and spectroscopic signatures provide a new understanding of the microstructural impacts that result from covalent modification. Angle-resolved photoemission spectroscopy reveals the effects of covalent modification on the electronic band structure of graphene materials. Overall, this work establishes fundamental knowledge on the manipulation of surface matter with molecular level insight.

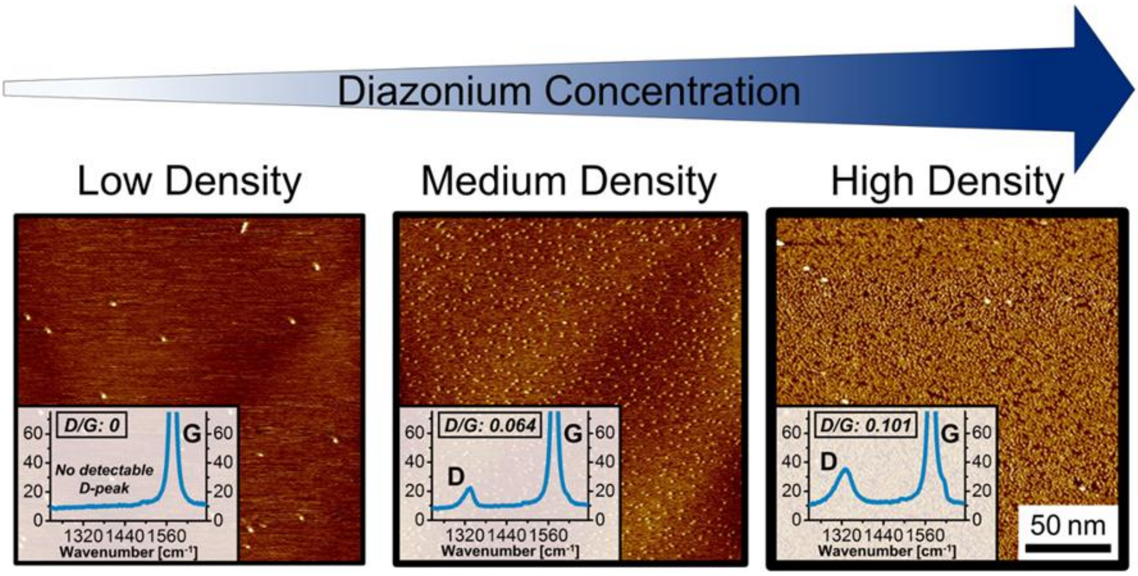

*Figure 1: STM visualizes varying densities of covalent aryl-functionalization of graphite surfaces. Inset represents the corresponding Raman spectrum indicating the degree of chemisorption by the rise of the D-peak around 1334 cm$^{-1}$.*

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# Self-Assembly 3D Electronic Structures on the 2D Supramolecular Tectons

Byeonggwan Kim,[a,b,c] Imad Arfaoui,[d] David Kreher,[c] André-Jean Attias,*[,a] and Eunkyoung Kim*[,b]

[a]*UMI Building Blocks for Future Electronics, CNRS - Sorbonne Université - Yonsei University - Ewha Womans University, 50 Yonsei-ro Seodaemun-gu, Seoul, Korea. E-mail: andre-jean.attias@upmc.fr*
[b]*Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, South Korea. E-mail: eunkim@yonsei.kr*
[c]*IPCM, UMR CNRS-Sorbonne Université 8232, 4 Place Jussieu, 75005 Paris, France.*
[d]*MONARIS, UMR CNRS-Sorbonne Université 8233, 4 Place Jussieu, 75005 Paris, France.*

Abstract:

Self-assembly of supramolecular 2D building blocks (tectons) has emerged as an important process to pattern well-organized monolayers on 2D materials.[1-2] One of the 2D materials, Graphene has good physical properties, especially electronic, optical, and mechanical properties, but bandgap tuning is required for semiconductor properties for a wider range of applications. As one of the tuning methods, it is possible to synthesize materials with unique characteristics by using a self-assembly. Electrically active molecules are synthesized through a molecular DFT calculation and design. The molecules were self-assembled in nanohole of the graphene with tecton array by drop-casting method. The self-assembly structures confirmed by scanning tunneling microscopy at the air/solid interface on the large-scale. This self-assembly 3D electronic structures can be applied for new electronic devices such as nano-thermoelectric harvesters, optoelectronics, and transistors.

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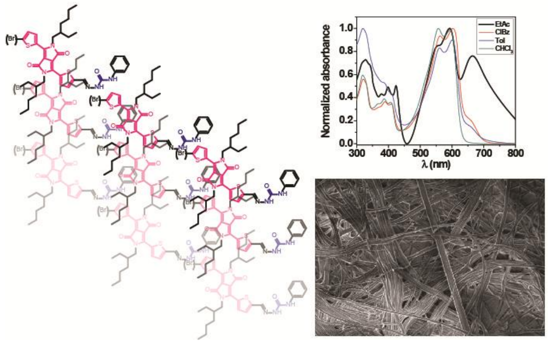
# Tuning the optical and self-assembly properties of small diketopyrrolopyrrole derivatives through multiple hydrogen bonding

Amparo Ruiz-Carretero,[a] Swann Militzer,[a] Thi My Phuong Tran,[a] Philippe Mésini

*[a]23 Rue du Loess, 67083 Strasbourg (France). Email:amparo.ruiz@ics-cnrs.unistra.fr*

## Abstract:

π-Conjugated systems, polymers and small molecules, are extensively employed in the field of organic electronics.[1] Both, the optoelectronic properties and the structural aspects of these systems have to be optimized to reach good performance in the final applications. Supramolecular chemistry is an alternative to achieve such control, especially when using small molecules. This way, it is possible to build semiconducting systems where the electroactive motifs are precisely organized by noncovalent interactions into functional supramolecular polymers.[2] The incorporation of highly directional noncovalent interactions, such as hydrogen bonds (H-bonds) can guide the self-assembly processes and vary the electronic properties. H-bonds are sensitive to solvent, concentration and temperature. Furthermore, the number, position and strength can deeply impact the self-assembly processes, influencing the final properties. H-bonds have been used in several types of organic electronic devices, such as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs) and solar cells. In these examples, the H-bonds afforded better connection among semiconductors, and thus very appropriate structures for charge transport.[3] Here we show that just by functionalizing simple thiophene-capped diketopyrrolopyrrole (DPP) derivatives with semicarbazone[4] or amide units, the optical and self-assembly properties can be tuned while controlling the formation of H-bonding. The appearance of J-type aggregates reaching the NIR region upon H-bonding formation made possible to vary the energy band gap and supramolecular structures formed in solution and on thin films. A combination of variable temperature UV-Vis spectroscopy, Fourier transform infrared (FTIR), circular dichroism (CD) and microscopy has been used to unravel the assemblies formation and the impact on the electronic properties.



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# Nonvolatile Memory Effect in Self-Assembled Monolayers Based Molecular Junctions

Yingmei Han[1], Senthil Kumar Karuppanna[1], Hong Zhang[1], Thorin Duffin[1,2], Damien Thompson[4] Christian A. Nijhuis[1,3,5*]

*[1] Department of Chemistry, National University of Singapore, 3 Science Drive, Singapore 117543.*
*Email:e0005491@u.nus.edu*
*[2] NUS Graduate School for Integrative Sciences and Engineering, National University of Singapore, 28 medical Drive Singapore, 117456.*
*[3] Centre for Advanced 2D Materials and Graphene Research Center, National University of Singapore, 6 Science Drive 2, Singapore 117546.*
*[4] Department of Physics, Bernal Institute, University of Limerick, Limerick V94 T9PX, Ireland*
*[5] NUSNNI-Nanocore, National University of Singapore, Singapore 117411.*
**Author : chmnca@nus.edu.sg*

Low-cost and chemically tunable organic materials are promising to construct memory devices[1,2]. Self-assembled monolayers (SAMs)[3] or single molecule[4,5] based memory devices have attracted considerable attention as they can provide new switching mechanisms. In general, it is still challenging to obtain reversible switching with large on/off ratios driven by electric field in molecular junctions. Here we report a voltage driven nonvoltatile memory effect in viologen SAM based molecular junctions with an ON/OFF ratio of $>10^3$. In addition, we also found that the memory effect is counterion dependent with $I^-$ gives the largest ON/OFF ratios, but $ClO_4^-$ results in junctions without a memory effect. Cyclic voltammetry was performed for the viologen SAMs and showed the dimer formation of the radical cation of the reduced viologen[6] which may be responsible for the conductance switching. In conclusion, this work can provide new insights for nonvoltatile voltage-driven SAM-based memory.

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# Polyoxometalate-functionalized vertically-oriented silica thin films for molecular electronics applications

Neus Vilà,[a] Israël M. Mbomekallé,[b] Pedro de Oliveira,[b] Alain Walcarius[a]

[a]Laboratoire de Chimie Physique et Microbiologie pour les Matériaux et l'Environnement (LCPME), UMR 7564,
CNRS-Université de Lorraine, 405 rue de Vandoeuvre, 54600 Villers-les-Nancy, France
Email: neus.vila@univ-lorraine.fr
[b] Equipe d'Electrochimie et Photo-électrochimie, Laboratoire de Chimie Physique, Université Paris-Sud, UMR
8000, CNRS-Université Paris Saclay, Orsay F-91405, France

## Abstract:

Metal-molecule junctions are the key components of molecular electronics circuits. Fundamental differences have been encountered between single-molecule and ensemble junctions. The main conceptual difference between idealized molecular and ensemble junctions is that in the latter case the interaction of individual molecules becomes important and determines the scaling of charge transport properties which depend on the number of molecules the junction contains. While in some experimental studies the conductance per molecule has been observed to scale directly with the number of molecules in the junction, in other cases the current per molecule in single molecule junctions has been found to be several orders of magnitude larger than for the monolayer.

Polyoxometalates (POMs) are inorganic building blocks analogous to molecular oxides.[1] They can accept and delocalize supplementary electrons within their molecular framework without undergoing structural damage.[2] We are currently investigating if an approach to address these issues would be the measurement of the conductance of molecular wires confined in vertically-oriented mesoporous silica films with pore diameters of 2-3 nm.[3] In this case, silica will play the role of a template allowing the isolation of molecular clusters immobilized inside the pores with a regular and convenient configuration for the measurement of the charge transport through the device. The proper choice of the molecular components and the host geometrical constraints produces a precise control of the supramolecular organization of the inserted molecules, thus tailoring the properties of the resulting system by preventing aggregation even at high concentration.

The convenient processability of silica sol-gels compounds, especially organic-inorganic hybrids, lead to interesting materials for optics, molecular electronics, catalysis or electro-catalysis.[4-7] The use of the vertically-oriented silica-based films will provide the possibility of creating an organized network which will be employed to confine POMs by using several strategies. Up to three different approaches to functionalize vertically-oriented silica thin films with polyoxometalates (POMs) will be presented. They are based either on the formation of covalent bonds or on the electrostatic interactions between the anionic polynuclear metal oxo-clusters. A full characterization of the POM-functionalized silica thin films will be presented in order to establish the best strategy to immobilize these species inside ordered and oriented silica matrices with potential applications in electronic devices due to their electron reservoir behavior.

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# Reversible photoisomerization inside a 2D self-assembled layer of diarylethene molecules

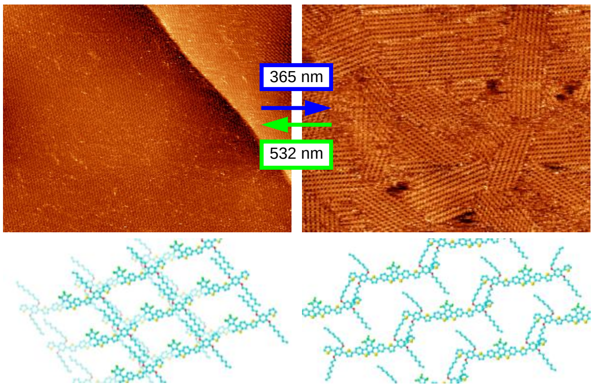
Marion Cranney,[a] François Calard,[b] Jean-Pierre Malval,[a] Thibaut Jarrosson,[b] Jean-Luc Bubendorff,[a] Arnaud Spangenberg,[a] François Vonau,[a] Jean-Pierre Lère-Porte,[b] Françoise Serein-Spirau,[b] Laurent Simon[a]

[a]*Université de Haute-Alsace, CNRS, IS2M UMR 7361, Mulhouse, France. Laurent.Simon@uha.fr*
[b]*ENSCM Montpellier, ICGM UMR 5253, Montpellier, France.*

## Abstract:

This study comes within the framework of design and study of smart surfaces. They are based on the self-assembly of functionalized molecules on a substrate, that will respond in a defined way to an external stimulus. As the use of light to control smart surfaces seems to hold promising prospects [1, 2], diarylethenes [3] are one of the most appropriate functionalized molecules for the achievement and study of smart surfaces. They are photochromic, i.e. they undergo a reversible phototransformation at specific wavelengths between two stable conformations with markedly different optical and electronic properties.

In this study, we report an in situ reversible photoisomerization inside a self-assembled layer of diarylethene molecules on a graphite surface at the solid-liquid interface. To achieve this aim, a new diarylperfluorocyclopentene derivative has been designed and synthesized, bearing benzothiophene groups in order to improve its fatigue resistance compared to diarylethenes with thiophenes [3]. Its photochromic properties have been investigated by a UV-visible study in solution. A submolecularly resolved scanning tunneling microscopy study shows that both open and closed isomers form a self-assembled layer on HOPG at the solid-liquid interface, with markedly different organizations. UV and visible light irradiations lead to reversible isomerizations of the molecules inside the 2D self-assembled layer. It is also possible to improve the self-assembly of the closed molecules by using light irradiation cycle. As photoswitching is proved to happen in the supramolecular self-assembly and not in solution through a desorption-readsorption process, these results may pave the way to get photoresponsive smart surfaces based on diarylethenes solely.



*STM pictures and corresponding schemes presenting the self-assembly of antiparallel-open (on the left) and of closed (on the right) diaryl-(TBT)$_1$ molecules on HOPG at the solid-liquid interface.*

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# Hybrid self-assembly of quantum dots and gold nanoparticles driven by protein pairing

Maxence Fernandez[a], Agathe Urvoas[b], Marie Valerio-Lepiniec[b], Agnès Burel[c], Tahar Bouceba[d], Philippe Minard[b], Erik Dujardin[e], Pascale Even-Hernandez[a], Valérie Marchi[a]
*[a]Univ Rennes 1' Inst Chem Sci, CNRS, UMR 6226, Rennes, France. valerie.marchi@univ-rennes.fr*
*[b]Univ Paris 11, I2BC, CNRS, CEA UMR 9198, Orsay, France.*
*[c]Univ Rennes, MRIC TEM BIOSIT, Rennes, France.*
*[d]Univ Paris 06, Prote Platform, Inst Biol Paris Seine, Paris, France*
*[e]CNRS, CEMES, UPR 8011, Nanosci Grp, Toulouse, France*

## Abstract:

The broad field of nanotechnology has resulted in the design of hybrid nanomaterials featuring exclusive properties such as sensing, data or energy storage and biocide activity. Molecule-driven self-assembly of biomolecules led to the design of colloidal assemblies thanks to the direct recognition of specific molecular partners grafted onto nanoparticles. Direct coupling of nanoparticles has been achieved using DNA strands hybridization, peptide coupling or archetypal protein interactions (streptavidin and biotin) but these methods are either expensive or either restricted to the limits of their assembly mediators. Recently, novel massive assemblies of gold nanoparticles were designed using artificial repeat protein pairs (αRep protein pairs).[1]

These new and promising assembly agents are able to organize functional colloids and provide control on the interparticle distance. Moreover, αRep proteins exhibit hypervariable amino acids positions that provide tremendous possibilities of interacting partners such as another protein or a specific crystalline surface.[2]

In this contribution, we present the design of new homogeneous and hybrid αRep proteins driven self-assemblies of semiconductor nanoparticles (Quantum dots, QDs) and gold nanoparticles (nPAu). First, the functionalization strategies of QDs and nPAu consists in using a polycystein peptide before grafting of the artificial proteins. The grafting on both αRep proteins onto these nanoparticles is characterized using agarose gel electrophoresis showing the saturation of their surface. The affinity of protein-functionalized nanoparticles is then characterized using surface plasmon resonance technique. Mixtures of complementary nanoparticles populations are observed under transmission electronic microscopy and show the formation of large colloidal assemblies (Figure 1). The optical properties of these aggregates are finally characterized by fluorescence spectroscopy. These results give hope to design other hybrid colloidal assemblies in order to be used as new optical nanostructures.

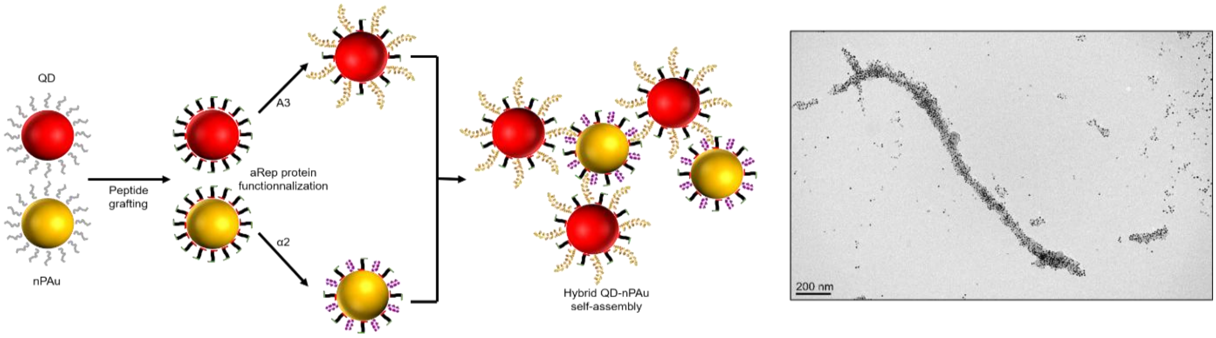

*Figure 1: Schematic representation of the three steps process of production of hybrid self-assemblies (left) and TEM image of self-assembled QDs and nPAu (right).*

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# Nanoconfinement of $[Fe(bpy)_3]^{2+}$ in ordered vertically aligned silica thin films

Samuel AHOULOU,[a,b] Neus VILA,[a] Sébastien PILLET,[b] Dominik SCHANIEL,[b]Alain WALCARIUS,[a]

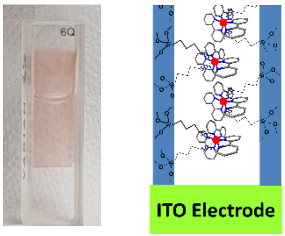
*[a]405 rue de Vandoeuvre, 54600 Villers-lès-Nancy, LCPMME, France.*
*Email: houa-franck.ahoulou@univ-lorraine.fr*
*[b]Boulevard des aiguillettes,54506 Vandœuvre-lès-Nancy, Laboratoire de Cristallographie, Résonance Magnétique et Modélisations, France*

## Abstract:

The phenomenon of spin crossover (SCO) for the $Fe^{II}$ consist to the change of molecular spin state by the effect of either photoexcitation, temperature or pressure[1]. $[Fe^{II}(bpy)_3]^{2+}$ is an SCO complex which can switch from low-spin (LS) to high-spin (HS) state only by photoexcitation.

We present here a novel methodology employed to confine this mononuclear complex, $[Fe^{II}(bpy)_3]^{2+}$, in the matrix of a sulfonate-functionalized vertically-aligned mesoporous silica thin film electrodeposited on indium-tin oxide electrode by an electrochemically-assisted self-assembly (EASA) method.[2] Transmission electronic microscopy (TEM) reveals that the mesostructure and orientation of the sulfonate-functionalized silica films is maintained up to 30% of mercaptopropylsilane in the starting sol.

The electrochemical characterization of the $[Fe^{II}(bpy)_3]^{2+}$ confined in the mesoporous silica shows a stable and reversible signal around 0.86 V. Comparison of the Raman spectrum of the $[Fe^{II}(bpy)_3]^{2+}$ functionalized silica thin films with the $[Fe^{II}(bpy)_3]^{2+}$ microcrystalline powder presents the same vibrational bands except in the low wavenumber region corresponding to Fe-N stretching vibrations modes suggesting a change of the conformation of the complex upon its confinement in the silica matrix. the UV-Vis shows the metal-to-ligand charge-transfer band at 526 nm Furthermore, the UV-Visible spectrum shows an absorption due to the metal to ligand charge transfer (MLCT) transition of $[Fe^{II}(bpy)_3]^{2+}$ in silica at 526 nm which is slightly shifted compared to the bulk observed at 519 nm indicating a possible drop of energy gap between LS and HS due to the confinement. This could be then exploited to induce unprecedented thermally induced SCO by modifying the bipyridine (bpy) ligand[3] with methyl group. Such compounds could be interesting for opto-magnetic or opto-electronic sensors.



*Picture of $[Fe(bpy)_3]^{2+}$confined in a mesoporous silica thin film*

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# Functionalized Resorcin[4]arene Cavitands: Electroswitchable Molecular Actuators

Jovana Milić,[a] Thomas Schneeberger,[a] Michal Zalibera,[b] Karolina Z. Milowska,[c–e] Nils Trapp, [a] Laurent Ruhlmann,[f] Corinne Boudon,[f] Carlo Thilgen,[a] François Diederich*[a]

[a] Dr. J. Milić, T. Schneeberger, Dr. N. Trapp, Prof. C. Thilgen, Prof. F. Diederich, Laboratory of Organic Chemistry, ETH Zurich, Vladimir-Prelog-Weg 3, 8093 Zurich, Switzerland. Email: diederich@org.chem.ethz.ch.
[b] Dr. M. Zalibera, Institute of Physical Chemistry and Chemical Physics, FCHPT STU, Radlinského 9, 81237 Bratislava, Slovakia. Email: michal.zalibera@stuba.sk.
[c] Dr. K. Z. Milowska, Department of Physics and Center for Nanoscience (CeNS), Ludwig-Maximilians-Universität (LMU), Amalienstaße 54, 80799 Munich Germany. Email: kzm21@cam.ac.uk.
[d] Nanosystems Initiative Munich (NIM), Schellingstraße 4, 80799 Munich, Germany.
[e] Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Rd, CB3 0FS Cambridge, UK. Email: kzm21@cam.ac.uk.
[f] Prof. Laurent Ruhlmann, Prof. Corinne Boudon. Université de Strasbourg, Laboratoire d'Électrochimie et Chimie Physique du Corps Solide, Institut de Chimie de Strasbourg, 4 rue Blaise Pascal, CS 90032, 67081 Strasbourg, France. Email: lruhlmann@unistra.fr.

The utility of molecular actuators in nanoelectronics requires responsiveness to electric charge by mechanical motion at the interface with conductive surfaces. We hence functionalized redox-active resorcin[4]arene cavitands with thioether groups and investigated their propensity to act as electroswitchable actuators that can adopt two conformations in response to changes in external potential. Molecular design was probed by Density Functional Theory (DFT) calculations that suggest covalent binding of the cavitands to the Au surface in a preferentially upward orientation. The electronic properties were experimentally studied by cyclic voltammetry on Au electrodes, while redox interconversion between the oxidized (quinone, **Q**) and reduced (semiquinone radical anion, **SQ**) state was monitored by UV-Vis spectroelectrochemistry and EPR spectroscopy. It was shown that the reduction to the **SQ** dianions induces a conformational change to a closed form, providing the basis for voltage-controlled molecular actuating devices in the future.

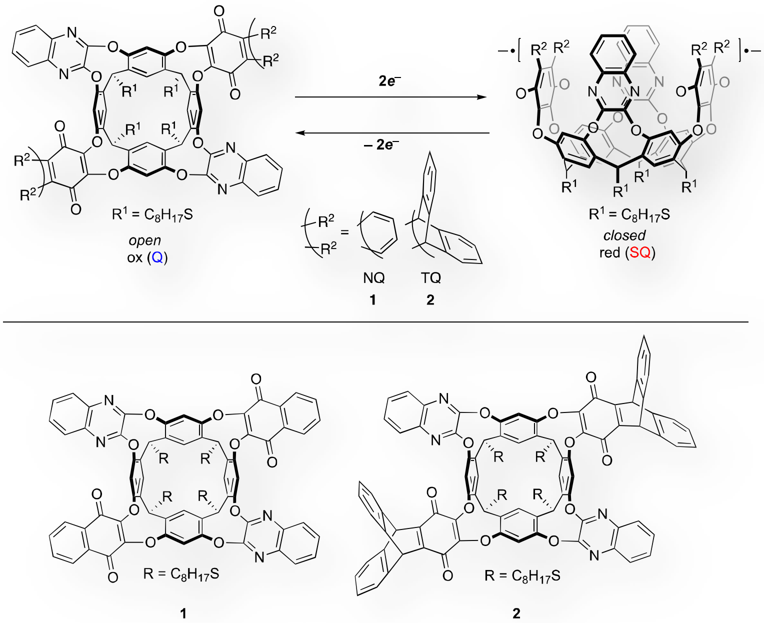

**Figure 1.** Top: Schematic representation of a binary switch between an open (kite) form in the oxidized **Q** state, and the closed (vase) conformation in the reduced **SQ** radical dianion state of quinone-based cavitands. NQ: naphthoquinone , TQ: triptycene-quinone Bottom: Structure of thioether-functionalized resorcin[4]arene cavitands **1**–**2** employed in this study.

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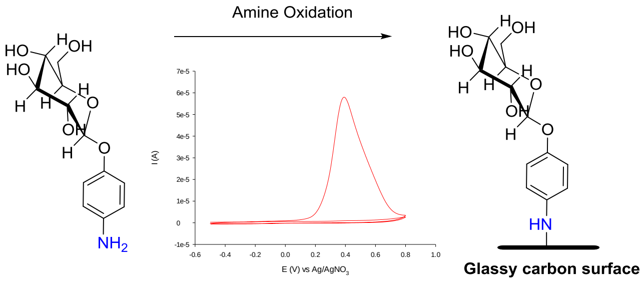
# Carbohydrates electrografting for antifouling applications

Fanny Peigneguy,[a] Charles Cougnon,[a] Christine Bressy,[b] Frédéric Gohier[a]

[a] *Université d'Angers, CNRS UMR 6200, Laboratoire MOLTECH-Anjou, 2 bd Lavoisier, 49045 Angers cedex, France Email :fanny.peigneguy@etud.univ-angers.fr*
[b] *Université de Toulon, Laboratoire MAtériaux Polymères-Interfaces-Environnement Marin (EA 4323 MAPIEM) CS 60584 -83041 Toulon cedex 9, France.*

## Abstract:

Marine fouling is a phenomenon that takes place when a surface is immersed in seawater. Thousands of marine organisms as bacteria, barnacles, algae settle on the surface causing environmental, economic and material issues.[1] Numerous solutions as self polishing paints based on tributyl tin (TBT) used as a biocide have been developed but are today banned for environmental reasons. E. M. Scanlan et al. have shown that carbohydrates grafted by reduction of salt diazonium on glassy carbon surface were able to limit the adhesion of proteins on surface.[2] Our research group has also demonstrated that electrical solicitations of terthiophene bound to polyacrylates could prevent bacteria from settlement on the surface by oxidation of conjugated system at low potential.[3]



Our project is about the immobilization of carbohydrates linked to electroactive systems on glassy carbon or PPF surfaces to target antifouling properties at different levels. Carbohydrate should have an effect on proteins whereas electroactive systems under electrical solicitations should prevent microorganisms from settlement on the surface. So, with reference to our study, we have synthesized 4-aminophenyl-β-D-glucopyranoside (Figure) and ferrocene derivative that have been electrochemically immobilized on glassy carbon and PPF surfaces by amine oxidation. The unprotected glucoside layers were analyzed by XPS, AFM, CV and contact angle experiments. Results demonstrate that the carbohydrate-functionalized surfaces retain the desirable properties of the glucoside compound, producing a wetting-enhancing effect and permitting the electrochemically controlled release of a glucosyl cation equivalent by oxidative cleavage of the anomeric glycosyl–O bond.[4]

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# Fluorescence switching *via* supramolecular plasmonic assemblies

Dana Kamzabek,[a] Brieuc Le Dé,[a] Fabien Miomandre[a] and Galina V. Dubacheva[a]

[a] *PPSM, ENS Paris-Saclay, 61 avenue du Président Wilson, 94230 Cachan*
*Email: galina.dubacheva@ens-paris-saclay.fr*

Tuning fluorescence reversibly and at nano-scale is of great interest for applications in sensing and photo-electronic devices. It is known that both fluorescence quenching and enhancement depend supra-linearly on the distance between the fluorophore and the plasmonic nanostructure. We thus propose to combine supramolecular self-assembly with plasmonics to design a dynamic system allowing reversible tuning of the nanoparticle/fluorophore distance and thereby the resulting fluorescence. We recently succeeded in the fabrication of gold nanoparticles (Au NPs) coated by thermoresponsive polymer poly(N-isopropylacrylamide) (pNIPAM) containing fluorescein (FAM) at the solution-facing end (Fig. 1). The size of the obtained nano-assemblies was characterized by AFM and DLS, while their optical properties were studied by UV-visible and fluorescence spectroscopies. The heat-induced shrinking of pNIPAM resulted in shortening Au NP/FAM distance, causing stronger fluorescence quenching, which was reversible upon cooling to room temperature (Fig. 1). Our current work is focused on the optimization of fluorescence modulation and extending the concept to other stimuli and plasmonic surfaces.

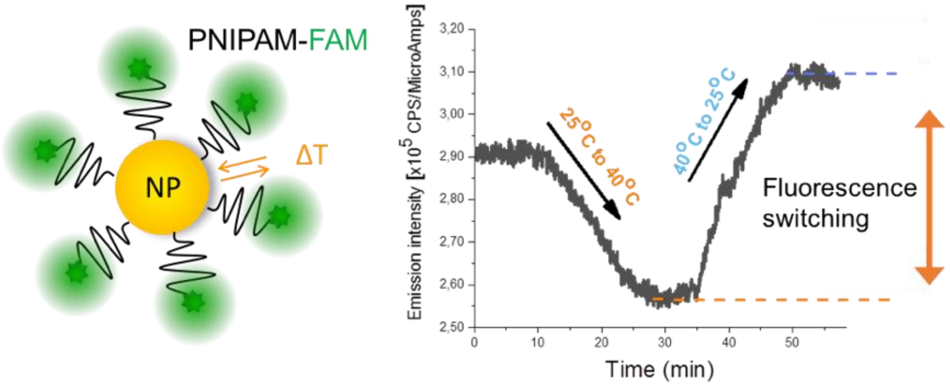

*Figure 1. T-driven nano-assembly (left) and the resulting fluorescence modulation (right).*

# Exploring a Combination of Halogen and Hydrogen Bonds in Two-Dimensional Self-Assembly at the Solution-Solid Interface

Sugosh R. Prabhu[a], Kunal S. Mali[a], Gabriella Cavallo[b], Pierangelo Metrangolo[b] and Steven De Feyter[a]

[a]*Division of Molecular Imaging and Photonics, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium.*

[b]*Laboratory of Nanostructured Fluorinated Materials (NFMLab), Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, I-20131 Milano, Italy*

## Abstract:

While hydrogen bonding is arguably the most predominantly encountered noncovalent interaction in molecular self-assembly processes, another type of intermolecular interaction called *halogen bonding* is rapidly evolving as a routine and predictable tool in supramolecular chemistry. Halogen bonds are formed between halogen atoms present on one molecule (typically Br, Cl, or I) and a nucleophilic atom/moiety present on the same or other molecule. Halogen bonds are weaker than typical hydrogen bonds but are highly directional, even more so than hydrogen bonds. These interactions have recently been used in the design of complex and functional supramolecular systems[1].

In the present research work, a combination of halogen and hydrogen bonds have been employed to fabricate complex two-component supramolecular architectures on a solid surface. Isonicotinamide has been used as a building block which has a hydrogen bonding unit in the form of the amide functional group and a halogen bond acceptor in the form of a pyridinic nitrogen. These unique structural features allow it to co-assemble with halogen bond donors such as **1** or **2** resulting in a two-component co-assembled system stabilized by halogen as well as hydrogen bonds (*see Figure 1 below*). The self-assembled monolayers so formed have been characterized using state-of-the-art scanning tunneling microscopy (STM) which reveals the contribution of the various above mentioned interactions in the self-assembly process.

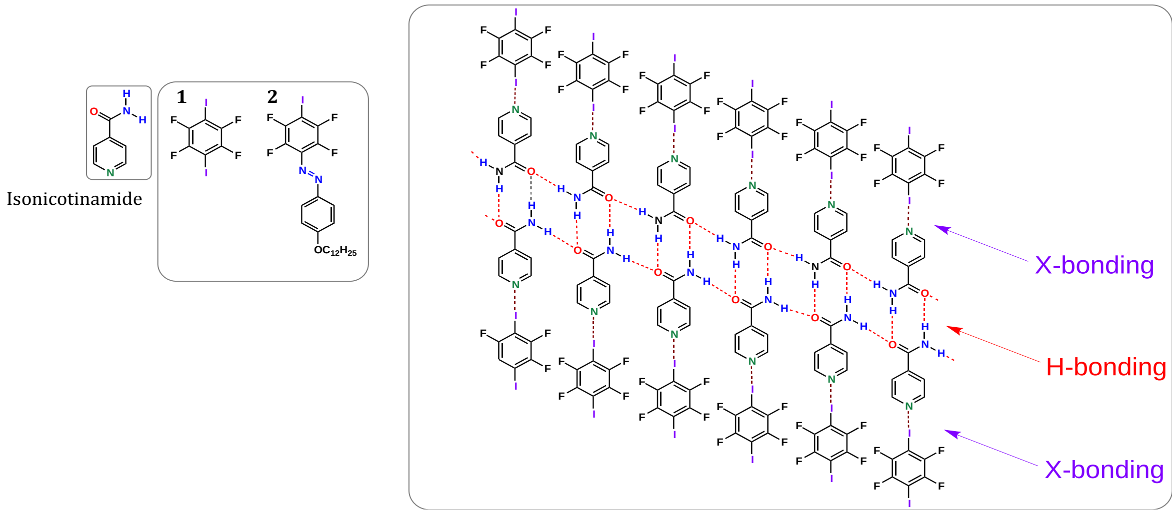

*Figure 1. Molecular structures of nicotinamide and the halogen bond-donating building blocks **1** and **2**. As depicted in the assembly schematic, halogen bonds (X-bonds) will be formed between the pyridinic nitrogen of nicotinamide and the iodine atoms*

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9th International Conference on Molecular Electronics
Paris, France
December, 17-20th 2018

# Synthesis and characterization of SAM's containing C60-Bodipy dyads bearing helical peptides for organic electronic applications.

Jad Rabah,[a] Van Bui,[a] Hélène Fensterbank,[a] Rachel Méallet-Renault,[b] Karen Wright,[a] Anne Vallée,[a] Emmanuel Allard.[a]

[a]*UVSQ, UMR-CNRS 8180 ILV, 45 avenue des Etats-Unis, 78035 Versailles cedex (France)*

[b]*Université Paris Sud, UMR 8214 ISMO, 15 rue Georges Clemenceau 91405 Orsay cedex (France)*

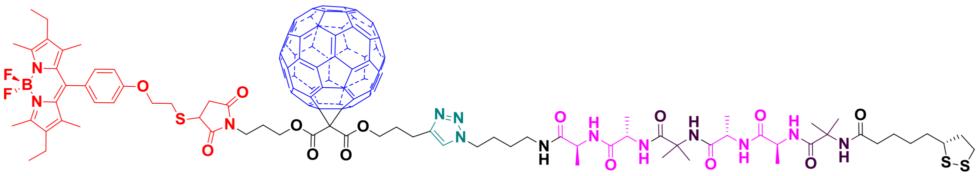
*jad.rabah@uvsq.fr*

## Abstract:

Photoinduced electron transfer (PET) in molecular systems plays a crucial role in converting solar energy to electricity through the use of photovoltaics or storing light energy in the form of chemical bonds. In this perspective, it is necessary to build artificial systems with good charge transfer efficiency and a long-lived charge separation state in order to improve the efficiency of energy conversion. [1-3]

Thus, we have developed donor-acceptor assemblies based on boron-dipyrromethene (BDY) as chromophore and electron donor and fullerene (C60) as electron acceptor. The photoinduced electron transfer process from $^1$BDY* to fullerene was confirmed by absorption, fluorescence, and transient absorption from femtosecond up to millisecond timescale. [4]

In order to investigate the potential of this dyad in the generation of photocurrent, these molecular systems were immobilized on gold surface by self-assembled monolayers (SAM) formation by attaching a helical hexapeptide that can be considered as surface structuring agent and a good electron mediator. The electrochemical and surface characterizations (XPS, QCM, and PM-IRRAS) of the SAMs show that the monolayers containing the peptidic chains are well packed and have a potential in photocurrent generation for photoelectrochemical devices. [5]



*Scheme 1: a) Chemical structure of (C60-BDY) dyad peptide.*

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# How Graphene and Hexagonal Boron Nitride get electrified in water?

B. Grosjean, R. Vuilleumier, M.L. Bocquet

*PASTEUR, Département de chimie,*
*École normale supérieure, PSL University, Sorbonne Université, CNRS, 75005 Paris, France*

## Abstract:

The recent emergence of nanofluidics has highlighted the exceptional properties of graphene and its boron-nitride counterpart as confining materials for water and ion transport [1-4]. Surprisingly ionic transport experiments have unveiled a considerable electrification of the water-BN surfaces, with a contrasting response for its water-carbon homologue [1]. This surface charging was conjectured to originate in the differential hydroxide adsorption at the surface of these twin materials, but the considerable challenge of simulating the elusive hydroxide ion has precluded a proper explanation up to now.

In this talk, we report free energy calculations based on *ab initio* molecular dynamics simulations of hydroxide $OH^-$ ions in water near graphene and hexagonal boron nitride (h-BN) layers. Our results disclose that both surfaces get charged through hydroxide adsorption, but via strongly different mechanisms. The hydroxide species shows strong chemisorption on the h-BN surface, but only weak physisorption on the graphene surface [5].

Interestingly $OH^-$ is accordingly shown to keep a very fast lateral dynamics and interfacial mobility in the physisorbed layer on graphene. This behavior sheds new lights on the experimental results on ionic transport in carbon channels. Taking into account the resulting large ionic surface conductivity, an analytical transport model allows to reproduce quantitatively the experimental data [5].

Our results offer new foundations for the chemical reactivity of carbon and BN materials in water and suggest new perspectives in the context of advanced membrane technologies for water purification and energy harvesting [6].

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# System level bistability of molecular Field-Coupled Nanocomputing

Yuri Ardesi, Mariagrazia Graziano, and Gianluca Piccinini

*Politecnico di Torino, Department of Electronics and Telecommunications, 10129 Turin, Italy*
*{yuri.ardesi, mariagrazia.graziano, gianluca.piccinini} @ polito.it*

## Abstract:

Chemists and physicists have investigated and demonstrated through simulations the possibility of exploiting redox centers to aggregate charge in precise regions of oxidized molecules. This property allows the information encoding and enables the information transfer, via electrostatic interaction, through ordered sequences of molecules. This evidence makes the implementation of molecular Field-Coupled Nanocomputing (FCN) possible[1]. The natural nanometric size of molecules and the absence of charge transport highlight molecular FCN as a possible technology for the future low power digital electronics. Our work consists in providing a methodology for the analysis, the design and the fabrication of molecular FCN devices, moving the focus from the single molecule, which has been already deeply discussed in the literature, to the molecular system. We develop an efficient model for studying systems of molecules organized as logic units, reducing the computational cost of ab initio simulations at the system level and keeping the chemical and physical properties of the assembled molecules.

More specifically in this work, we characterize the single molecule through DFT analyses and we use the results to analyze the capability of a molecular FCN wire to propagate digital information (Fig 1A). A self-consistent algorithm[2] based on the aggregated charge[3,4] (evaluated from the electrostatic potential surfaces) is used to model the electrostatic behavior of the molecules. It provides quantitative results about the information propagation and the energy associated with the electrostatic interaction among molecules (Fig 1B). We demonstrate the bistability of the molecular cell when inserted in a molecular system: it retains the digital information when the polarization of an input molecule is varied (Fig 1C). The bistability is enhanced by increasing the number of molecules in the wire and shortening the intermolecular distance (i.e. by strengthening the electrostatic interaction).

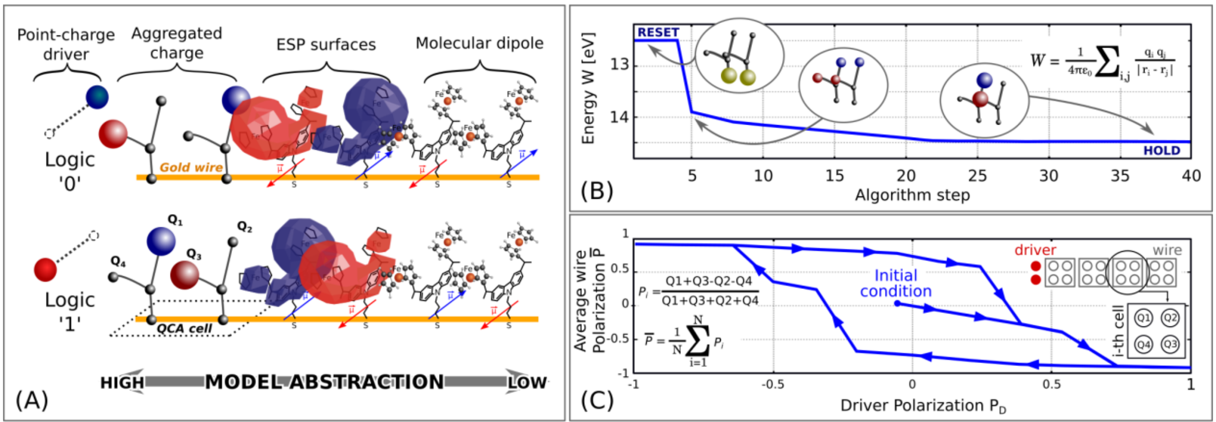

*Figure 1. (A) : molecular FCN wires, made up with bis-ferrocene molecules[5], propagating '1' and '0' bits. (B) : Electrostatic Energy trend among molecules in a wire when polarizing (from RESET to HOLD state). (C) : average polarization of cells in an FCN wire composed of 8 molecules with 1.0 nm intermolecular distance.*

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# Extending the applicability of Marcus theory in molecular junctions

Jakub K. Sowa,[a] Jan A. Mol,[a] G. Andrew D. Briggs,[a] Erik M. Gauger[b]

[a] *Department of Materials, University of Oxford, Oxford, UK. Email: jakub.sowa@materials.ox.ac.uk*
[b] *SUPA, Institute of Photonics and Quantum Sciences, Heriot-Watt University, Edinburgh, UK*

## Abstract:

It is ultimately desirable for single-molecule technologies to operate at around room temperature. In these conditions it should be possible to describe the charge transport through single-molecule junctions [schematically pictured in Fig. 1(a)] using Marcus-type theories which treat the nuclear motion classically, and account for the electron-vibrational interactions through the overall reorganization energy, λ. However, as we demonstrate here the conventional approach used in this context – Marcus-Hush-Chidsey (MHC) theory – gives rise to a number of artefacts resulting from (i) coupling to high-frequency vibrational modes (for which the high-temperature assumption of MHC is not justified), and (ii) the absence of lifetime broadening.[1] We suggest alternative transport theories (still in the spirit of Marcus theory) which rectify the above shortcomings while largely retaining the mathematical simplicity of MHC approach.[1] In particular, we derive a low-temperature correction to the semi-classical Marcus rates and show its importance in the resonant transport regime [Fig. 1(b)].[1] Furthermore, we demonstrate how lifetime broadening can be incorporated into Marcus theory, and use this approach to describe the phenomenon of thermoelectricity in molecular junctions [Fig. 1(c)].[2]

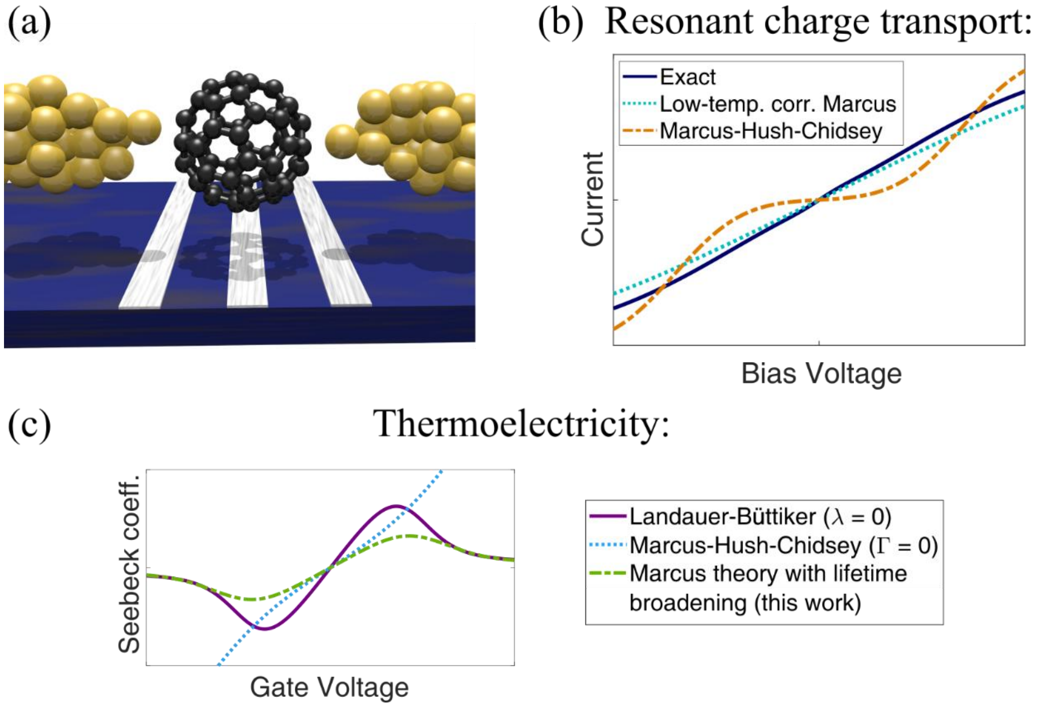

*Figure 1 : (a) Schematic of a fullerene-based molecular junction. (b) Resonant IV characteristics in the presence of electron-vibrational coupling calculated using various methods. (c) Seebeck coefficient calculated using the Landauer-Büttiker approach, Marcus-Hush-Chidsey theory and our approach.*

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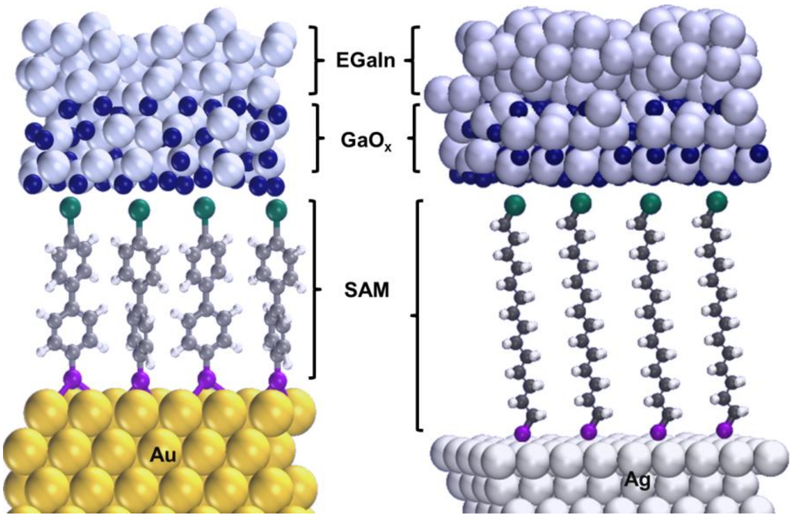
# Halogen terminated self-assembled monolayers in molecular electronics – impact of backbone

Harshini V. Annadata,[a] Xiaoping Chen,[a] David A. Egger,[b] Christian A. Nijhuis[a, c, d]

[a] Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore.
[b] Institute of Theoretical Physics, University of Regensburg, Universitätsstraße 31, 93040 Regensburg, Germany.
[c] Centre for Advanced 2D Materials and Graphene Research Centre, National University of Singapore, 6 Science Drive 2, Singapore 117546, Singapore.
[d] NUS Nanoscience & Nanotechnology Initiative, Faculty of Engineering, 2 Engineering Drive 3, Singapore 117581, Singapore.

## Abstract:

Introducing halogen atoms into the backbones of self-assembled monolayers (SAMs) is an important step towards tuning intermolecular interactions by virtue of the molecular polarizability.[1] However, predicting charge transport behaviour from polarizability from a text-book relationship is not straightforward.[2-5] Here, we use density functional theory (DFT) with periodic boundary conditions to understand how work-function modifications and energy-level alignment of halogenated SAMs influence the device performance. We examine electrostatic and electronic properties of the molecular precursor and its corresponding SAM from both DFT and electrostatic modelling. Our results show that strategically terminating SAMs with halogens proved to be a particularly promising way to tune the dielectric and tunnelling rates of the SAMs. These findings are discussed in the context of effects that arise from the chemical nature of the backbone, and the role of effective mass of the tunnelling electron, while also being correlated to experimental data.



Cartoons of ideal junctions of the form M/SAM//$GaO_x$/EGaIn. On the left, M = Au and SAM = $S(C_6H_4)_2T$. On the right, M = Ag and SAM = $S(CH_2)_{14}T$ where T = H, F, Cl, Br and I.

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# Tuning of gold work function by carborane self-assembled monolayers using a Density Functional Theory

Martin Hladík,[a] Héctor Vázquez,[a] Aliaksei Vetushka,[a] Antonín Fejfar,[a]

[a] *Institute of Physics, Czech Academy of Sciences, Na Slovance 1999/2, CZ 182 21, Prague, Czech Republic.*
*Email: hladikm@fzu.cz*

## Abstract:

Self-assembled monolayers (SAMs) act as tuners of surface properties useful for utilization in material research and nanotechnology[1,2]. Upon adsorption, the tuning of molecular level positions of SAMs composed of electronically active molecules occur and can be associated with the changes of the photovoltaic (PV) cells efficiency[3,4]. Carboranes among the SAMs building blocks attract attention due to a significant molecular dipole which can be oriented towards the surface or away from it. The investigation of the adsorption of carborane SAMs on Au(111) and resulting structures is performed through the first principle calculation based on a Density Functional Theory (DFT)[6]. The adsorption process is controlled by the electron density rearrangement from the surface gold layer to the sulfur anchoring groups of the carboranes leading to the Au-S chemical bond formations. These chemical bonds contribute to the dipole of the SAMs and thus also to the resulting work function (WF) changes that reach up to units of electronvoltes (eV). Previous experiments using Kelvin Probe Force Microscopy (KPFM) showed a similar range of the WF changes which is sufficient for the change in the PV cells potential[5]. The resulting adsorption geometries strongly affect the final total energy. The minimal total energy is achieved at the slightly inclined geometry of the molecule relative to the surface. Such an arrangement can lead to a possible prediction of geometries generated during experiments.

## Acknowledgement:

This work used facilities provided by TH02020628 project of the Technological Agency of the Czech Republic, project 17-27338Y of the Czech Science Foundation. Computational resources were provided by the National Grid Infrastructure MetaCentrum and the "Projects of Large Research, Development, and Innovations Infrastructures" program (CESNET LM2015042 and LM2015087).

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# Transport properties of oligothiophene isomers

Pascal Martin[a], Yannick J. Dappe[b], François Maurel[a], Jean Christophe Lacroix[a], Mahamadou Seydou[a]*

*[a]Université Paris Diderot, Sorbonne Paris Cité, ITODYS, CNRS-UMR 7086, 15 rue J.-A. de Baïf, 75205 Paris Cedex13, France.*
*[b]SPEC, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France*

*mahamadou.seydou@univ-paris-diderot.fr

## Abstract:

We present here longitudinal electronic transport properties in linear polymeric oligothiophenes stranded between carbon nanotube and gold electrodes. In particular, the effect of bias, electrodes and isomerization of oligomers in the device on transport properties is investigated. These grafted oligothiophenes, are currently investigated in large area junctions and at the single molecule levels. The geometries of oligomers are optimized by means of the DFT/LCAO− $S^2$+ vdW formalism, to take into account weak interactions. The probability of electron transmission in function of applied voltage is computed by using a non-equilibrium Green's functions formalism [1,2]. The results are compared to recent experimental measurements [3].

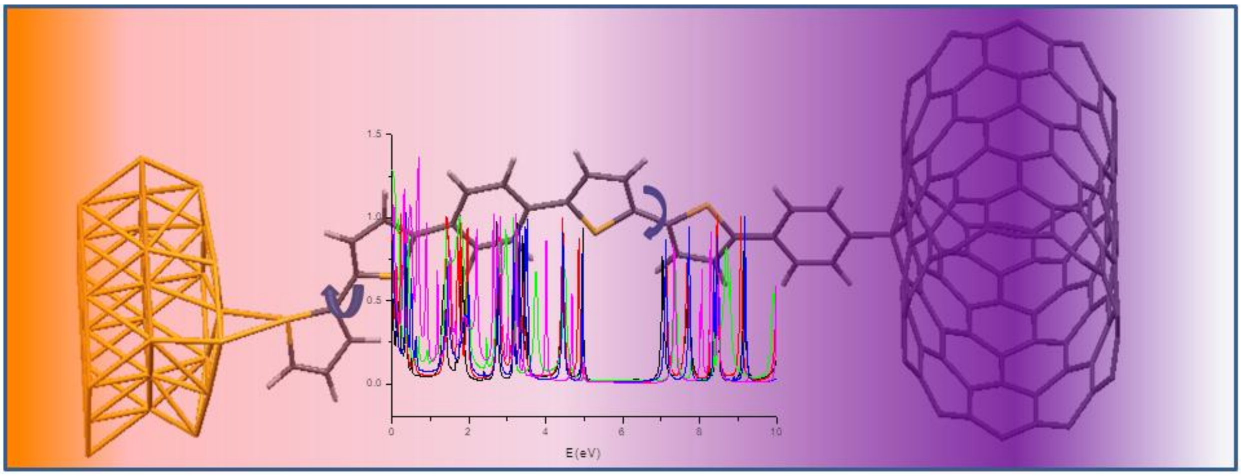

*Figure: grafted oligothiophenes stranded between gold and carbon nanotube electrodes*

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# Carbon nanostructures for biosensing and biological energy conversion

Michael Holzinger,[a] Andrew Gross [a], Jules Hammond [a], Alan Le Goff [a]

[a] CNRS-University Grenoble Alpes, 570 rue de la Chimie, 38041 Grenoble, France
Email: michael.holzinger@univ-grenoble-alpes.fr

Abstract:

Due to the increasing need to monitor health and environment in real time and to energize small electronic devices, carbon nanotubes (CNTs) and graphene are, between other, promising alternatives as building blocks in bioelectrochemical devices due to their unique electrical, mechanical properties, biocompatibility and high specific surface. In the past years, we focused the development of biosensors and biofuel cells based on such carbon nanostructures [1-3]. Our efforts in this domain aim the construction of nano-architecture at molecular scale associating different nano-objects via organic or organo-metallic connectors to immobilize redox enzymes and bioreceptors [4-5]. Furthermore, our efforts focus redox enzyme wiring on nanotubes and graphene to enable efficient electron transfer with the electrode [2, 6].

The possibility to generate electrical power out of living organisms directed biofuel cell research towards glucose biofuel cells (GBFC) since the two required compounds (glucose and oxygen) are present in both, vegetal and body fluids [7]. However, in spite of this promising evolution, there are still too many issues to be resolved before enzymatic biofuel cells become competitive in practical applications. We follow the strategy to design GBFCs as an eco-friendly power source for disposable biomedical devices as alternative application where the proof of concept is presented [8].

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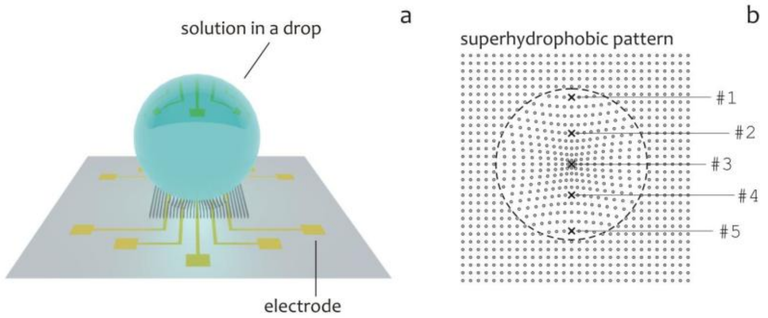
# Cancer cell culture medium identification by super hydrophobic properties of organic electrochemical biosensor

Nicola Coppedè,[a] Natalia Malara,[b] Francesco Gentile,[c] Andrea Zappettini,[a] Colluccio Maria Laura,[b] Enzo di Fabrizio,[b d]

*[a]IMEM-CNR Parco Area delle Scienze 37/A - 43124 Parma, Italy. Email: nicola.coppede@imem.cnr.it*
*[b]Department of Experimental and Clinical Medicine, University of Magna Graecia, 88100 Catanzaro, Italy.*
*[c]Department of Electrical Engineering and Information Technology, University Federico II, Naples, Italy.*
*[d]King Abdullah University of Science and Technology, Thuwal, Saudi Arabia.*

## Abstract:

Conductive polymers demonstrate their ability as biosensor devices in Organic Electrochemical Transistors architecture. With sensible dependence in ions size[1], similar devices break down if challenged with complex mixtures, due to the lack of spatial resolution. Here, we modified a conductive PEDOT:PSS polymer to include extra non-continuous scales in the device. Super-hydrophobic SU8 pillars positioned on the substrate to form a non-periodic square lattice[2], allow increased super hydrophobic properties. Then a finite number of micro-electrodes produces a multiple local detection[3]. The sample solution on device surface maintains a spherical shape. Main Marangoni convective flows could develop in the solution drop. The competition between convection and diffusion will cause a spatial separation of biological species, depending on the size and charge. Here we analyze the "waste deposit" of cell culture medium upon interaction with circulating cell isolated form peripheral blood sampling of health, sub-clinical and colon cancer patients. The analysis of culture medium, as an accessible source of biological markers, focuses on the concentration of positive ions. Understanding the cells metabolism, is a crucial topic to be useful for cancer early detection. Here, we demonstrate a super-hydrophobic organic electrochemical device may measure cell culture, showing significative differences between tumor and non-tumour patients. This assay could impact on cancer risk management, individual's diagnosis and/or help clarify risk in healthy populations.



*Super Hydrophobic OETC design*

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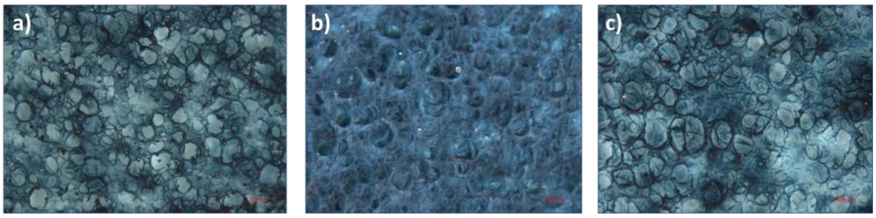
# Polymeric scaffold for wound healing monitoring based on biocompatible textile organic electrochemical transistor

Nicola Coppedè,[a] Paola Losi,[b] Andrea Zappettini,[a] Marianna Buscemi,[b] Tamer Al Kayal,[b] Giorgio Soldani [b]

[a]*IMEM-CNR Parco Area delle Scienze 37/A - 43124 Parma, Italy. Email: nicola.coppede@imem.cnr.it*
[b]*Institute of Clinical Physiology, National Research Council (CNR), Massa, Italy.*

## Abstract:

Recently, wearable devices have grown in importance, especially in healthcare, for their ability to collect crucial data, with noninvasive detection, to monitor patient's physiological conditions. An emerging application is the monitoring of dangerous wounds, to detect the ulcer status. For chronic or infected wounds, the literature reports a pH interval between 6.5 and 9, with a high dependence on the healthy development of the wound. Our objective is to realize an innovative scaffold capable of monitoring ulcers healing, starting from high biocompatible materials to ensure a correct interaction with the physiology of the wound. The scaffold has been constituted by a synthetic biocompatible material, poly(ether)urethane-polydimethylsiloxane (PU-PDMS), was manufactured by spray, phase-inversion technique. This scaffolds has been successfully used in combination with fibrin as delivery system for VEGF, bFGF and platelet lysate in preclinical wound healing experiments. A micro-fibrillar tubular scaffold was obtained using a 1% polymer solution and H2O as non solvent (I layer) and 2% and H2O (II layer) and was lyophilized. The morphological analysis of PU-PDMS scaffold surfaces was performed by stereo-microscope after Sudan Black B staining, to ensure a correct shape surface interaction. The scaffold realized in such a way has been functionalized with a biocompatible conductive polymer (PEDOT:PSS), used as detector in Organic Electrochemical Transistor architecture. This polymer presents a high sensitivity to positive ions in liquid environment and allows to determine ions concentration in easy and stable way. The fiber textile electrochemical device has been realized by a dipping process and connected with specific electric contact to create a channel and a gate electrode to control the modulation changes of the sensor. The device functionality was proved on human serum at different pH (between 4 and 10). The morphological analysis showed a dense, non porous surface obtained with the 2% solution, while a porous surface was obtained with the 1% solution where the PEDOT:PSS was positioned. This feature was maintained after lyophilization and re-hydratation. The characteristic of the device was tested showing the sensitivity to saline concentration and the effective functionality of the device. The device shows a sensitivity to pH change. The functionalized scaffold could be used as a wearable detector for wound healing monitoring in patients affected by chronic lesions.



Patch after Sudan Black B staining: a) after fabrication, b) lyophilized, c) re-hydratated

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2 Sensors and Imaging for Wound Healing: A Review Tim R. Dargaville, Brooke L. Farrugia, James A. Broadbent, Stephanie Pace, Zee Upton and Nicolas H. Voelcker

# POSTERS SESSIONS

## Wednesday 19 December, 10:00 – 11:00
## 15:50 – 16:50

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9th International Conference on
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# Influence of Intermolecular Interaction on Spontaneous Orientation Polarization in Evaporated Films of Organic Light-Emitting Diode Materials

Kohei Osada,[a] Hisao Ishii,[b] Yutaka Noguchi [a]

[a]*School of Science &Technology, Meiji Univ., Kawasaki, Japan. Email: ce171018@meiji.ac.jp.*
[b] *Center for Frontier Science, Chiba Univ., Chiba, Japan.*

## Abstract:

Molecular orientation in organic films is very important because it influences the properties of organic light-emitting diodes (OLEDs) [1]. We have reported that spontaneous orientation polarization (SOP) is commonly observed in the evaporated films of OLED materials [2]. The surface potential of such films grows proportionally to their film thickness because of spontaneous order of permanent dipole moment (PDM) of the molecules. This phenomenon is known as giant surface potential (GSP) [3]. We discussed the relationship between GSP slope and PDM or intermolecular interaction and indicated the intermolecular interaction such as intermolecular hydrogen bond and dipole-dipole interaction may suppress SOP [2]. However, the formation mechanism and control method of SOP are still unknown. In this study, we measured GSP characteristics of the mixed film of polar and nonpolar molecules (TPBi and CBP, respectively) to investigate effects of the intermolecular interaction. We also examined GSP properties at hetero interfaces with varying substrate conditions.

Fig.1 shows the mixing ratio dependence of the normalized orientation degree of PDM and GSP slope in the mixed film of TPBi and CBP. Relationship of GSP slope (*V/d*) and PDM (*p*) can be described as $V/d=n\langle\cos\theta\rangle p/\varepsilon$, where *n* is the density of polar molecule, $\varepsilon$ is dielectric constant and $\langle\cos\theta\rangle$ is the average orientation degree of PDM with respect to the surface normal direction. Interestingly, the GSP slope shows nearly constant in the mixed films, that is, orientation degree of PDM is increased with decreasing mixed ratio of TPBi. Since co-evaporation with CBP increases the intermolecular distance between TPBi molecules, dipole-dipole interaction decays in the mixed film. As the result, the probability that PDMs cancel each other may be reduced and the orientation degree is enhanced.

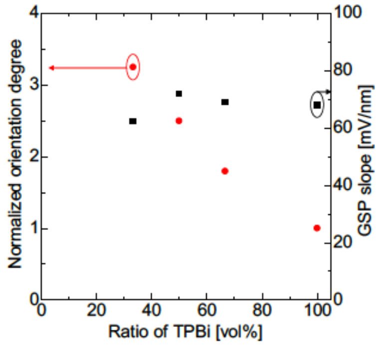

*Fig.1 Mixture ratio dependence of orientation degree in mixed film of TPBi and CBP.*

We also measured the local potential distribution of the TPBi film on the Au substrate with/without 1-Dodechanethiol self-assembled monolayer (SAM) by using Kelvin probe force microscopy. A relatively small surface potential was observed near the boundary between the TPBi film and the SAM treated substrate. The weak interaction with the substrate may induce the molecular packing of TPBi with reducing electrostatic energy, consequently SOP.

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# Towards single POM photoswitch for data storage

Michele Mattera,[a] Imad Arfaoui,[b] David Kreher,[a] Anna Proust,[a] Florence Volatron[a]

[a] *Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, IPCM, 4 Place Jussieu, F-75005 Paris, France. Email:michele.mattera@upmc.fr*
[b] *MONARIS, UMR CNRS-Sorbonne Université 8233, 4 Place Jussieu, 75005 Paris, France.*

## Abstract:

In this actual era of fast technological advances, the need for more powerful computers and denser memories contrains to push further the limits of the traditional electronics, going down to the molecular level. Polyoxometalates have remarkably electronic properties which makes them good candidates, as molecular components for data storage, since they have already been exploited in flash memory devices.[1]

The Keggin family of phosphomolybdates with different alkylammonium-based counter cations will be studied (see Fig 1a).[2] Interestingly this family can be reduced in the presence of an UV light, without any external reducing agent.[3,4] This process is reversible and could be exploited to program these polyoxometalates, and the reading process can take place by appling a small bias current.

Because we want to use each polyoxometalate as a bit of information, we will show how is it possible to work at the sub monolayer level, by isolating each cluster from each other, covering areas in the order of the centimeter square. The successful isolation is obtained by using a porous bidimensional network, based on aromatic stilbene units, that will immobilize and host the clusters, by means of hydrophobic weak interactions (see Fig 1b). Depending on the side chains present on the stilbene units, the network can adjust itself to the guest that want to accommodate.[5,6]

We studied different parameters in order to optimize the overall coverage of the surface: the concentration of the POM, the solvent used, the pore diameter of the network and also the deposition method.

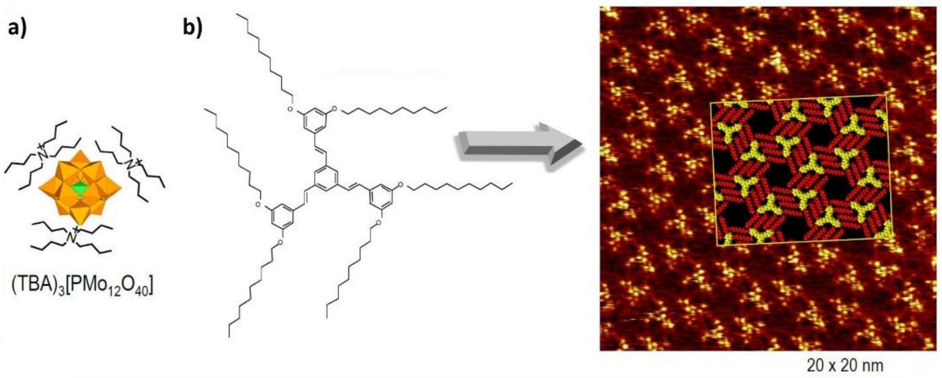

Figure 1 - a) Example of Keggin Family Phosphomolybdate with alkylammonium countercation. b) Bidimensional aromatic stilbene-based porous network.

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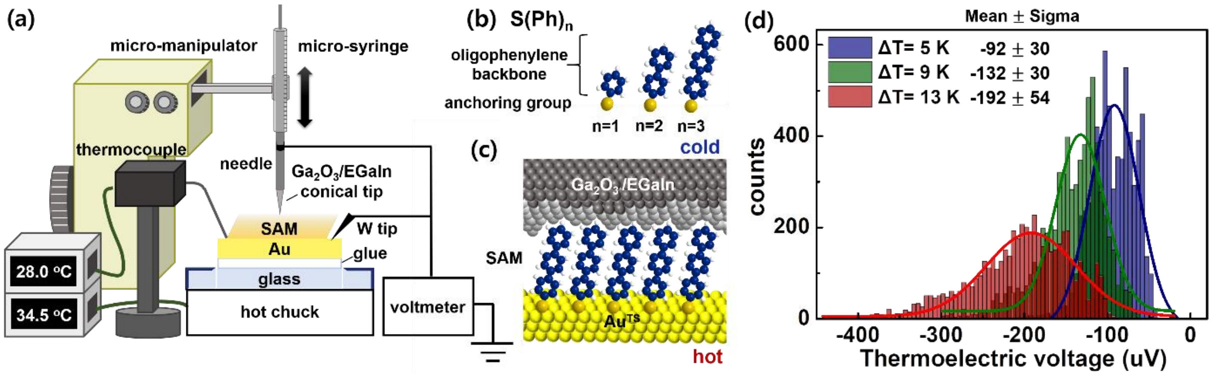
# Large-area Thermoelectric Junctions Formed with Eutectic Gallium-Indium Electrode

Sohyun Park, and Hyo Jae Yoon*

*Department of Chemistry, Korea University, Seoul, 02841, Korea, hyoon@korea.ac.kr*

## Abstract:

A challenge in organic thermoelectrics is to relate thermoelectric performance of devices to the chemical and electronic structures of organic component inside them on a molecular scale.[1,2] To this end, a reliable and reproducible platform relevant to molecular-level thermoelectric measurements is essentially needed. This paper shows a new, efficient approach for thermoelectric characterization of large-area of molecular monolayers using liquid eutectic gallium-indium (EGaIn). Cone-shaped EGaIn[3] microelectrode permits access to non-invasive, reversible top-contact formation onto organic surfaces in ambient conditions, high yields of working devices (up to 97%), and thus statistically sufficient thermoelectric data sets (~6000 data per sample in a few hours). We here estimated thermopowers of EGaIn (3.4 ± 0.1 µV/K) and the $Ga_2O_3$ layer (3.4 ± 0.2 µV/K) on the EGaIn conical tip and successfully validated our platform with widely studied molecules, oligophenylenethiolates. Our approach will open the door to thermoelectric large-area molecular junctions.



(a) *Schematic describing our thermoelectric measurement system*. (b) *Molecules used in this study*. (c) *Schematic describing the structure of large-area thermoelectric junction*. (d) *Exemplary histograms of ΔV for* $S(Ph)_3$ *SAM*.

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T2 - 4

# Effects of ionic liquid layers on morphologies, structures and electrical properties of thin films of pentacene and fullerene

Keitaro Eguchi,[a] Michio M. Matsushita[b] and Kunio Awaga[b]

[a]*James-Franck Str. 1, Garching, Department of Physics, Technical University of Munich, Germany.*
*Email:keitaro.eguchi@tum.de*
[b]*Furo-cho, Chikusa-ku, Nagoya, Department of Chemistry, Nagoya University, Japan.*

## Abstract:

Ionic liquids (ILs), which consist of mobile cations and anions, and hybrid IL and polymer materials have been used as gate dielectric materials in OFETs to accumulate a high carrier density (ca. $10^{15}$ $cm^{-2}$) in the active layer due to their high capacitances [1,2]. These specific properties originate from their mobile characteristics and the formation of electrical double layers (EDLs) at the electrified solid-IL interfaces [1]. However, these properties of ILs are known to break down under confined conditions, resulting in the formation of characteristic structures and orderings, which are quite different from those of bulk ILs [3]. In this work, we investigated the effects of an IL, *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME–TFSI, Fig. 1a), sandwiched between substrates and organic layers, on the morphologies, structures, and electrical properties of thin films of organic layers.

DEME-TFSI was deposited on the FET substrates with a bottom gate, bottom-contact-device architecture having $SiO_2$ insulating layers (300 nm) thermally grown on highly doped n-Si substrates (gate electrodes) and comb-shaped Pt electrodes (width/length = 7.9 cm/20 μm). Subsequently, the thin films of pentacene (10 ML) wwere prepared on the substrates without exposure to air (Fig. 1b). FET measurements were performed *in situ* under high vacuum conditions without exposure to air at room temperature in the dark, using a source-measure unit (Advantest Corp. R6245A). *Ex situ* structural and morphological characterization were performed for the thin films under ambient conditions using an X-ray Diffractometer (XRD) and an atomic force microscope.

The thin films of pentacene prepared on IL-coated Si substrates exhibited dendritic structures but the growth of dendritic structures was strongly suppressed on the DEME–TFSI layers. The XRD of the thin film of pentacene on the bare substrate showed a peak at $2\vartheta = 5.7°$, which corresponds to the (001) plane of the thin-film phase of pentacene. The intensity of the peak decreased with the thickness of the DEME–TFSI layers. In addition, an additional peak corresponding to the bulk phase was observed in the XRD of the thin film on 5 ML DEME–TFSI. The pentacene FET without the DEME–TFSI layer exhibited a typical p-type channel behavior with a small hysteresis loop, while the pentacene FETs with the DEME–TFSI layers displayed p-chanel behaviors with larger hysteresis loops. The size of the hysteresis showed a dependence on the thickness of the DEME–TFSI layers. The OFETs with the DEME–TFSI layers has the potential for use in memory deices.

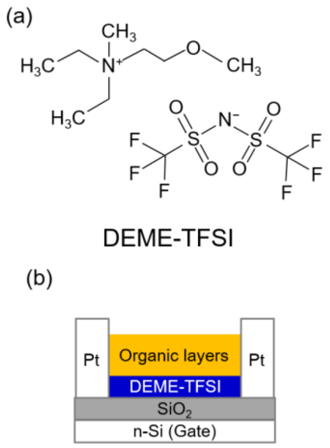

*Figure 1. (a) Chemical structure of DEME–TFSI. (b) OFET device structure showing the incorpolation of a DEME–TFSI layer.*

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# Organic-inorganic thin multilayer for organic light emitting diode passivation film by a single deposition chamber

Yoonseuk Choi,[a] Min-Hoi Kim,[b] and Jae-Hyun Lee,[b]

*[a]Department of Electronic and Control Engineering, Hanbat National University, 125 Dongseo-daero, Yuseong-gu, Daejeon 305-719, South Korea. Email: ychoi@hanbat.ac.kr*
*[b]Department of Creative Convergence, Hanbat National University, 125 Dongseo-daero, Yuseong-gu, Daejeon 305-719, South Korea.*

## Abstract:

We investigated poly-para-xylylene (parylene) and Aluminium Nitride (AlN) multilayer thin film as passivation for organic light emitting diodes (OLED), fabricated in a short process time at room temperature using a single deposition chamber. We deposited the parylene and AlN layers using an optimized chemical vapor deposition technique and sputtering respectively. The passivation film has an optical transmittance of 90%. Moisture barrier performance was improved with increasing thickness and number of layers. OLED devices with half-life of 30 hours passivated with Parylene(6.4μm)/AlN(50nm)/Parylene(0.6μm)/AlN(50nm)/Parylene(0.6μm)/AlN(50nm) films showed preserved shelf-life, in excess of 48 hours under 37.8 °C and 90% RH conditions.

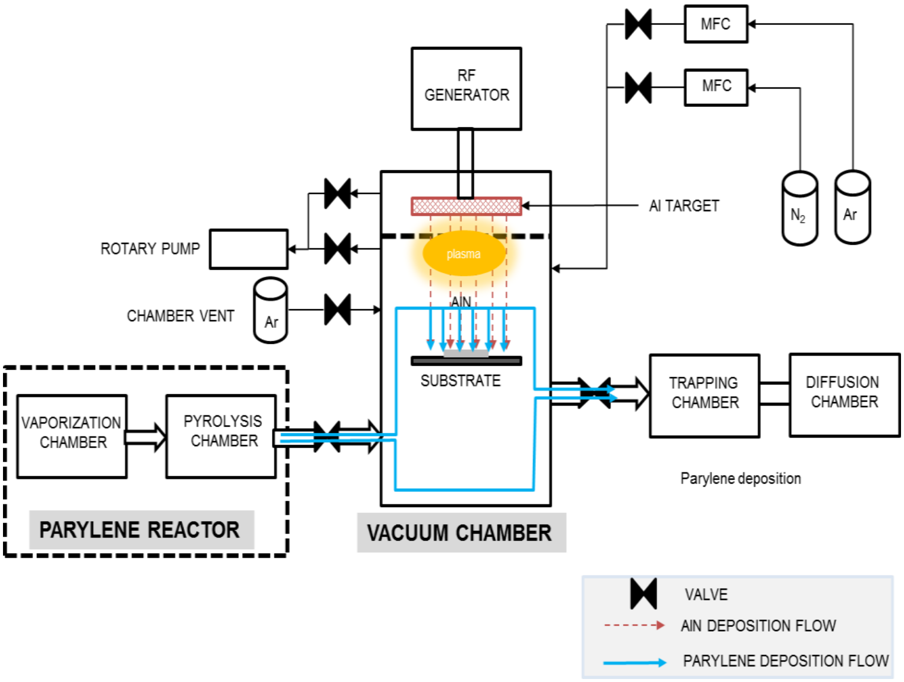


*Figure. Schematic diagram of a single system for multilayer passivation thin film deposition*

## Acknowledgement:

This work was supported by the Korea Institute of Energy Technology Evaluation and Planning(KETEP) and the Ministry of Trade, Industry & Energy(MOTIE) of the Republic of Korea (No. 20183010013840)

# Tunneling-Based Access Resistance in Layered Single-Crystal Organic Semiconductor

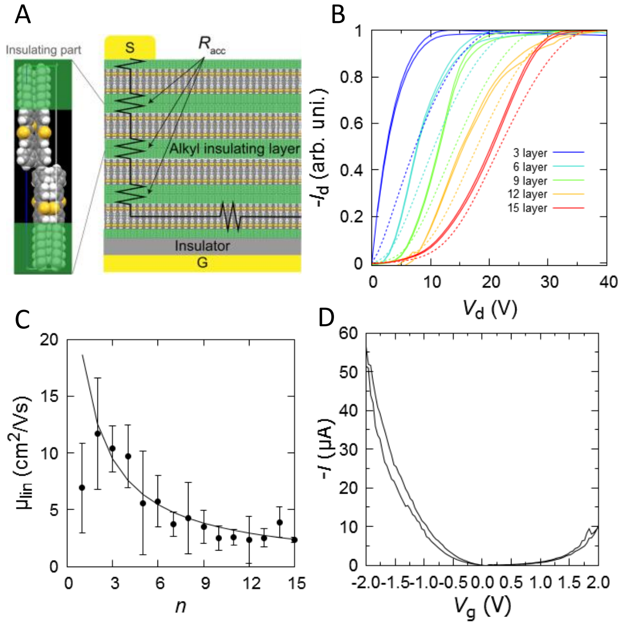
Takamasa Hamai,[a] Shunto Arai,[a] Hiromi Minemawari,[b] Satoru Inoue,[b, c] Tatsuo Hasegawa[a, b]

[a] *Department of Applied Physics, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, Japan.*
*Email: hamai@hsgw.t.u-tokyo.ac.jp*
[b] *National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Japan.*
[c] *Nippon Kayaku Co., Ltd., 3-31-12 Shimo, Kita-ku, Tokyo, Japan.*

## Abstract:

Organic thin film transistors (OTFT) are the key component of flexible and printed electronics with its processability under room-temperature and ambient pressure. Recent studies revealed that π electron core substituted by long alkyl chain shows optimal characteristics such as high layered crystallinity, solubility to conventional organic solvent, and high carrier mobility. However, a potential problem which comes from the insulating nature of substituted alkyl chains are not elucidated.

Here, we report the effects of vertical tunnel transport across alkyl-chain layers in single-crystal OTFT of Ph-BTBT-C10 [1, 2]. In OTFTs with staggered geometry (Fig. A), ohmic contact in ultrathin films systematically changes to highly nonlinear contact with the increase of the layer number (*n*) (Fig. B). The device mobility is also layer-number-dependent: The device mobility in linear regime of thick film with *n*=15 (~80 nm thick) is 5 times smaller than that of ultrathin film with *n*=2 (10.6 nm thick) (Fig. C). These drastic change of device characteristics were reproduced by numerical calculation with a simplified model which assumes that the nonlinear access resistance is derived from tunneling conduction across the alkyl-chain insulating layers. We also experimentally confirmed that the vertical transport is dominated by tunneling by measurement with template-stripped Au ($Au^{TS}$) and eutectic gallium indium (EGaIn) electrodes (Fig. D) [3]. In the presentation, we discuss the completely different two carrier conduction mechanism in intra-layer and inter-layer transport in Ph-BTBT-C10.



*A, Schematic of interlayer access resistance. B, Normalized $I_d$-$V_d$ characteristics of Ph-BTBT-C10 OTFT with various layer-number thickness. Solid curves : measured data, broken curves : calculated data. C, Layer-number dependence of device mobility in linear regime between n=1 and 15. Solid curve indicates fitting curve. D, I-V characteristics of $Au^{TS}$/Ph-BTBT-C10/EGaIn vertical device.*

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# The Role of Molecule–Electrode Interfacial Defects in Large-Area Tunneling Junctions

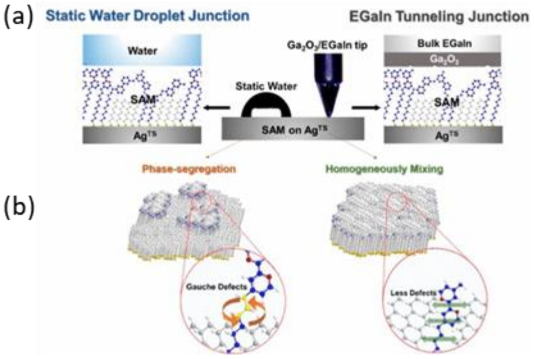
Hyunsun Song [a] , Gyu Don Kong [a] , Junji Jin [a] , Martin Thuo [b] , Joonyoung F. Joung [a] , Sungnam Park [a] , and Hyo Jae Yoon* [a]

*[a] Department of Chemistry, Korea University, Seoul 02841, Korea, hyoon@korea.ac.kr*

*[b] Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011, United States*

## Abstract:

Herein, we compare two analogous junctions formed with identical organic thin film and different liquid top-contacts (water droplet vs eutectic gallium indium alloy[1]) and elucidate the puzzling interfacial characteristics. Specifically, we fine-tune the surface topography of the organic surface using mixed self-assembled monolayers (SAMs)[2]: single component SAM composed of rectifier (2,2′-bipyridyl-terminated n-undecanethiolate; SC11BIPY[3]) is systematically diluted with nonrectifying n-alkanethiolates of different lengths (denoted as SCn where n = 8, 10, 12, 14, 16, 18). Characterization of the resulting mixed SAMs in wettability and tunneling currents with the two separate liquid top-contacts allows us to investigate the role of phase segregation and gauche defect in the SAM//liquid interfaces. The results reported here show the difference in length between SC11BIPY and SCn translated into nanoscopic pits and gauche-conformer defects on the surface, and the difference in contact force—hydrostatic vs user pressures—and hence conformity of contact account for the difference in wettability and rectification behaviors. Our work provides an insight into the role of molecule–electrode interfacial defects in performance of molecular-scale electronic devices.



*(a) Schematic describing similarity and discrepancy between AgTS|mixed SAM//liquid interfaces where AgTS is template-stripped silver and liquid is either pure deionized water droplet or liquid eutectic gallium indium (EGaIn). (b) Schematic illustration of mixed SAMs on AgTS derived from competitive adsorption of two molecules having different or similar chain lengths.*

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# Understanding Cross-Conjugation for Organic Electronics

Samara Medina,[a] Jean-François Morin,[b] Xiaozhang Zhu[c], Juan Casado[a]

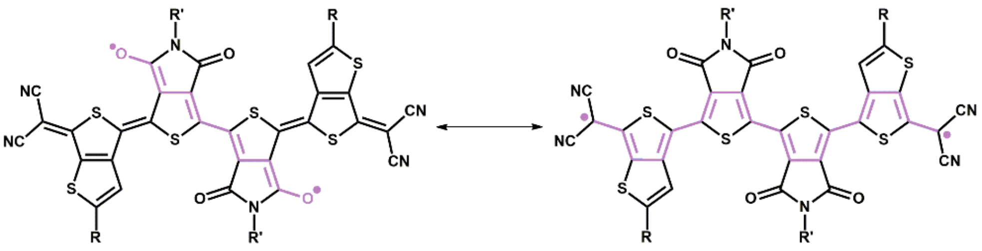
[a] Univ. Malaga, Dept. Phys. Chem., Campus Teatinos S-N, E-29071 Malaga, Spain, samara@uma.es.
[b] Département de Chimie, Université Laval, 1045 Ave de la Médecine, Québec, G1V 0A6, Canada.
[c] Chinese Acad. Sci., Inst. Chem., CAS Key Lab Organ Solids, Beijing 100080, Peoples R China.

## Abstract:

π-Conjugated organic molecules have been the focus of interest since they have been probed as potential semiconducting materials,[1] suitable for replacing the widely used silicon technologies. Their structural, optical and conductive properties are now under study to improve their application in organic electronics and to make possible their *ad hoc* synthesis. In this sense, the knowledge of the π-electron delocalization is crucial to stablish the relation between the properties and the function, enabling the development of a synthesis guide based on the specific application.

The most acknowledged conjugated organic materials are those which present extended, linearly-conjugated π-systems.[1,2] However, this is not the only way of π-electron delocalization: homoconjugation, cross-conjugation, curved-conjugation, etc. constitute different electronic designs to achieve new organic materials.

There is a relative high abundance in the organic world of cross-conjugated but limited comprehension.[1,2,3] Thus, the understanding of how cross-conjugation works in π-electronic systems is of importance. Following this idea, in this project we show 4 different structures which present two perpendicular π-conjugated paths and how the cross-conjugated property is revealed. On the one hand, two molecules based on thieno[3,4-c]pyrrole-4,6-dione quaterthiophenes[2,3] allow us to accomplish the subject from the aromatic/quinoidal outlook, and, on the other hand, two molecules with an anthanthrone core make possible the study from the perspective of the substituent groups.[4]



*Cross-conjugated paths in a quaterthiophene-based molecule.*

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# Electrochemical surface modification for the modulation of electrical properties of organic devices

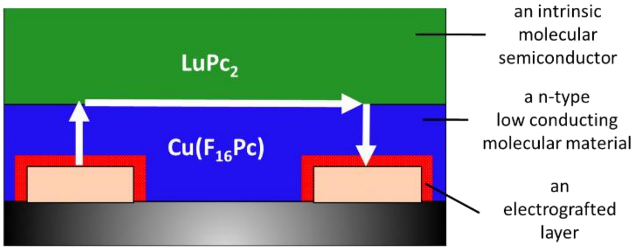
Rita Meunier-Prest, Mickaël Mateos, Marcel Bouvet

*Institut de Chimie Moléculaire de l'Université de Bourgogne, UMR CNRS 6302,*
*Univ. Bourgogne Franche-Comté, Dijon, France*
*rita.meunier-prest@u-bourgogne.fr*

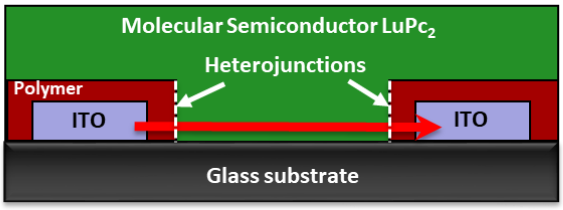
## Abstract:

Organic electronics is a field of intensive research thanks to the diversity of molecular structures reachable by organic synthesis. Molecular materials offer convenient shaping processes, such as solution processing techniques, which can be used for the fabrication of organic devices on plastic substrates.

We present the elaboration of two original conductometric devices: a conductometric gas sensor called MSDI heterojunction[1] and a polymer – phthalocyanine double lateral heterojunction. The properties of these devices are highly dependent on the interfaces. Electrochemistry was used both to modify the electrode surface of the MSDI and to synthesize the polymer.



*Modified CuF$_{16}$Pc – LuPc$_2$ n-MSDI*



*Polymer – LuPc$_2$ double lateral heterojunction*

We studied the impact of the electrode surface modification on the electrical and sensing properties of the devices.

Previous works on the development of MSDI emphasized the primary role of interfaces, particularly in the case of n-MSDI that contained a p-n heterojunction. We grafted different substituted benzenes by reduction of the corresponding diazonium salts on interdigitated electrodes. The various surface modifications mainly acted as an insulating barrier that amplified the nonlinear behavior of the current-voltage characteristics of MSDI. The grafting of 2,5-dimethoxybenzene significantly improved the ammonia sensitivity of MSDI based on copper hexadecafluorophthalocyanine and lutetium bisphthalocyanine, with a limit of detection of around 200 ppb.

We also developed polymer - phthalocyanine lateral heterojunctions based on polyaniline or substituted polyanilines having either electron withdrawing, the poly (2,3,5,6-tetrafluoroaniline)[2], or electron donating groups, the poly (2,5-dimethoxyaniline). Their electrical behavior, studied by impedance spectroscopy and the record of the I(V) characteristics, differs according to the nature of the substituents of the electrodeposited polyaniline. Their sensing measurements revealed their efficiency to detect ammonia in humid atmosphere, with a sub-ppm limit of detection.

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# Ag nanoparticles for application to electronic device materials

Kazuaki Hiroki,[a] Shigetaka Katori,[a] Kazuhiro Takemura,[a]
Mai Ooe,[b] Yasukazu Kawamoto,[b] Kaito Yasuda,[b] Kazumi Yasuda[b]

[a] National Institute of Technology, Tsuyama College,
*Numa 624-1, Tsuyama,Okayama,Japan,708-8509. Email: hiroki@tsuyama-ct.ac.jp*
[b] Fect Inc., *Nishiyoshida 558-3, Tsuyama,Okayama,Japan,708-0856. Email: info@fect.jp*

## Abstract:

In recent years, metal nanoparticles have been paid much attention, which have various and superior characteristics. The materials, including gold, silver and copper, can be applied to the fabrication of nano inks. Those are especially worthy of method to fabricating electronic devices. By coating or inkjet printing of metal nano ink, a dense circuit can be drawn on a small electronic substrate. It can also be fabricate a multilayer device by using metal nano ink with conductive polymers, organic EL materials. In this study, we report the simple method for preparation and properties of silver nano ink.

The method for preparation of metallic nano ink was developed by Fect Inc. It uses a common silver oxide as a precursor. Although an unusual solvent and a polymer dispersant (surfactant) are required, the method is a very simple. TEM image of silver nanoparticles contained in the silver nano ink obtained by this method is shown in figure 1. The particle size of silver nanoparticles were relatively uniform at around 50 nm, and it can be confirmed that they were uniformly dispersed. These silver nano particles were covered with a polymer dispersant (surfactant) used in the process for preparing of silver nanoparticles. Therefore, when this silver nano ink is applied, it has a beautiful silver metallic luster, however the silver nano layer did not exhibit electroconductivity.

A polymer dispersant (surfactant) can be easily removed by linsing with a common solvent. TEM image of silver nanoparticles contained in the silver nano ink obtained after linsing process method is shown in figure 2. The particle size of silver nanoparticles was relatively growing. It can be confirmed that they are aggregated and are stripped off a polymer dispersant (surfactant). Thus, the silver nano layer, which is fabricated from new silver nano ink, has both of a beautiful silver metallic luster and electroconductivity.

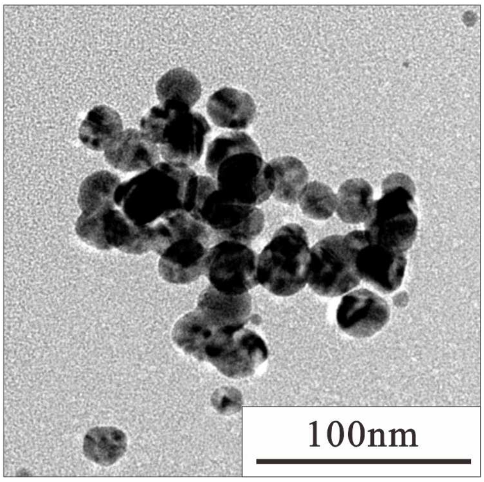

*Fig.1 TEM image of silver nanoparticles with the surfactant.*

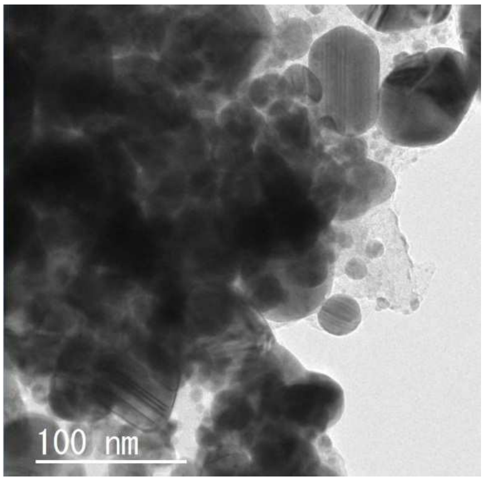

*Fig.2 TEM image of silver nanoparticles with no surfactant.*

# A study of leakage current behavior according to blade-coating velocity in a metal-polymer dielectric-metal capacitor

Do-Kyung Kim, Hyeon-Seok Jeong, and Jin-Hyuk Bae*

*School of Electronics Engineering, Kyungpook National University, Daegu, South Korea, Email: jhbae@ee.knu.ac.kr*

## Abstract:

Solution process of organic electronic materials have attracted significant attention for their potential of flexible and large-scale electronics in low-cost [1]. Among many solution coating techniques, meniscus-guided coating have been actively studied due to easy controllability of thickness and electrical characteristics in large-scale [2]. However, many researches have been focused on semiconductors to improve field-effect mobility of transistors, and less attention has been paid to the dielectrics even though dielectric properties highly effect on leakage current and operational voltage of capacitor or transistor [3]. Therefore, understanding of relationship between coating parameters and electrical characteristics of dielectric film in meniscus-guided coating is essential for large-area, high-performance organic electronics.

Here, we demonstrate the leakage current behavior according to coating velocity which is one of the major parameters in meniscus-guided coating method in a metal-polymer dielectric-metal capacitor structure. The representative polymer insulator, cross-linkable poly(4-vinyl-phenol) (c-PVP) was blade-coated at the speeds of 2, 5, and 10 mm/s over a large indium-tin-oxide coated glass substrate (10x10 cm$^2$) as shown in Fig. 1(a) to fabricate metal-insulator-metal capacitors. The current density was measured in electric field range of 0 - 1.2 MV/cm as shown in Fig. 1(b). The current densities for the coating speeds of 2, 5, and 10 mm/s at the electric field of 0.3 MV/cm were 8.3x10$^{-5}$, 1.6x10$^{-6}$, and 1.4x10$^{-5}$ A/cm$^2$, respectively. The capacitor with c-PVP coated at the speed of 5 mm/s shows the lowest leakage current density regardless of the electric field.

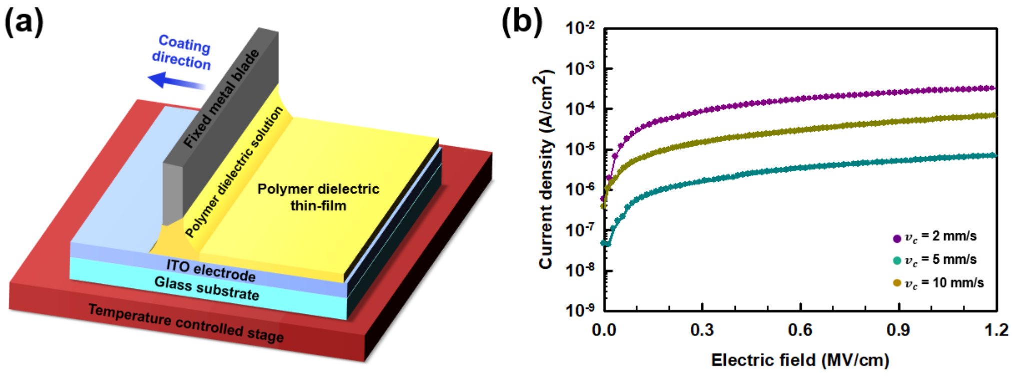

*Figure 1. (a) Schematic of blade-coated metal-polymer dielectric-metal capacitor and (b) current density of fabricated capacitors as a function of electric field.*

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# Computational Design of Novel Organic Semiconductors

Pascal Friederich,[a] Franz Symalla,[a] Franz Symalla,[a] Artem Fediai,[a] Velimir Meded,[a] Alexander Colsmann,[b] Mario Ruben,[a] Wolfgang Wenzel[a]

[a]*Institute of Nanotechnology, Karlsruhe Institute of Technology, Germany.*

[b]*Light Technology Institute, Karlsruhe Institute of Technology, Germany.*

*Email: Wolfgang.wenzel@kit.edu*

Abstract:

Small-molecule organic semiconductors are used in a wide spectrum of applications, ranging from organic light emitting diodes[1] to organic photovoltaics. A number of factors determine mobility, such as molecular packing, electronic structure, dipole moment and polarizability. Presently, quantitative ab-initio models to assess the influence of these molecule-dependent properties, including the influence of dopants, are lacking. Here, we present a multi-scale model, which provides an accurate prediction of experimental data over ten orders of magnitude in mobility [2], and allows for the decomposition of the carrier mobility into molecule-specific quantities. The model consists of a multi-step procedure, incorporating single molecule parameterization, generation of atomistic morphologies,[3] DFT based electronic structure calculations yielding site energies, energy disorder, electronic couplings and reorganization energies.[4] These parameters are used in an analytic model[5] to compute the charge carrier mobility of the amorphous materials. We also provide molecule-specific quantitative measures how two single molecule properties, the dependence of the orbital energy on conformation and the dipole induced polarization determine mobility for hole-transport materials. On the basis of this methodology we are able to computationally predict novel pure ETL materials with three orders of magnitude higher mobility than their precursors [6] and elucidate the molecular mechanism of doping these materials with kinetic Monte-Carlo simulations. The availability of first-principles based models to compute key performance characteristics of organic semiconductors may enable in-silico screening of numerous chemical compounds for the development of highly efficient opto-electronic devices.

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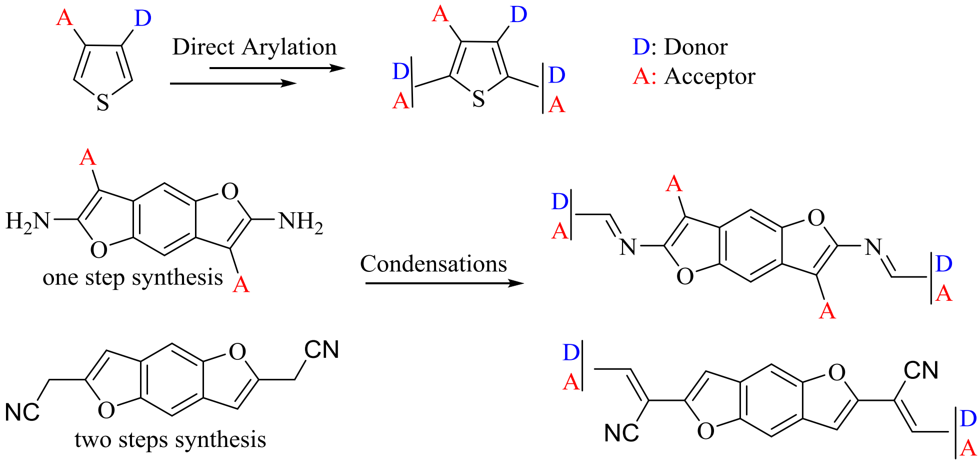
# Rapid access to organic semi-conductors based on benzodifurane/thiophene for OPV applications

Frédéric Gohier[a], Chady Moussalem[a], Alexandre Faurie[a], Jérémie Grolleau[a] and Pierre Frère[a]

[a] *Université d'Angers, MOLTECH-Anjou, UMR CNRS 6200, groupe SCL, UFR Sciences, 2 bd Lavoisier, Angers, France*
*frederic.gohier@uiv-angers.fr*

## Abstract:

Organic semiconductors (OSC) are the basis for the development of plastic electronics whose applications are linked to LED displays systems, to low voltage lighting (white light emission), to microelectronics (field effect transistors) or to solar energy (photovoltaic cells) conversion [1]. In the context of clean energy, access to organic semi-conductors should be very rapid (few steps) and based on green synthetic methods [2] such as cycloaddition reactions (atom economy), condensation reactions (only water as waste), cascade reactions or direct arylation reactions (atom economy). We have used these methodologies to build organic semi-conductors containing donor-acceptor groups to tune electronic levels. First examples were based on direct arylation of substituted thiophenes to afford donor-acceptor-donor (D-A-D) materials [3]. Other examples consist of benzodifurane moieties [4] from which donors and acceptors have been linked by condensation reactions. The electronic properties of the different compounds have been studied, and some solar cells have been realized.



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# Electronically condictive polymers in electroanalytical chemistry : from potentiometric to biologic gates

Gaetan Scheiblin[a], David Gosselin[a], Maxime Gougis[a], Romain Coppard[b], R. Owens[c], G. Malliaras[c], Jean Berthier[a], Pascal. Mailley[a]

*[a]Univ. Grenoble Alpes,CEA LETI DTBS, F-38000, Grenoble, France. Pascal.mailley@cea.fr*
*[b]Univ. Grenoble Alpes,CEA LITEN DTNM, F-38000, Grenoble, France*
*[c]University of Cambridge, UK.*

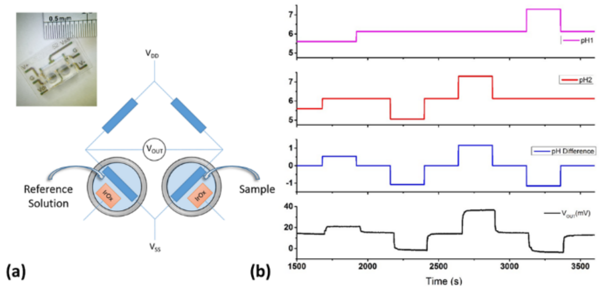
Abstract:

Electronically conductive polymers represent an interesting class of materials for the design of electroanalytical tools owing to their intrinsic electrical/electrochemical properties and doping behavior. More particularly, our attention was devoted to the design of low cost and accurate electrochemical (bio)sensors that could be implemented for example in point of care devices for patient survey at home or in pathogen detection in food using molecular biology principles.

Screen printing technology is a very efficient process for the high rate fabrication of electroanalytical systems. Moreover, electronically conductive polymers such as Polyaniline and PEDOT are now commercially available as screen printable inks. In such a context, we developed printed potentiometric sensors and organic electrochemical transistors (OECT) for the selective detection of metabolites in complex media.

First PANI based pH electrodes were developed for the monitoring of isothermal polymerase chain reaction (PCR LAMP). We recently shown the possibility to detect accurately 10 copies/mL of bacterial DNA in less than 30 min using a µfluidic PCR reaction chambers embedding PANI pH electrodes[1].

Secondly, we demonstrated the possibility to develop printed OECT with similar performances than classical lithographed systems using screen printed PEDOT inks. We first focused on the development of fully printed biosensors for lactate and glucose[2]. But, away from classic biosensing, OECT offer the unique possibility to be combined for the design of more complex electronic circuitry. Thereby, some basic electronic architectures, Wheatstone bridge, as well as NAND and NOR gates, were designed. The former circuit was implemented for the referenceless measurement of pH in sweat[3]. An original NOR gate was finally assayed for the design of an enzymatic logic gate using lactate and glucose as input signals.



*Referenceless pH measurement using OECT based Wheatstone bridge. (a) Layout of the sensing function and picture of the device. (b) Drawing of the pH evolution in the two wheatstone bridge chambers and differential pH and recorded output signal.*

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# Water-Gated Organic Field-Effect Transistors: Biosensing Applications

B. Piro[a], T.T.K. Nguyen[a,b], T.N. Nguyen[a,b], G. Anquetin[a], S. Reisberg[a], V. Noël[a], G. Mattana[a], J. Touzeau[a], F. Barbault[a], M.C. Pham[a]

[a] *Univ. Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS, 15 rue J-A de Baïf, 75205 Paris Cedex 13, France.* piro@univ-paris-diderot.fr

[b] *Department of Advanced Materials Science and Nanotechnology (AMSN), University of Science and Technology of Hanoï (USTH), Vietnam Academy of Science and Technology (VAST), 18 Hoang Quoc Viet, Nghĩa Đô, Cầu Giấy, Hanoi, Viet Nam.*

## Abstract:

In the field of organic transistors, Electrolyte-Gated OFETs have recently emerged, where the classical dielectric of an OFET is replaced by water. Polarization of the gate causes formation of an electrical double layer (EDL) at both the gate/water and semiconductor/water interfaces, causing accumulation of carriers in the semiconductor, thus a drain current ($I_D$) increase. Due to the extreme thinness of the EDLs, operating potentials are of a few hundreds of mV only. It is known, for classical OFETs, that $I_D$ depends on the dielectric capacitance. Interestingly, for a water-gated OFET, the overall capacitance depends on two interfaces: the organic semiconductor/water and the water/gate capacitances.

As a consequence, physicochemical processes occurring at the water/gate interface, such as changes in interfacial capacitance induced by molecular recognition of a target molecule onto an immobilized receptor, or accumulation of ions, can be transduced and, most importantly, amplified into a drain current variation. This paves the way for applications in the field of biosensors.

At first in this work, we will focus on different methods able to biofunctionalize the semiconductor interface, which is challenging because covalent or even non-covalent functionalization of semiconductors led to significant degradation of charge carriers' mobility. For applications such as immunosensing, we will show that gate modification is pertinent and that microelectrodes or even ultramicroelectrodes can gate such organic transistors. Two approaches of gate functionalization and two transduction mode will be illustrated, with practical examples such as selective detection of small organic molecules or even ions in water.

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# [4]Cyclo-9-ethyl-2,7-carbazole: Synthesis, characterization and application of a nanoring

Fabien Lucas,[a] Cassandre Quinton,[a] Emmanuel Jacques,[b] Joëlle Rault-Berthelot,[a] Cyril Poriel[a]
[a]*Univ Rennes, CNRS, ISCR - UMR 6226, F-35000 Rennes, France*
[b]*IETR, Département Microelectronique & Microcapteurs UMR CNRS 6264, F-35000, France*
*E-mail: fabien.lucas@univ-rennes1.fr ; website : https://iscr.univ-rennes1.fr/macse/people/students-and-postdocs/article/fabien-lucas*

## Abstract:

Since the first reported synthesis of a cycloparaphenylene (CPP) by R. Jasti *et al* in 2008,[1] many nanorings made of various units such as fluorene[2], naphthalene[3] or stilbene[4] have been synthesized and studied. This type of cyclic nanostructure arouses a large keen interest because of their unexpected properties. For example, in linear oligophenylenes, we observe a decreasing of the HOMO-LUMO gap while increasing the number of phenyl units, whereas the HOMO-LUMO gap of the CPPs increases with the size of the ring (and the number of phenyl units). Considering that linear organic semi-conductors are the molecular pillars which have allowed the development of organic electronics, investigating their cyclic counterparts appears as an exciting challenge. Thanks to its appealing properties (particularly its electron rich character), the carbazole fragment has been widely used in the design of functional materials for organics electronics and appears therefore as an interesting building unit to construct nanorings. The first examples of cyclocarbazoles have been reported by Yamago *et al* in 2016.[5] In these examples, nitrogen atoms were substituted with methyl and phenyl groups and this work mainly concerned the ring currents induced by the peculiar cyclic geometry. In this present work, we report an improved synthesis of a cyclocarbazole nanoring including four carbazole fragments possessing nitrogen atoms substituted with ethyl chains. The electrochemical, photophysical and their interplay will be detailed and rationalized thanks to molecular modelling. Thus a redox-fluorescent switch will be presented. Incorporation of [4]cyclo-9-ethyl-2,7-carbazole in an organic field-effect transistor (OFET) is finally presented. As organic devices based on nanorings are barely explored to date, this work shows that nanorings can be successfully introduced as an active layer in an OFET but also provides a first benchmark for nanorings.

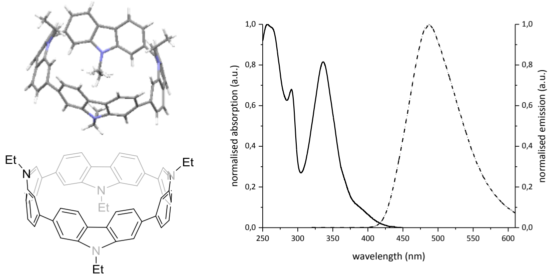

***Figure 1.*** *(left)* X-Ray crystal structure of [4]cyclo-9-ethyl-2,7-carbazole and (right) UV-Vis absorption (solid line) and emission (dashed line) at RT in cyclohexane

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# Air stability of p-doped organic semiconductors: can they be processed under ambient conditions?

Tamara Nunes Domschke,[a] Alexandre Pereira,[a] Raphael Clerc[b], Alexandre Carella [a] and Anass Benayad[a]

[a] *Univ. Grenoble Alpes, CEA-LITEN, Grenoble, 38000, France. Email:tamara.nunesdomschke@cea.fr*
[b]*Université de Lyon, UJM-Saint-Etienne, Laboratoire Hubert Curien, Saint-Etienne, 42100, France.*

## Abstract:

Chemical doping allows tuning the electrical and optoelectronic properties of organic semiconductors (OSC) and conductive polymers, offering a promising solution for improving the electrical contact quality of organic electronic devices. However, controlled and efficient doping of OSC by solution-processed methods remains challenging[1]. In addition, in order to be adapted for large-scale printing and patterning techniques, these doped layers should be stable to short periods of air exposure.

Depending on their energy levels, organic materials can undergo redox reactions with water and/or oxygen species from ambient air[2,3]. For example, it is well known that n-dopants are susceptible to suffer from immediate oxidation in air due to their low ionization energies (IE), compromising the air stability of n-doped OSCs [4]. In contrast, efficient p-dopants are supposed to be air-stable molecules thanks to their high IE (> 5eV), but the stability of p-doped OSCs has never been investigated in detail so far.

Here, we study the impact of the processing atmosphere (air vs. $N_2$) on the p-type doping of the low bandgap polymer poly[(4,8-bis-(2-ethylhexyloxy)-benzo(1,2-b:4,5-b')dithiophene)-2,6-diyl-alt-(4-(2-ethylhexanoyl)-thieno[3,4-b]thiophene-)-2-6-diyl) (PBDTTT-c) with the molecular dopant tris[1-(trifluoroethanoyl)-2-(trifluoromethyl)ethane-1,2-dithiolene] ($Mo(tfd\text{-}COCF_3)_3$). For p-doped layers prepared in inert atmosphere, the conductivity increased over six orders of magnitude.

First, we report on an anomalous thickness dependency of the conductivity observed for the air-processed layers, which increased over two orders of magnitude with the layer thickness (varied from 15 - 200nm). This behavior was not present in $N_2$-processed doped layers. Hence, air-processed PBDTTT-c: $Mo(tdf\text{-}COCF_3)_3$ layers showed a conductivity drop over time. Additional ageing experiments carried out under different atmospheres (nitrogen, anhydrous air, air) indicated that humidity plays a major role in the observed degradation mechanism.

In a second part, X-ray photoemission spectroscopy (XPS) allowed us to demonstrate that once in the p-doped system, $Mo(tdf\text{-}COCF_3)_3$ is prone to oxidation under ambient conditions. In conclusion, our results highlighted an unexpected air instability of thin p-doped layers, opening the field for future investigations.

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# High Thermoelectric Harvesting From Ionic Conductive Polymer

Byeonggwan Kim,[a,b,c] Jongbeom Na,[b] Hanwhuy Lim,[b] Younghoon Kim,[b] Jinbo Kim,[b] and Eunkyoung Kim*,[b]

[a]*UMI Building Blocks for Future Electronics, CNRS - Sorbonne Université - Yonsei University - Ewha Womans University, 50 Yonsei-ro Seodaemun-gu, Seoul, Korea.*
[b]*Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 03722, South Korea. Email: eunkim@yonsei.kr*
[c]*IPCM, UMR CNRS-Sorbonne Université 8232, 4 Place Jussieu, 75005 Paris, France.*

## Abstract:

Thermoelectric effect of conductive polymer films were explored by controlling the dopant content for poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS).[1-2] Highly doped conductive polymer films were synthesized in the presence of high molecular weight PSS under an optimized temperature and humidity. As prepared polymer films showed high Seebeck coefficient and ionic conductivity, which led high power factor of thermoelectric conversion. Simultaneously, it showed large electrochemical and thermal capacitance due to the mixed ionic carriers. Surprisingly, the thermal charging afforded a high thermal voltage and current output, reproducibly, to show thermocapacitive properties in the absence of external capacitors. This suggests that such proton transport in TE materials represent a new way to exceed the limitations of traditional TE harvesters, including electronic, ionic, or mixed ionic thermoelectric harvesters, and it could be useful for body-worn or hand-held electronics

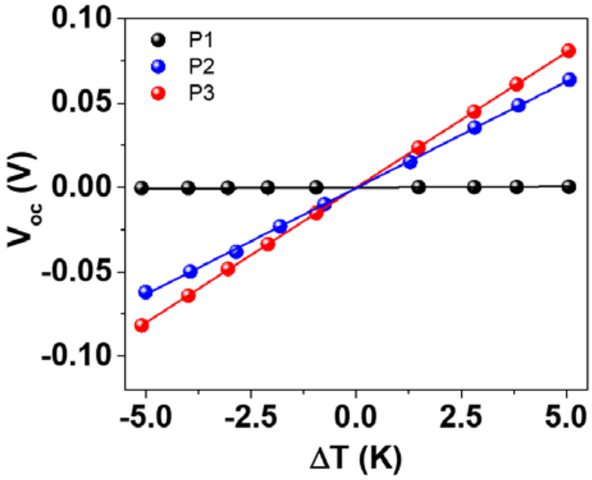


*Figure. Thermovoltage at different ΔT and 90% RH. The slope of the linear fitting to the data for the Seebeck coefficient.*

## References:

[1] D. Zhao, S. Fabiano, M. Berggren, X. Crispin, *Nat. Comm.*, 8, 14214 (2017).

[2] T. Park, C. Park, B. Kim, H. Shin, E. Kim, Energy Environ. Sci., 6, 788 (2013)

# Towards the fabrication of all-inkjet-printed, flexible Electrolyte-Gated Organic Field-Effect Transistors

Giorgio Mattana,[a] Marco José Olarte Lopez,[a] Justine Pallu,[b] Samia Mekhmoukhen,[a] Samia Zrig,[a] Benoît Piro,[a] Vincent Noël,[a]

*[a] Université Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS, 15 rue Jean-Antoine de Baïf, 75205 Paris Cedex 13, France*
*Email: giorgio.mattana@univ-paris-diderot.fr*
*[b] Université Paris Diderot, Sorbonne Paris Cité, LEM, UMR 7086 CNRS, 15 rue Jean-Antoine de Baïf, 75205 Paris Cedex 13, France*

Abstract:

Electrolyte-Gated Organic Field-Effect Transistors (EGOFETs) have recently attracted considerable attention. The very low biasing potentials (< 1 V) and the possibility of employing fast-response polymer electrolytes make EGOFETs ideal candidates for the next generation of electronic switches and amplifiers.[1] At the moment, the large majority of EGOFETs reported in the literature were fabricated on rigid substrates with extensive use of clean-room photolithographic processes.[2] These factors clearly limit the transistors portability and also considerably increase the cost per device. Surprisingly, the utilisation of the inkjet-printing (IP) technique for the fabrication of EGOFETs has received up to now little attention: no examples of fully inkjet-printed EGOFETs on flexible, plastic substrates have been described so far. In this communication, we report on the fabrication of fully inkjet-printed EGOFETs, realised on flexible, plastic substrates (namely Kapton®). The first part of the presentation will be devoted to the formulation and rheological characterisation of semiconducting inks, inkjet-printed on source and drain electrodes fabricated by means of photolithography on silicon wafers. After demonstrating the feasibility of printing the semiconducting layer (Fig. 1a), the second part of the talk will be focused on the inkjet-printing of the source, drain and gate electrodes, using an original, coplanar configuration where the three electrodes lie on the same plane (Fig. 1b). Inkjet-printed EGOFETs were electrically characterised in terms of output and transfer curves and the most important electrical figures of merits were extracted (Fig. 1c). Our results could pave the way for the fabrication of the next generation of low-cost, flexible and portable printed circuits and devices.

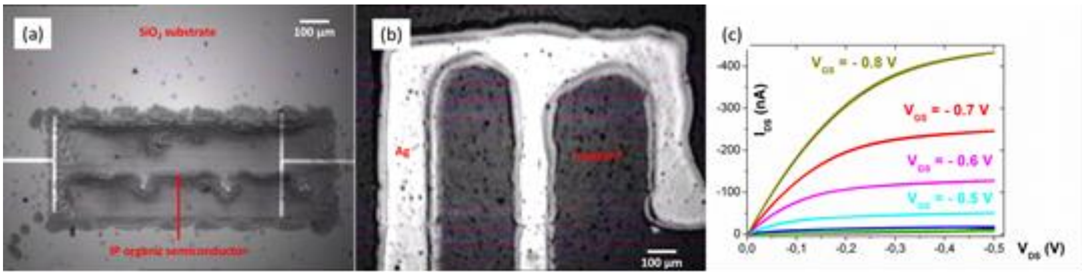


*Figure 1. (a) Inkjet-printed organic semiconductor; (b) detail of inkjet-printed electrodes on Kapton; (c) output curves of the transistor shown in (a).*

References:

[1] D. H. Kim et al, Adv. Mater. 25, 1822 (2013).

[2] L. Kergoat et al, Anal. Bioanal. Chem. 402, 1813 (2012).

# Characterization of Memristor Behavior based on $TiO_2/TiO_{2-x}$ Layers

Han-Sang Kim[1], Fei Shan[1], Zi-Tong Ao[1], Hong-Bo Guo[1], Jae-Yun Lee[1], Eundo Kim[2],

Geunho Kim[2] and Sung-Jin Kim[1,*]

[1]*College of Electrical and Computer Engineering, Chungbuk National University, Cheongju 28644, Korea*
[2] *The one science, Asan, 31466, Korea*
*Email: ksj@cbnu.ac.k*

## Abstract:

For several decades the size of transistors has been continuously decreasing as a result of advances in digital electronics as expressed by Moore's Law, and innovation has ultimately pushed CMOS technology to the 12-nm feature width that presently exists [1,2]. In this work, we have investigated the effect of the thickness of the oxide active layers with device architecture of Al (top electrode)/ $TiO_2/TiO_{2-x}$/ heavily doped bottom electrode for the behavior of memristor. $TiO_2$ insulating thin film was deposited using ALD system and $TiO_{2-x}$ active layers were deposited at 5 nm, 10 nm, and 15 nm by an RF sputtering system. When the electrical characteristics of the memristor were observed, the memristor based 10 nm thick active layer is exhibited the most complete hysteresis curve at the I-V curve applied -3 to 3 V. A As the surface with 10 nm thickness was analyzed with atomic force microscopy, it is noted that the roughness was small and the grain boundary was clear. In addition, the electrical characteristics of nonvolatile memory were confirmed by measuring the retention stability.

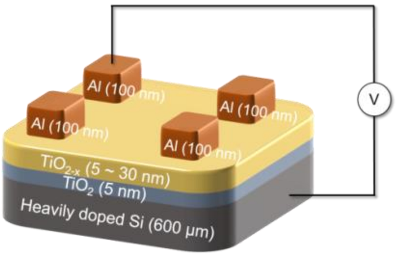


*Fig. 1 Schematic representation of $TiO_{2-x}/TiO_x$ based memristor device.*

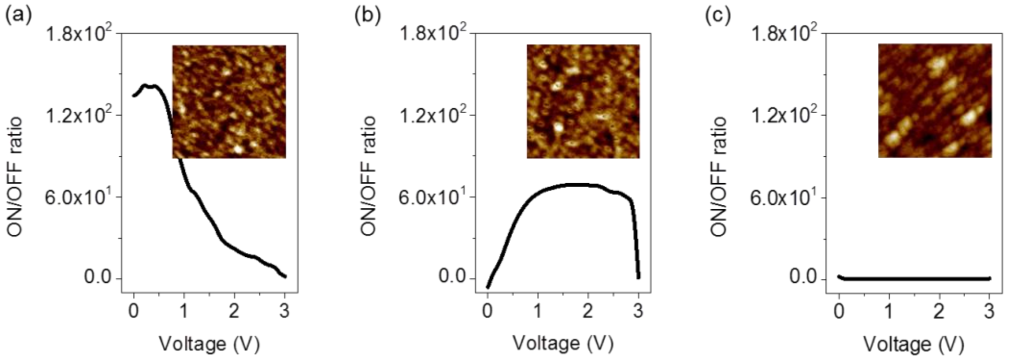


*Fig. 2 ON/OFF ratio and AFM image of the memristor with $TiO_{2-x}$ layers of (a) 5 nm, (b) 10 nm, and (c) 15 nm.*

## References:

[1] N. H. E. Weste and K. Eshraghian, Principles of CMOS VLSI Design: A Systems Perspective, Addison-Wesley, Reading, MA, USA (1992).
[2] D. B. Strukov, G. S. Snider, D. R. Stewart, and R. S. Williams,Nature 453, 80 (2008).

# Multi-Layer Stacked Indium Zinc Oxide Thin-Film Transistors with Femtosecond Laser Post-Annealing Treatment

Zi-Tong Ao, Fei Shan, Han-Sang Kim, Hong-Bo Guo, Jae-Yun Lee and Sung-Jin Kim*

*College of Electrical and Computer Engineering, Chungbuk National University, Cheongju 28644, Korea*
*Email: ksj@cbnu.ac.kr*

## Abstract:

Post-annealing process is a reliable and effective treatment in active film fabrication, it has greatly affected on surface shape and roughness of indium zinc oxide (IZO) thin-film and low surface roughness may improve the electrical properties of thin-film transistors (TFTs) [1,2]. In this research, the three-layer active film stack IZO TFTs with femtosecond laser post-annealing process treatment, so as to investigate of the post-annealing treatment with femtosecond laser of multi-layer active film stack IZO TFTs on the electronic properties. The multi-stacked IZO TFT exhibited field-effect mobility of approximately 5 cm$^2$/Vs and current on/off ratio of approximately 2 × 10$^6$, especially the electrical performance after 14 days still maintains a decent status with field-effect mobility of approximately 4 cm$^2$/Vs and current on/off ratio of approximately 2 × 10$^4$. The experimental results of electrical properties show that the voltage gain, switching response and electrical properties of IZO TFTs with femtosecond laser post-annealing treatment were significant improved. In particular, the TFTs with post-annealing process treatment by femtosecond laser for 100 s has good stability and still maintains good electrical properties after several weeks.

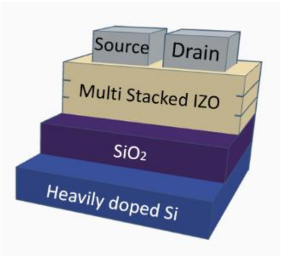


*Fig. 1 Schematic representation of the three-layer active film stack IZO TFTs structure*

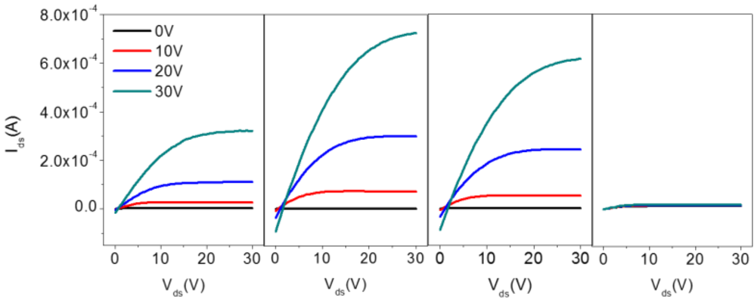


*Fig. 2 Output characteristic curves of IZO TFTs after 0 s, 50 s, 100 s, and 200 s femtosecond laser post-annealing process treatment.*

## References:

[1] Z. B. Fang, Z. J. Yan, Y. S. Tan, X. Q. Liu and Y. Y. Wang, Applied Surface Science 241 (3), 303 (2005).

[2] Y. Hwan Hwang, J.-S. Seo, J. Moon Yun, H. Park, S. Yang, S.-H. Ko Park and B.-S. Bae, Npg Asia Materials 5, e45 (2013).

# Comprehensive Analysis of Indium Zinc Oxide Thin Film Transistor with Multi-layers Active Film Stack Structure

Hong-Bo Guo, Fei Shan, Zi-Tong Ao, Han-Sang Kim, Jae-Yun Lee and Sung-Jin Kim*

*College of Electrical and Computer Engineering, Chungbuk National University, Cheongju 28644, Korea*
*Email: ksj@cbnu.ac.kr*

## Abstract:

Indium zinc oxide (IZO) thin film transistor (TFT) has the advantages of exceptional field-effect mobility, large on–off current ratio ($I_{on}/I_{off}$), exceptional uniformity, excellent light transmittance and outstanding electrical stability [1]. In recent years, it has been used more in fabrication process of the Thin Film Transistor. With continuous development, the IZO TFT with multi stack active layer structure is detected decent electronic performance than single active layer TFT [2]. Multi-IZO-layer is proposed as a new active film stack structure for more optimized electrical performance of IZO TFTs. The surface roughness of thin film formed by multi-IZO-layer was measured by using Atomic Force Microscope (AFM), giving a low root-mean-square (RMS) roughness of 0.465 nm. Compared with the single layer (RMS = 0.695 nm), it has smaller folds and a smoother surface. The results show that the multi active layer TFT is higher than singgle active layer TFT as shown in field-effect mobility of 7.75 ± 0.2 $cm^2/V \cdot s$, threshold voltage($V_{th}$) is 0.35 ± 0.42V, and light transmittance stable at more than 85 percent. Consequently, the electrical characteristics are improved by multi-layers active film stack structure of IZO TFTs, and the multi-IZO-layer is a promising sturcture for next-generation semiconductor devices that simultaneously can improve electrical characteristics and stability.

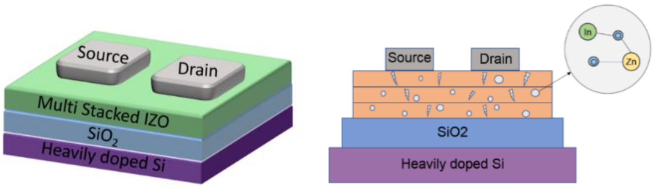


*Fig. 1 Schematic representation of Multi Stacked Structure IZO TFT.*

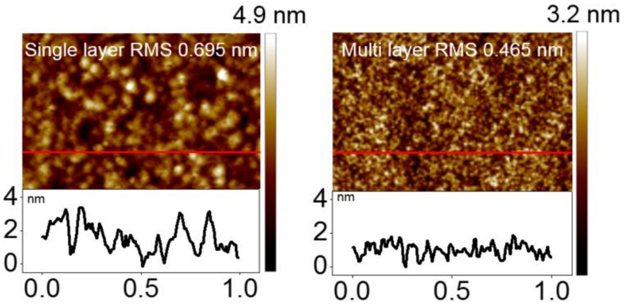


*Fig. 2 (Color online) AFM topographies and cross sections for single layer and multi layer thin film.*

## References:

[1] H. Xu, L. Lan, M. Xu, J. Zou, L. Wang, D. Wang, and J. Peng, “High performance indium–zinc-oxide thin-film transistors fabricated with a backchannel-etch-technique,” Appl. Phys. Lett., vol. 99, no. 25, 2011, p. 253 501.

[2] I. Baek, D. Kim, M. Lee, H.-J. Kim, E. Yim, M. Lee, J. Lee, S. Ahn, J. Seo, S. Lee, J. Park, Y. Cha, S. Park, H. Kim, I. Yoo, U. Chung, J. Moon, and B. Ryu, “Multi-layer cross-point binary oxide resistive memory (OxRRAM) for post-NAND storage application,” in IEDM Tech. Dig., 2005, pp. 750–753.

# New high triplet energy 2,7-dimethoxycarbazole-based materials for blue organic light-emitting diodes

Audrius Bucinskas[a], Dmytro Volyniuk[a], Oleksandr Bezvykonnyi[a], Juozas Vidas Grazulevicius[a]

[a]*Department of Polymer Chemistry and Technology, Kaunas University of Technology, Kaunas, Lithuania*
*Email:audrius.bucinskas@ktu.lt, web site: http://www.ktu.edu/*

## Abstract:

Nowadays organic light emitting diodes (OLED) are gaining more popularity in the global market as an alternative for LED. The use of thermally activated delayed fluorescence (TADF) is a promising approach to efficient blue electroluminescence. Improving the performance of blue organic light-emitting diodes electrochemically and thermally stable materials are needed, as well.

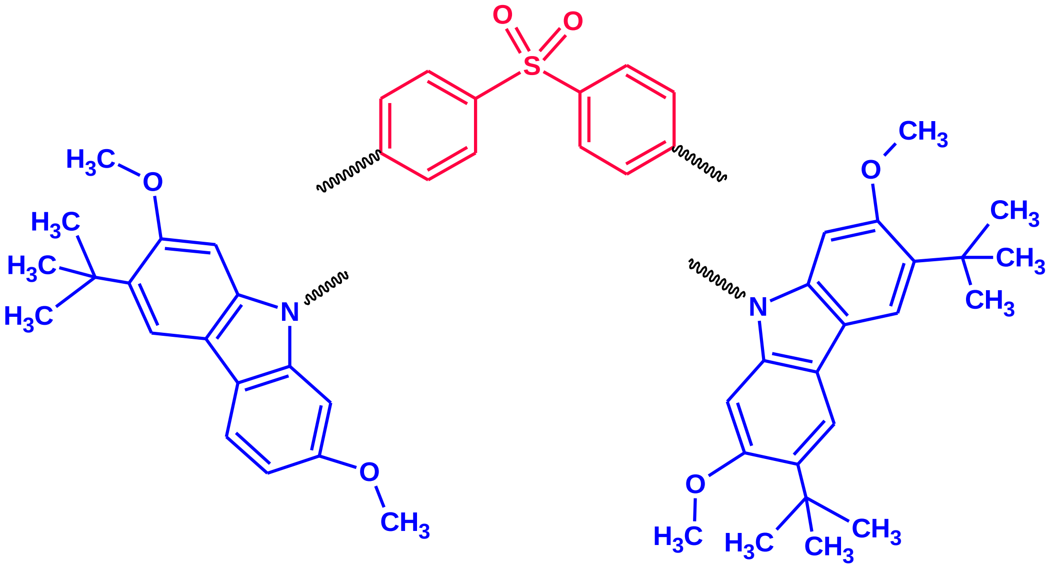


*Figure 1. New high triplet energy materials for OLEDs*

Since Adachi et al. [1] synthesized D-A-D emitters for efficient blue TADF OLEDs based on carbazole and diphenylsulfone, in our work, we designed and synthesized various new compounds using newly designed carbazole moieties, such as 2,7-dimethoxy-3,6-di-tert-butylcarbazole and 2,7-dimethoxy-3-tert-butylcarbazole (Fig.1). It is known that 2,7-substituted derivatives of carbazole show irreversible oxidation. [2] Therefore, we introduced tert-butyl groups to obtain higher thermal and electrochemical stability. All compounds have been investigated using density functional theory and the comparative experimental study was performed Due to very small theoretical/experimental singlet-triplet energy splitting (~0.1-0.2 eV) new D-A-D molecules were analyzed as potential candidates for thermally activated delayed fluorescent effect.

## References:

1. Wu, S. et al. J. Mater. Chem. C. 2014, 2(3), 421.
2. J. Qu et al. Polymer, 2007, 48, 4628.

T3 - 2

# Quinoline and carbazole based materials for non-doped white OLEDs

Galyna Sych [a], Oleksandr Bezvikonnyi [a], Dmytro Volyniuk [a] and Juozas Vidas Grazulevicius [a]

[a] *Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilenu pl. 19, LT-50254, Kaunas, Lithuania; E-mail: sych.galyna@gmail.com*

## Abstract:

Bipolar conjugated molecules with donor-acceptor architecture are of great interest of scientists due to its wide potential application in optoelectronic devices. A significant interest has focused on development of white organic light emitting diodes (WOLEDs), as possible low-cost, highly efficient alternatives for back-lights in flat panel displays [1]. Tunable combination of two or three exciplex systems affords simple way to obtain efficient white light emission [2].

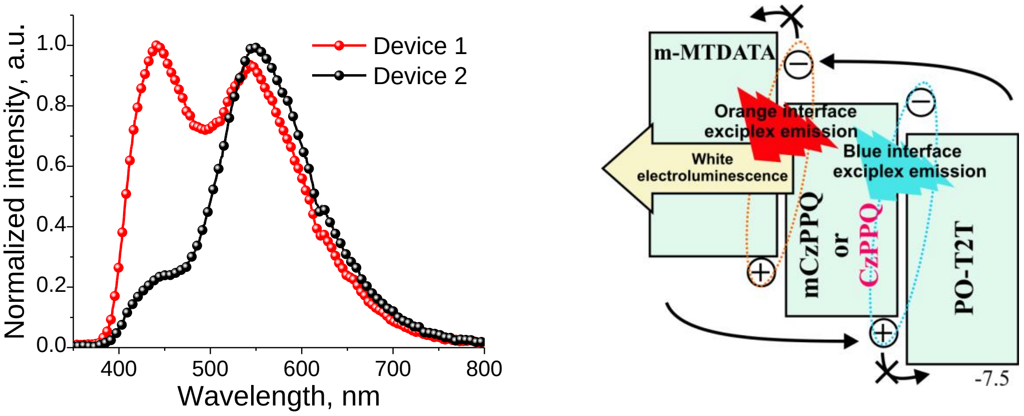


*Fig. Electroluminescence Spectrum of the devices*

We designed and synthesized donor-acceptor bipolar molecules based on carbazole and quinoline moieties, which behave as acceptor (A) or donor (D) respectively. The synthesized materials CzPPQ and mCzPPQ demonstrate maximum fluorescence intensity at 417 nm and 413 nm in the solid state, and 396 and 402 nm in the toluene solution with fluorescence quantum efficiency of 67%, 8%, respectively. Investigated molecules pCzPQ and mCzPQ showing bipolar nature and form blue excited complexes (464 nm and 458 nm) with 2,4,6-tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazine (PO-T2T) acceptor and orange (551 nm and 546 nm) with 4,4′,4′′-tris[3-methylphenyl(phenyl)amino]-triphenylamine (m-MTDATA) donor. White organic devices comprised of two interface exciplexes m-MTDATA : mCzPPQ (orange exciplex) and mCzPPQ : PO-T2T(blue exciplex) in the three-layers sandwich-type OLED allowed us to obtain warm-white electroluminescence. Fabricated and optimized white non-doped devices with the structure consisting of m-MTDATA/ orange exciplex/mCzPPQ/blue exciplex/PO-T2T light-emitting system demonstrated white electroluminescence with a high colour rendering index of 76 and colour temperature of 8400 K and maximum external quantum efficiency of 3.15 %.

## References:

1. Goushi K., Adachi C. Appl. Phys. Lett., 2012, 101, 023306.
2. Hung W., Fang G., Lin S., Cheng S., Wong K., Kuo T., Chou P., Sci. Rep., 2014, 4, 5161.

# Diphenylsulfones *para*-substituted by diverse electron-donating fragments as TADF emitters

Dalius Gudeika,[a,b] Dmytro Volyniuk,[a] Martins Rutkis,[b] Juozas V. Grazuleviciusa[a]

[a]*Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilėnų pl. 19, LT-50254 Kaunas, Lithuania.*
[b]*Institute of Solid State Physics, University of Latvia, 8 Kengaraga St., Riga LV-1063, Latvia.*
*Email: dalgude@ktu.lt.*

## Abstract:

Thermally activated delayed fluorescence (TADF) [1] is shown by organic molecules due to the reverse intersystem crossing from triplet excited to singlet excited states caused by the thermal motion of atoms and the following charge transfer emission [2]. This approach allows to employ triplet excitons by converting them to singlet excitons for luminescence and overcome spin statistical 25% limit of internal quantum efficiency of organic light emitting diodes (OLEDs). Employment of TADF emitters for the fabrication of OLEDs became widespread in recent years due to the possibility of replacing high-cost phosphorescent emitters based on rare metals. In 2012 Adachi *et al* [3] reported on the first class of deep-blue TADF emitters designed using diphenylsulfone moiety as an acceptor. The advantage of this type of acceptor moiety is in tetrahedral geometry of sulfonyl group which helps to avoid conjugation in the compound thus leading to strong intramolecular charge transfer. In addition, diphenylsulfone moiety has electron-withdrawing properties caused by significant electronegativity of oxygen atoms [4]. We synthesized and characterized a series of new donor-acceptor-donor type diphenylsulfone-based TADF materials and studied them in host-guest systems in order to test the optimized systems in OLEDs. The optical, thermal, electrochemical and photoelectrical properties of the synthesized compounds have been investigated. All the compounds were found to be capabale to form glasses with glass transition temperatures ranging from 68 to 162 °C. They exhibited high thermal stabilities, with 5% weight loss temperatures exceeding 433 °C. Ionization potentials of the solid samples were ranged from 5.03 to 5.74 eV. The charge-transporting properties of the synthesized materials were studied by time-of-flight method. Some of the synthesized compounds exhibit ambipolar charge transport properties. These compounds were tested as emissive species for the fabrication of OLEDs.

Acknowledgment: This research was supported by the the ERDF PostDoc project No. 1.1.1.2/VIAA/1/16/177.

## References:

[1] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, Nature 492 (2012) 234-238.

[2] K.K. Rohatgi-Mukherjee, New Delhi, India: Wiley Eastern Limited, 1978, p. 105.

[3] Q. Zhang, J. LI, K. Shizu, S. Huang, S. Hirata, H. Miyazaki, C. Adachi, J. Am. Chem. Soc. 134 (2012) 14706-14709.

[4] Z. Yang, Z. Mao, Z. Xie, Y. Zhang, S. Liu, J. Zhao, J. Xu, Z. Chi, M. P. Aldred, Chem. Soc. Rev. 46 (2017) 915-1016.

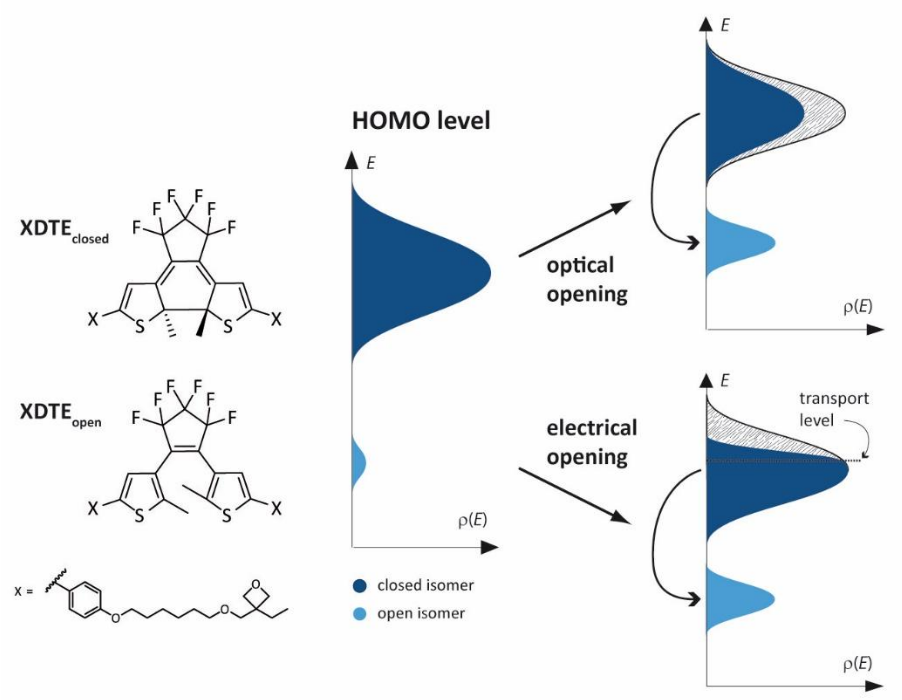
# Influence of trapping effects on organic memory devices

Ulli von Goscinski,[a] Kavita Singh Ghotra,[a] Maxim Kempf,[a] Klaus Meerholz [a]

[a] *University of Cologne, Institute of Physical Chemistry,*
*Luxemburger Str. 116, 50939 Cologne, Germany*
*E-mail: klaus.meerholz@uni-koeln.de*

## Abstract:

Organic memory devices (OMEMs) are realized by integrating a layer of the crosslinkable dithienylethene XDTE in a solution-based multilayer OLED stack. The photochromic XDTE molecule can be switched reversibly by a photo- and/or electrically induced ring-opening/-closing reaction to two thermally stable states featuring different physical properties.[1] The change in the energy level positions, which is responsible for controlling the hole injection by shifting the hole injection barrier,[2] enables a high ON/OFF ratio approaching $10^6$. For future application as data storage element, electrically induced switching is of great importance, but the charge trapping landscape is affected by this switching mechanism. By incremental switching via current densities pulses, intermediate switching states are accessible.[3] The current-response is analysed as a function of the fraction of closed isomer obtained via in-situ reflectance absorption spectra. In combination with impedance spectroscopy measurements, we study the role of trapping effects in this energetically anisotropic switching process.



*Energetic difference of the photo- and electrically induced opening process of XDTE based OMEMs*

## References:

[1] Zacharias, P. et al. “Photoprogrammable Organic Light-Emitting Diodes”, *Angew. Chemie - Int. Ed.* 48, 4038–4041 (2009).

[2] Shallcross, R. C. et al. “Photochromic Transduction Layers in Organic Memory Elements”, *Adv. Mater.* 25, 469–476 (2013).

[3] Körner, P. O., et al. „Optical and electrical multilevel storage in organic memory passive matrix arrays”, *Org. Electron.* 15, 3688–3693 (2014).

# Fabrication of a nanogap light-emitting electrochemical cell

Yoshinari Takenouchi,[a] Yutaka Noguchi,[a]
[a]*School of Science & Technology, Meiji Univ., Kawasaki, Japan. Email: ce171042@meiji.ac.jp*

## Abstract:

Electrically driven single-molecule light-emitting devices are expected to be applied to new single molecular electronics devices and single-photon sources. However, it is generally difficult to fabricate a single molecular junction between fixed electrodes and realize bipolar charge injection from a nanogap electrode which consists of same metals to the molecule. In this study, we propose a nanogap light-emitting electrochemical cell (LEC) [1], that is to be a new single-molecule light-emitting device without using single-molecular junctions. In LECs, due to the motion of the electrolyte mixed in the light-emitting polymer, highly efficient bipolar charge injection and light emission occur regardless of the work function of the electrodes and interelectrodes distance. We fabricated a LEC by using a mixed film of light-emitting polymer (F8BT) and ionic liquid ($P_{66614}$-TFSA) between nanogap electrodes and observed an electrically driven light-emission.

A gold electrode pattern was drawn on the $SiO_2$ substrate by a conventional electron beam lithography technique, and it was immersed in Octadecyltrichlorosilan (OTS) solution (1 mM, dehydrated cyclohexane solvent) for 24 hours to control the deposition pattern of the organic film. The nanogap electrode was then formed by the electromigration method. F8BT and $P_{66614}$-TFSA were mixed at a weight ratio of 4 : 1 and spin-coated (3000 rpm) on the substrate. The device characteristics were measured at a room temperature under the atmosphere. Fig. 1 shows the AFM image of the device. The organic film is formed only on the electrodes and nanogap owing to the OTS surface treatment on $SiO_2$. Therefore, the electrically-driven light-emission is expected to occur at the nanogap electrode. Fig.2(a) and 2(b) shows current-time and luminescence intensity-time characteristics of the nanogap LEC, respectively. A constant voltage of 10 V was applied after 20 s. Spike like current and light emission were simultaneously observed, indicating that the current-driven light-emission occurred.

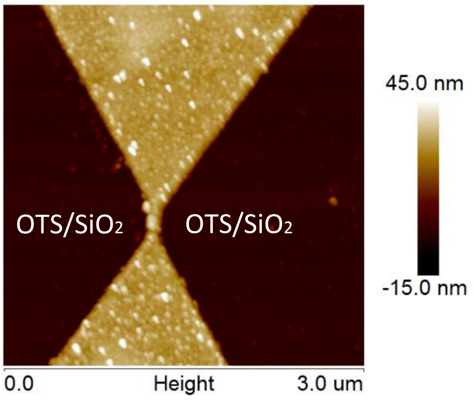


*Fig.1 AFM image of the nanogap LEC.*

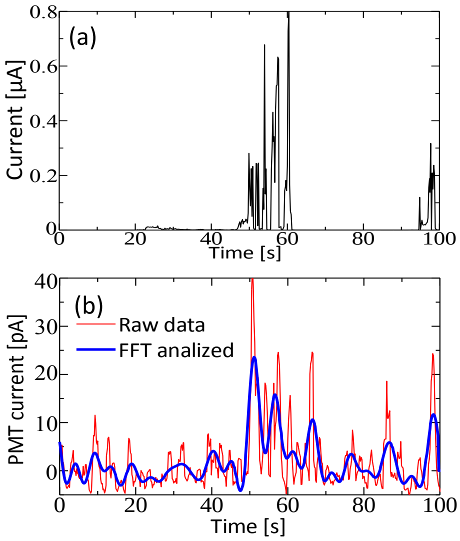


*Fig.2 Current-time (a) and photomultiplier tube (PMT) current-time (b) characteristics of the nanogap LEC.*

## References:

[1]Q. Pei et al., Science 269, 1086 (1995).

# A Comprehensive Study of Structurally Engineered Double-layer Memristors

Fei Shan, Zi-Tong Ao, Han-Sang Kim, Hong-Bo Guo, Jae-Yun Lee and Sung-Jin Kim*

*College of Electrical and Computer Engineering, Chungbuk National University, Cheongju 28644, Korea*
*Email: ksj@cbnu.ac.kr*

## Abstract:

The memristor is believed to be the fourth two-terminal fundamental passive element, and a memristor model was successfully developed by Hewlett-Packard scientists in 2008 on the basis of the original theoretical framework of the memristor, which was published by Leon Chua in 1970 [1]. We demonstrate the fabrication of a memristor device based on Al/$TiO_2$/$TiO_x$/Al/$TiO_x$/$TiO_2$/Al double-layer structure. $TiO_2$ thin film was deposited using an atomic layer deposition technique, and the $TiO_x$ thin film was coated on the $TiO_2$ layer with radio frequency magnetic sputter technology. The Al/$TiO_2$/$TiO_x$/Al/$TiO_x$/$TiO_2$/Al double-layer memristors will be able to make nanoscale switching capability to change their resistance state between high and low as a switching device within crossbar arrays and showing a forming-free resistance switching behavior [2]. The crossbar arrays structure is observed to affect the switching mechanism in the memristor device. The research presented here can provide a new memristor structure for exploring the possibility of a high-performance memristor device for electronic applications.

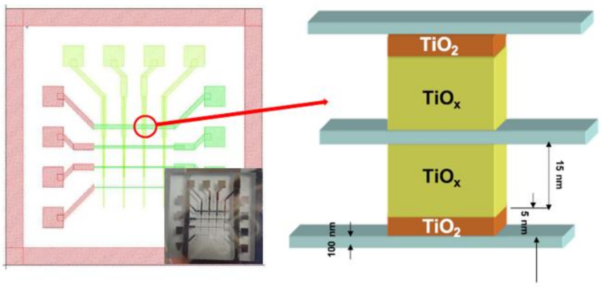


*Fig. 1 Schematic representation of $TiO_2$/$TiO_x$ based memristor device.*

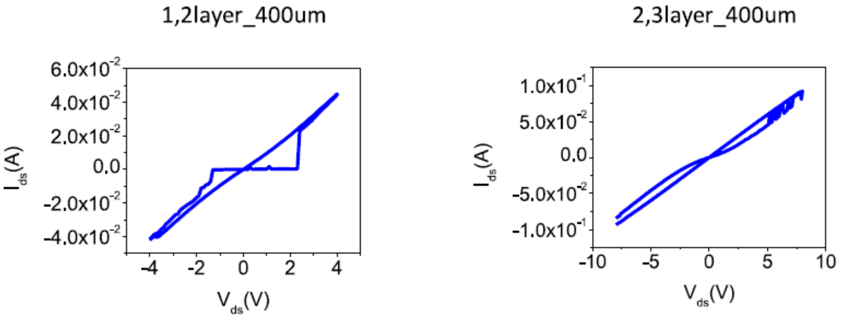


*Fig. 2 Switching I-V curves of the double-layer memristor with 1-2 layer and 2-3layer, respectively.*

## References:

[1] L. O. Chua, “The missing circuit element,” IEEE Trans. Circuit Theory, vol. 18, no. 5, pp. 507-519, Sep. 1971.

[2] K. D. Liang et al., “Single $CuO_x$ nanowire memristor: forming-free resistive switching behavior,” ACS Appl. Mater. Interfaces, vol. 6, no. 19, pp. 16537-16544, Aug. 2014.

# Control of molecular orientation in diindenoperylene films by underlying few-layer $MoS_2$ substrate

Nada Mrkyvkova,[a] Jakub Hagara,[a] Peter Nádaždy,[a] Ashin Shaji,[a] Peter Siffalovic,[a]
Matej Jergel,[a] Eva Majková,[a] Peter Hutár,[b] Michaela Sojková,[b] Martin Hulman,[b]
Martin Hodas,[c] Frank Schreiber,[c]

*[a]Institute of Physics, Slovak Academy of Sciences, Bratislava (Slovakia).*
*Email:nada.mrkyvkova@gmail.com*
*[b]Institute of Electrical Engineering, Slovak Academy of Sciences, Bratislava (Slovakia).*
*[c]Institute of Applied Physics, University of Tübingen, Tübingen (Germany)*

## Abstract:

Recently developed one-zone sulfurization technique [1] enables fabrication of uniform, large-area few-layer $MoS_2$ films with a high degree of crystallinity. In this contribution, we show that the crystallographic orientation of $MoS_2$ *c*-axis is directly influenced by the layer thickness and/or sulfurization temperature. To be more specific, the *c*-axis varies from the *out-of-plane* to *in-plane* orientation for samples with the $MoS_2$ thickness of 3 and 9 nm, respectively. Furthermore, we found out that the *c*-axis orientation subsequently controls the orientation of small organic molecules, such as diindenoperylene (DIP), grown on the top of $MoS_2$ layer. Employing the grazing-incidence wide-angle X-ray scattering (GIWAXS), we observed that the DIP molecules are oriented in the *lying-down* configuration when the *c*-axis is normal to the substrate plane and adopt the *standing-up* orientation when the *c*-axis is oriented parallel to the substrate plane, see Figure 1. To the best of our knowledge, the molecular orientation was so far manipulated exclusively by selecting an appropriate substrate [2], but a different molecular orientation on the same kind of substrate was not observed up to now. This result has direct implications for a tailored preparation of small-molecule organic films for diverse applications in (opto)electronics.

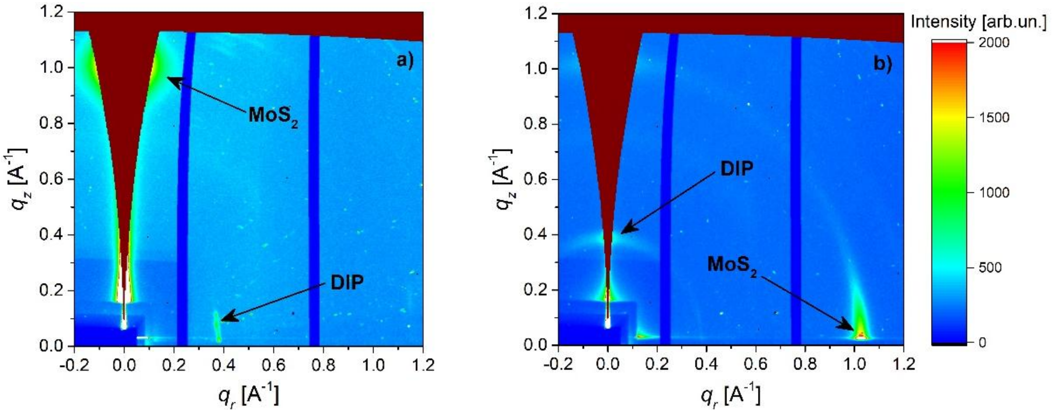


*Figure 1 : Reciprocal space map shows 002 diffraction peak, coming from the $MoS_2$ layer with a thickness of a) 3 nm and b) 9 nm, and 001 reflection of the 13 nm thick layer of DIP.*

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# Through-space charge-transfer of carbazole-imide derivatives resulting in aggregation enhanced and thermally activated delayed fluorescence.

Dmytro Volyniuk[a], Yan Danyliv[a], Iryna Hladka[a], Oleksandr Bezvikonnyi[a], Juozas V. Grazulevicius[a]
[a]*Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilenu rd. 19, LT-50254, Kaunas, Lithuania. Email: dvolynyuk@gmail.com*

Abstract:

All-organic emitters exhibiting thermally activated delayed fluorescence (TADF) have great potential for applications in organic light-emitting diode (OLEDs) since they allow harvesting of both singlets and triplets generated under electrical excitation [1]. Using TADF materials, 100% transformation of electricity to light can be achieved. High photoluminescence quantum yields (PLQY) and small singlet-triplet energy splittings ($\Delta E_{ST}$) of TADF emitters have to be obtained which are not trivial tasks.

Aiming to maximize PLQY and minimize $\Delta E_{ST}$ of TADF emitters, we designed and synthesized two carbazole-imide derivatives in which chromophores are linked via spacer. Such molecular design can allow to separate electrons and holes on two different donor and acceptor units which results in extremely low $\Delta E_{ST}$ values. It was shown by time dependent density functional theory (TD-DFT) calculations that HOMOs of the compounds are mainly located on the electron-donating carbazole moieties while LUMOs are located on the electron-deficient imide fragments. The molecules were found to be twisted with calculated torsion angle close to 75° in the ground state, which usually leads to small $\Delta E_{ST}$. The results of single crystal X-Ray analysis revealed that torsion angles for one carbazole-imide derivative between carbazole and benzene ring planes was 69° while carbazole plane and benzene ring plane formed angle of 86°. Additionally, N-C interatomic distance was estimated to be 3.227 Å and this distance was found to be less than the sum of the van der Waals radii of C and N (3.25 Å) which usually leads to $n \rightarrow \pi^*$ interaction between carbon atom of carbonyl group and nitrogen atom of carbazole. For the solid sample PLQY value of 20% was observed. The emission enhancement can apparently be explained by the restriction of intramolecular rotations without the planarization of the molecular structure. To investigate the nature of charge transfer in the studied molecules, photoluminesce (PL) spectra and PL decays of the derivatives dispersed in ZEONEX matrix were recorded. The obtained results show intramolecular nature of the through-space charge transfer resulting in TADF. TADF properties of the studied molecules were additionally characterized by steady-state and time resolved measurments at different temperatures. Using the developed emitters, The best greenish-blue OLED fabricated using the developed emitters exhibited maximum current, power and external quantum efficiencies of ca. 6.7 cd/m$^2$, 4 lm/W and 2.3 %, respectively, without out-coupling.

Acknowledgements

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# Exciplex-based approache for highly efficient organic light-emitting devices

Juozas V. Grazulevicius[a], Galyna Sych[a], Oleksandr Bezvikonnyi[a], Dmytro Volyniuk[a], Ausra Tomkeviciene[a], Gintare Grybauskaite-Kaminskiene,[a] Khrystyna Ivaniuk [b], Pavlo Stakhira [b]

[a]*Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilenu rd. 19, LT-50254, Kaunas, Lithuania. Email: juozas.grazulevicius@ktu.lt*

[b]*Lviv Polytechnic National University, S. Bandera 12, 79013 Lviv, Ukraine.*

## Abstract:

Organic exciplex-based systems that display thermally activated delayed fluorescence (TADF) are widely used in highly efficient organic light-emitting diodes (OLEDs) [1]. Since electrons and holes are positioned on two different molecules, in exciplex-based systems small singlet-triplet splitting ($\Delta E_{ST}$~0–0.03 eV) can be realized much easier than in single TADF molecules. TADF contribution in exciplex-based OLEDs can be maximized and theoretical internal quantum efficiency of 100% can be achieved [1].

In this presentation, several approaches of application of exciplex-forming systems in high-efficiency oleds exhibiting TADF will be demonstrated. Interface exciplex host, was applied for optimization and enhancement of performance of non-doped OLEDs based on new emitters showing aggregation induced emission enhancement (AIEE) [2]. The color-tunable OLEDs with the minimal number of the functional layers were designed and fabrocated [3]. The voltage-dependent green-blue electrofluorescence was obtained due to unique physical properties of the new ambipolar fluorophore 3,6-di(4,4'-dimethoxydiphenylaminyl)-9-(1-naphthyl)carbazole. Electroluminescence spectrum of the devices contained the blue fluorescence band, strong interface exciplex emission band with the emission maximum at ca. 540 nm, and voltage-dependent electroplex emission bands in the region of 550-650 nm [3]. OLEDs based on carbazole and tetraphenylethylene derivatives exhibiting emission from both excitons and exciplexes based on aggregation-induced emission were designed fabricated and charaterized [4]. Extremely efficient warm-white OLEDs with harmless for the human eyes electroluminescence spectra designed [5]. In the designed OLEDs, sky-blue TADF of a carbazole derivative is combined with the yellow-orange exciplex emission of this derivative and a commercial donor material. The best device demonstrated very high brightness of 40900 Cd/m$^2$ (at 15 V), current efficiency of 53.8 Cd/A, power efficiency of 19.3 lm/W. Eexternal quantum efficiency of the device reached 18.8 %.

## Acknowledgements

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# Could we improve the stability and the luminescence of copper (I) diimine complexes by a new chemical design of the phenantrolines?

Léa Gimeno, Errol Blart, Yann Pellegrin,

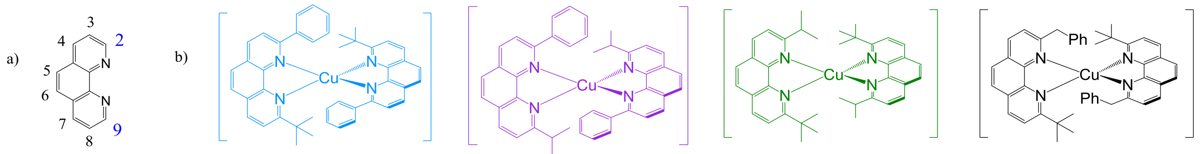
*Nantes University, 2 Chemin de la Houssinière, France.*
*Email: lea.gimeno@univ-nantes.fr*

## Abstract:

Copper(I) complexes $CuL_2^+$ where L is a diimine ligand are low cost and non-toxic species, which are well known for their interesting photo-physical properties. Our main interest concerning these complexes is the luminescence, that is mainly ruled by the steric hindrance at positions 2 and 9 of the phenanthroline (figure 1a). The bulkier the substituent, the more the luminescence quantum yield is notable because non-radiative deactivation pathways are disfavored. We can quote for example $[Cu(dsbtmp)_2]^+$ (dsdtmp=2,9-di(sec-butyl)-3,4,7,8-tetramethyl-1,10-phenantroline)[1,2] whose high quantum yield, about 6.3% with a lifetime of 2.8 µs were demonstrated by Castellano et al.. However, one of the major issues of these molecules is their stability. In the same way that steric hindrance in positions 2 and 9 of phenanthroline increases luminescence, it also increases the instability of the complexes. Burstyn et al. have demonstrated with Bis(2,9-di-tert-butyl-1,10-phenanthroline)copper(I) complex[3,4] that really impressive photophysical performances could be reached by using tert-butyl substituents in positions 2 and 9 of phenanthroline, but the former complex proved very unstable because of the huge steric strain imposed by tert-butyl groups.

**Could we improve the stability and the luminescence of copper (I) diimine complexes by a new chemical design of the phenanthrolines**?

In order to solve this problem, we imagine a new chemical engineering for phenanthrolines, namely substituting position 2 by a bulky aliphatic group (to promote luminescence) and position 9 by an aromatic group (to stabilize the coordination sphere). Thus, we designed three new ligands (1), (2) and (4) composed of one aromatic stabilizing group able to do π-staking with vicinal phenanthroline ligands in the copper(I) complex and one bulky ramified alkyl group. We studied the impact of the latter (using both iPr and tBu) as well as the effect of a spacer between phenanthroline and the aromatic ring ($CH_2$ vs. direct bonding). This presentation will focus on the synthesis, photophysical characterizations and stability study of this family of four copper(I) complexes with asymmetric phenanthrolines ligands.



(1) (2) (3) (4)

*Figure 1: a) Phenanthrolines numbering b) Family of copper(I) complexes.*

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# Carbazole-based hole transporting material for efficient and stable perovskite solar cell

Fatima Al-zohbi,[a] Youssef Jouane,[b] Nicolas Berton,[a] François Tran-van,[a] Johann Bouclé,[b] Bruno Schmaltz[a]

*[a]Laboratoire de Physico-Chimie des Matériaux et des Electrolytes pour l'Energie (EA 6299), Université de Tours, Parc de Grandmont 37200 Tours, France*

*[b]XLIM UMR 7252, Université de Limoges/CNRS, Faculté des Sciences et Techniques de Limoges, Limoges, France*

## Abstract:

The organometal halide perovskite solar cell (PSC) is currently widely studied due to its good photovoltaic performance and low cost fabrication technique [1]. However, PSCs still need to overcome several drawbacks like instability of the device performances [2]. The stability of PSCs is influenced by several factors, such as the perovskite materials, moisture, the hole transporting materials (HTMs), … [1].

The HTMs layer impacts the power conversion efficiency of the devices and can act as a perovskite protective layer avoiding diffusion of moisture [2,3]. The litterature reference HTM (Spiro-OMeTAD) as well as most of organic HTMs are usually doped with bis(tri-fluoromethylsulfonyl) amine lithium salt (Li-TFSI) and 4-tertbutylpyridine (TBP) to enhance the electrical properties of the HTM layer [1]. However, the addition of hygroscopic Li-TFSI decreases the hydrophobicity of HTMs and limit its role as a protective layer [2, 4], decreasing the stability of the device. The scientific community tend to solve this problem by synthesizing hydrophobic HTMs [4]. In the present work, we synthesized novel hydrophobic HTMs based on carbazole moiety, which improve the device stability even though they are doped with Li-TFSI and TBP. All the devices were fabricated with FTO/TiOx/ $MAPbI_{3-x}Cl_x$ /HTM/Au electrode configuration. These HTM show improvement of the stability compared with Spiro-OMeTAD reference. Therefore, they can be considered as promising candidates as HTM in perovskite solar cells (PSCs).

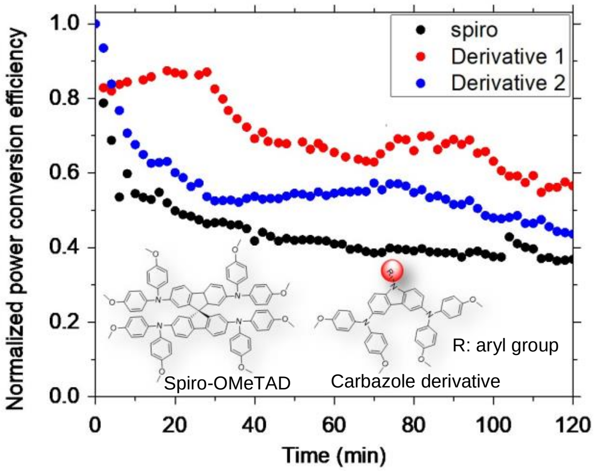

*Figure 1 : Normalized stability curves of the device efficiencies ($\eta$) of novel HTM based on carbazole moiety under AM 1.5 illumination conditions*

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# Polarized Emission of Mesogenic Conjugate Polymer by Photo-Commanding Layer

Jong-Ha Woo, Jae-Hoon Kim, and Chang-Jae Yu

*Department of Electronic Engineering, Hanyang University, Seoul 04763, Republic of Korea.*
*Email: cjyu@hanyang.ac.kr*

## Abstract:

The control of orientational ordering of conjugate polymer has been of interest for improving the performance of light-emitting diodes [1]. Liquid crystalline (LC) conjugate polymers have been widely studied due to their self-orientational ordering, obtained by rubbing method [2]. Although the rubbing method is a promising technique for aligning the LC, this could give rise to perfromance degradation in the electro-photonic devices since an electrostatic effect and an large surface roughness.

In this work, we demonstrate highly polarized emission of LC conjugate polymer, poly(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-(benzo[2,1,3]thia-diazol-4,8-diyl) (F8BT), via photoalignment method. Here, the photoalignment layer is acted as a hole transport layer and an electron blocking layer in a conventional organic light emitting diode (OLED). Also, the photo-commanding layer is easily governed by controlling the polarization of ultra-violet (UV) light. The surface anchoring energy was measured to be similar to the anchoring energy by the rubbing method. However, the surface roughness was remarkably reduced from 3.1 nm to 0.8 nm (rms). Figure 1 shows the microscopic textures of the F8BT film on the photo-commanding layer under crossed polarizers and the polarized spectra. When the photo-aligning direction was parallel to one of crossed polarizers, an excellent dark state was observed. In addition, a polarization ratio of the photoluminescence (PL) was measured to be similar to that of the rubbed F8BT film. This method would be applicable to the emitting devices with the patterned polarization such as stereoscopic 3D display [3].

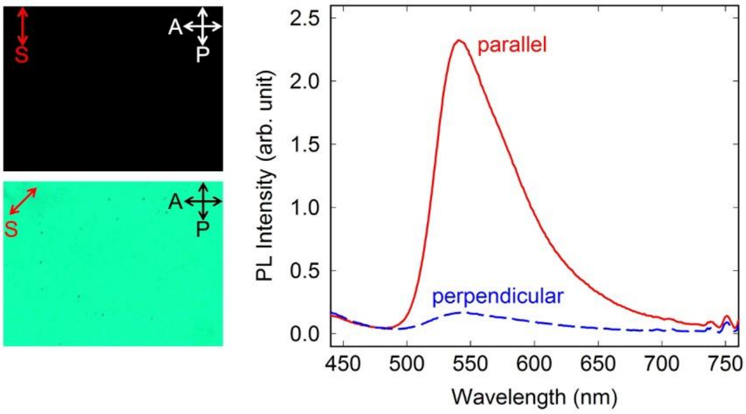

*Figure 1. Microscopic textures under crossed polarizers and polarized PL spectra parallel and perpendicular to a sample-orienting direction. Letters P, A, and S represent the directions of the polarizer, the analyzer, and the sample orientation (photo-aligning direction), respectively.*

This work was supported by a National Research Foundation of Korea (NRF) grant (NRF- 2018R1A2A3075276).

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# How can non fullerene acceptors help to print stable high efficiency polymer solar cells?

Elena Barulina,[a] Pavlo Berkhun,[a] Sadok Ben Dkhil,[b] Pascal Pierron,[b] Birger Zimmermann,[c] Uli Würfel,[c] Olivier Margeat,[a] Jörg Ackermann, [a] Christine Videlot-Ackermann[a]

*[a]Aix Marseille Univ, CNRS UMR7325, CINaM, Marseille, France. Email: videlot@cinam.univ-mrs.fr*
*[b]Dracula Technologies, 4 rue Georges Auric, 26000 Valence, France.*
*[c]Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofdtrasse 2, 79110 Freiburg, Germany.*

Abstract:

Non fullerene acceptors (NFAs) have recently attracted high intention due to their strong potential to improve power conversion efficiency (PCE) of organic solar cells (OSCs). Indeed an unprecedented increase in the device performance of OSCs since 2015 could be observed through the arising of new NFAs leading now to PCEs > 13 % in single junction solar cells [1], while even 17.3 % efficiency could be reached in tandem solar cells [2]. As now theirs performances make OSCs as photovoltaic technology highly promising for a large number of niche markets, it is important to study aspects such as processing of OSCs with industrial relevant materials and techniques and even more important stability of the NFA based OSCs. Some first results presented during the last years have shown that OSCs based on NFA held great promise for improve device stability compared to fullerene based acceptors [3]. More recently Brabec *and coll.* have studied the stability of one of the most representative NFA family, namely ITIC, blended with the PBDB-T donor polymer under light soaking test. It was found that ITIC-Th and ITIC-2F blended with PBDB-T lead to OSCs with lifetime approaching 10 years [4]. However in all those studies, the device structure was composed of partly evaporated layers (hole extraction layer and Ag electrode) and solution processing of the devices was performed under inert atmosphere demanding therefore more details investigation under more industrial relevant material and processing conditions.

In this work, we study two ITIC derivatives in combination with PBDB-T as well as PTB7-Th towards stable fully solution processed high efficiency OSCs. The stability of the NFA based OSCs is compared to device using PTB7-Th:PCB$_{70}$BM blend as highly stable reference material [5] that has recently demonstrated constant high efficiency under light soaking over 10 years. First we demonstrate that replacement of MoOx as HTL by PEDOT:PSS introduce only performance losses from 9.4% for PBDB-T:ITIC to 7.7% making fully printed OSCs possible. As interfacial layers plays important role in the stability of OSCs [6,7], their impact as well as that of the donor polymer and processing conditions on the device stability are investigated under ISOS L-1, ISOS T1 and ISOS D1 using simulated AM1.5 lighting as well as UV @ IR free LED lighting. Finally, the stability of fully inkjet printed ITIC based solar cells is evaluated

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T3 - 14

# Ambipolar organic field-effect transistors based on the dicyanodistyrylbenzene copolymers

Hwa Sook Ryu,[a] Min Je Kim,[b,c] Moon Sung Kang,[d] Jeong Ho Cho[b,c*] and Han Young Woo[a*]

*[a]Department of Chemistry, Korea University, Seoul 136-713, Republic of Korea. hywoo@korea.ac.kr*

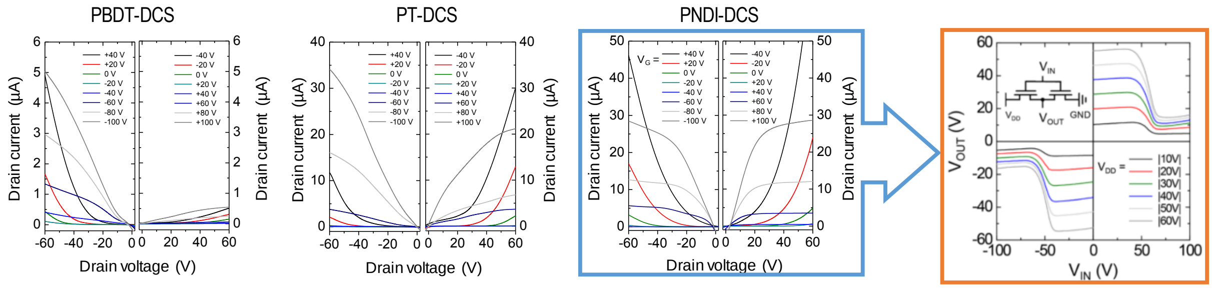
*[b]SKKU Advanced Institute of Nanotechnology (SAINT),[c]Department of Nano Engineering, Sungkyunkwan*

*University, Suwon 16419, Republic of Korea. jhcho94@skku.edu*

*[d]Department of Chemical Engineering, Soongsil University, Seoul, 156-743, Korea.*

## Abstract:

Three types of dicyanodistyrylbenzene (DCS) -based copolymers (PBDT-DCS, PT-DCS, and PNDI-DCS) present ambipolar charge transport characteristics in organic field-effect transistors (OFETs). Because introduction of the DCS moiety in a polymer backbone not only lowers the lowest unoccupied molecular orbital (LUMO) level, but also increases the crystalline ordering via interchain dipole-dipole interactions. As a result, the highest occupied molecular orbital (HOMO) energy levels of polymers were determined to be −5.53, −5.56, and −5.70 eV, respectively. The lowest unoccupied molecular orbital (LUMO) energy levels of PBDT-DCS, PT-DCS and PNDI-DCS are estimated to be -3.76, -3.84 and -3.92 eV, respectively. The three polymers showed HOMO and LUMO levels close to -5.5 eV and -4.0 eV, respectively, which can show efficient injection of electrons and holes from the Au electrode to improve ambipolar charge transport. The determined hole/electron mobilities of the OFETs were 0.064/0.014, 0.492/0.181, and 0.420/0.447 cm2/Vs for PBDT-DCS, PT-DCS, and PNDI-DCS, respectively, after thermal annealing at 250 °C. By incorporating the electron-deficient naphthalene diimide (NDI) unit in the copolymers, the n-channel transport was enhanced, with decreasing frontier molecular orbitals with enhanced electron injection from the Au electrode. Therefore, PNDI-DCS provided equivalent hole and electron mobilities with completely symmetric output curves in the positive and negative drain voltage regions. A complementary inverter was successfully fabricated, which benefitting from the balanced ambipolar feature of the PNDI-DCS OFETs.



*Output characteristics of the OFETs based on 250 °C-annealed film*
*and voltage transfer characteristics of the complementary inverter based on the PNDI-DCS OFETs.*

T3 - 15

# Growth morphologies and thermalization pathways of nitrogen based oligoacene derivatives on (0001) sapphire

Aydan Çiçek [a], Aleksandar Matković [a], Markus Kratzer [a], Zhongrui Chen [b] ,Olivier Siri [b] , Conrad Becker [b] , Christian Teichert [a]

*[a]Institute of Physics, Montanuniversität Leoben, Leoben, Austria. aydan.cicek@studmail.ac.at*
*[b]Aix Marseille Univ., CNRS, CINaM, Marseille, France*

## Abstract:

Oligoacenes (as pentacene) and their derivatives are considered as potential candidates in the field of organic electronics due to their molecular packing that favors charge transport and thus high field-effect mobilities. Here, dihydro-tetraaza-pentacene (DHTA5) and dihydro-tetraaza-heptacene (DHTA7) molecules are considered [1,2]. Both molecules exhibit a similar dipolar momentum and hydrogen bonding in the crystal, but have a different size of the backbone. Molecular arrangement, nucleation densities, sizes, and shapes of the resulting crystallites are analyzed as a function of the deposition temperature [3].

The molecules are deposited using a hot wall epitaxy system. As substrate, vicinal (0001) sapphire is used with an average step distance of 50 nm, and step height of 0.2 nm. The morphology of the grown films is investigated ex-situ by atomic force microscopy. Coverages from sub-monolayers to several layers are analyzed, and evolution of needle-like and island-like crystallites is examined as a function of the deposition temperature. An activation energy of (1.23 ± 0.12) eV was found for the nucleation of DHTA7 islands (composed of upright standing molecules), while (1.16 ± 0.25) eV was obtained for DHTA5 needles (composed of lying molecules). The observed disparity in the temperature dependent nucleation densities of the two molecular species is attributed to the different thermalization pathways of the impinging molecules [4].

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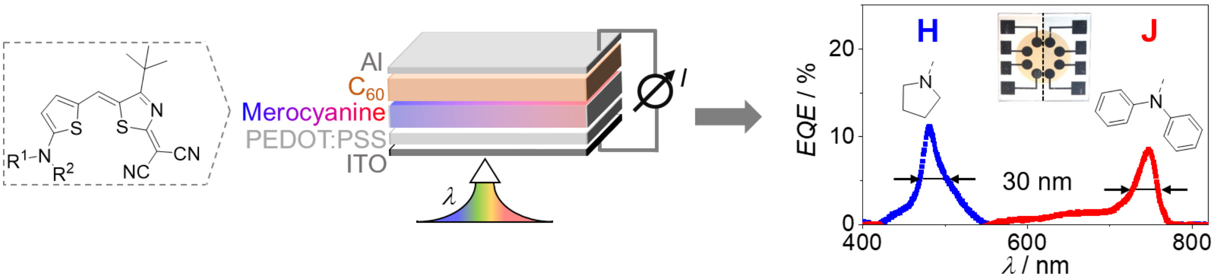
# Ultra-narrow Bandwidth Organic Photodiodes by Exchange Narrowing in Merocyanine H- and J-aggregate Excitonic Systems

Andreas Liess,[a,b] Alhama Arjona-Esteban,[a] Astrid Kudzus,[b] Julius Albert,[b] Ana-Maria Krause,[b] Aifeng Lv,[b] David Bialas,[a,b] Vladimir Stepanenko,[a,b] Matthias Stolte,[a,b] Frank Würthner[a,b]

[a] *Universität Würzburg, Institut für Organische Chemie, Am Hubland, Würzburg, Germany.*
[b] *Universität Würzburg, Center for Nanosystems Chemistry (CNC), Theodor-Boveri-Weg, Würzburg, Germany.*
*Email: wuerthner@uni-wuerzburg.de*

## Abstract:

The solid-state packing structure of π-conjugated organic molecules highly affects the materials' properties.[1] For merocyanine dyes, usually arranging in an H-coupled antiparallel fashion,[2] more interesting J-coupling structures have rarely been reported. Here we show for nine highly dipolar merocyanines with the same π-scaffold and thus equal monomer properties in solution, that the packing arrangement can be controlled by the bulkiness of the donor substituent, leading to strong exciton coupling within a card stack (H) or zig zag (J) packing.[3] Both bands in the blue (H) and NIR (J) spectral ranges arise from a single exciton band and are not just a mere consequence of different polymorphs within the same thin film. By fabrication of organic thin-film transistors, these dyes are demonstrated to exhibit hole transport behavior in spin-coated thin films. Moreover, when used as organic photodiodes in planar heterojunctions with $C_{60}$ fullerene, they show wavelength-selective photocurrents with external quantum efficiencies up to 11 % and ultra-narrow bandwidths down to 30 nm.[4] Thus, narrowing the linewidths of optoelectronic functional materials by exciton coupling provides a powerful approach to yield ultra-narrowband organic photodiodes.



*Application of merocyanine dyes in planar heterojunction photodiodes with corresponding EQE data of the best devices exhibiting an ultranarrow H- or J-band.*

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# Infrared studies of device relevant layers - energetic and morphological insights

Valentina Rohnacher,[a,b] Florian Ullrich,[b,c] Sebastian Beck,[a,b] Annemarie Pucci[a,b]

[a] *Kirchoff Institute for Physics, Heidelberg University, Germany. valentina.rohnacher@kip.uni-heidelberg.de*
[b] *InnovationLab Heidelberg, Germany*
[c] *Surface Science Division, Technical University Darmstadt, Germany*

Abstract:

Organic optoelectronic devices consist of stacked organic and inorganic materials. The device performance is mainly influenced by the interface of these layers. Increasing the interfacial compatibility especially between the transparent conductive oxide electrode and the organic semiconductor layer can improve the charge carrier transport through the stack and thus the efficiency of the device. The investigation of the structure-function relationship of these layers is a major key to the basic understanding of the fundamental mechanisms in organic electronics.

Thin films of metal oxides are known to be excellent charge-selective interlayers in optoelectronic devices.[1,2] In this study, solution-processed nickel oxide as hole transport layer and tin oxide as electron transport layer were investigated by infrared spectroscopy. This method gives insight into the composition of the investigated material and can monitor orientation of characteristic vibrations or functional groups. We studied the influence of annealing temperature on bulk and surface properties of the metal oxide layers.[2] In comparison with photoelectron spectroscopy, atomic force microscopy and device characteristics a better understanding of the energetic, chemical and morphological properties at the interface can be achieved helping to improve device performance.

References:

[1] E.H. Anaraki al., "Highly efficient and stable planar perovskite solar cells by solution-processed tin oxide." Energy & Environmental Science, 2016 9 (10), pp3128-3134

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# Naphthothiazine and Acridine spiropyrans for electronic applications

Yana Glukhova[a], Alexander Ponyaev[b]

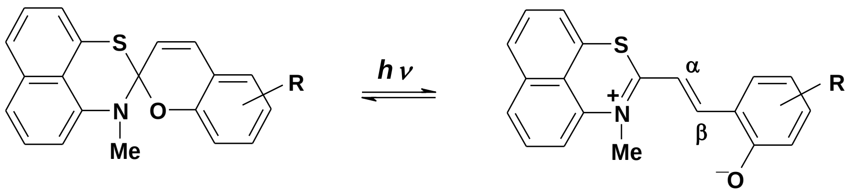
*[a]190013, Saint-Petersburg, Moskovsky pr. 26, Russia. Email: Jancha@mail.ru*
*[b]190013, Saint-Petersburg, Moskovsky pr. 26, Russia. Email: Ponyaev2002@mail.ru*

Abstract:

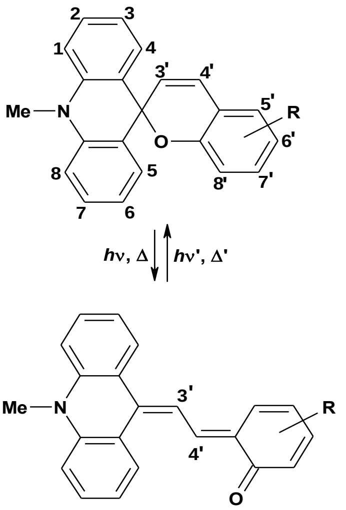
Molecular electronics requires systems capable of receiving, storing and processing information. Photochromic processes can be considered as “elementary” acts of recording information by actinic light.

$$\mathbf{0} \rightleftharpoons \mathbf{1} \qquad \mathbf{A} \underset{h\nu',\,\triangle}{\overset{h\nu}{\rightleftharpoons}} \mathbf{B}$$

In this work, we synthesized and investigated photochromic materials based on spiropyrans, with improved for practical application of spectral-kinetic properties. Their photoinduced form is a merocyanine dye (**B**).



**A** **B**



***1***-**R=H,** ***2***-**R=5',6'-benzo,** ***3***-**R=8'-OMe,** ***4***-**R=7'-NEt$_2$**

Photochromic properties of spiropyrans of the naphthothiazine (***1–4)*** and acridine series in liquid solutions have been studied. Flash photoexcitation of solutions of ***1A–4A*** in toluene and ethanol at room temperature induced absorption in visible region, and the absorption pattern did not change to an appreciable extent if air was present in the system. The absorption maximum of the colored form in more polar solvent appeared at longer wavelengths. Unlike indoline and phenanthridine spiropyrans, colored isomers ***2B–4B*** exhibit positive rather than negative solvatochromism, indicating their predominantly quinoid structure. The absorption maxima of the colored form of unsubstituted derivative (***1B***) in ethanol and toluene are almost similar. On example of the naphthothiazine (***1–4)*** and acridine spiropyrans, the factors contributing to the improvement of light resistance are experimentally illustrated: the absence of a nitro group in the structure of the molecule, the singlet path of photocoloration, a quinoid structure, and a short lifetime of the photoinduced form.

The study was supported by the Russian Ministry of Education and Science (Project 4.4697.2017/6.7), Committee on Science and Higher School of St. Petersburg and Russian Foundation for Basic Research (Project 16-08-01299).

# Resonance Raman spectra of molecules exhibiting ultrafast excitation energy transfer

Martin Michl,[a] Tomáš Staněk,[a] Miroslav Dvořák,[a] Numan Almonasy,[b] Miloš Nepraš,[b]

[a] *Department of Physical Electronics, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, V Holešovičkách 2, 180 00 Prague 8, Czech Republic Email: martin.michl@fjfi.cvut.cz*

[b] *Institute of Organic Chemistry and Technology, Faculty of Chemical Technology, University of Pardubice, Studentská 95, 532 10 Pardubice, Czech Republic*

Abstract:

It has been found that the rate of intramolecular excitation energy transfer in many molecules where the donor and acceptor moieties are connected via a conjugated bridge exceeds by up to several orders of magnitude the rate which would correspond to purely Förster type energy transfer (see e.g. [1]). For this process, the term „through-bond“ energy transfer has been coined. It differs from the „through-space“ Förster energy transfer also by its independence on spectral overlap and mutual orientation of corresponding transition dipole moments. However, the true nature of the „though-bond“ energy transfer remains unclarified. One of the considered contributing mechanisms is superexchange interaction where the molecular orbitals of the bridge are involved in the Dexter-like energy transfer mechanism (see e.g. [2]). Another approach introduced by Okuno [3] considers the energy transfer as a non-adiabatic transition. Recently, Athanasopoulos and coworkers performed excited-state molecular dynamics simulations of a donor-acceptor molecule exhibiting the „through-bond“ energy transfer [4]. Their results show that the molecule undergoes transient delocalization within several femtoseconds after photoexcitation of the donor and then gradually relaxes towards the state with the excitation energy localized on the acceptor moiety. According to Heller’s time-dependent formulation of the Raman scattering, such early dynamics of the excited state should be reflected in resonance Raman intensity pattern of the molecule [5]. Thus, in this contribution we describe our attempt to measure resonance Raman spectra of compounds containing 1-aminopyrene donor(s) and 3-aminobenzanthrone acceptor connected via *sym*-triazine bridge [6] using 355 nm excitation wavelength. These compounds were shown by transient absorption and transient lens measurements to undergo very efficient excitation energy transfer on timescale shorter than 200 femtoseconds [7].

References:

[1] Kim, TG, et al., J. Phys. Chem. A 2006, 110(1):20-27.

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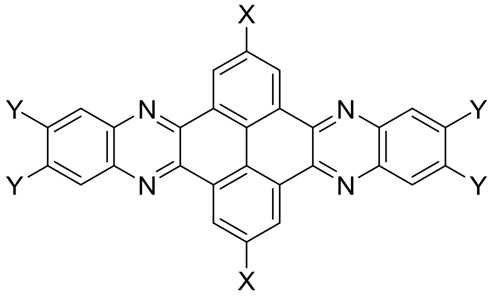
# Pyrene-Based Compounds In Organic Optoelectronic Applications

Bilal R. Kaafarani[a]

[a] *Department of Chemistry, American University of Beirut, Beirut 1107-2020, Lebanon. Email:* *bilal.kaafarani@aub.edu.lb*

Abstract:

Fused, ladder-type organic materials have inherent advantages, such as extended ⍰⍰-frameworks, favorable stacking behavior in the solid state, conductivity, and high field-effect mobility. We report a wide range of extended pyrene-based compounds so called quinoxalinophenanthrophenazine (TQPP), Figure 1. The introduction of nitrogen atoms in the TQPP core decreases the HOMO-LUMO gap making the compounds of more interest in electronic applications. Besides, the planarity of the core in the TQPP compounds facilitates the efficient cofacial stacking of the materials in the solid state and increases the intermolecular $\pi$-orbital overlap. Combining the electronic properties of the electron-deficient TQPP chromophore and the predisposition of the TQPP compounds to self-organize into efficient self-assembled $\pi$-$\pi$ columnar stacks in a single molecule offer an interesting combination of physical properties and, perhaps, a route to new materials for electronic applications. In this talk, we will discuss the different properties and features of the TQPP compounds.



**TQPP-$[X]_2$-$[Y]_4$**

Figure 1. Chemical structure of TQPP-$[X]_2$-$[Y]_4$.

# Improvement of organic photovoltaic cells performances by the insertion of dipolar SAMs-functionalized metal oxides

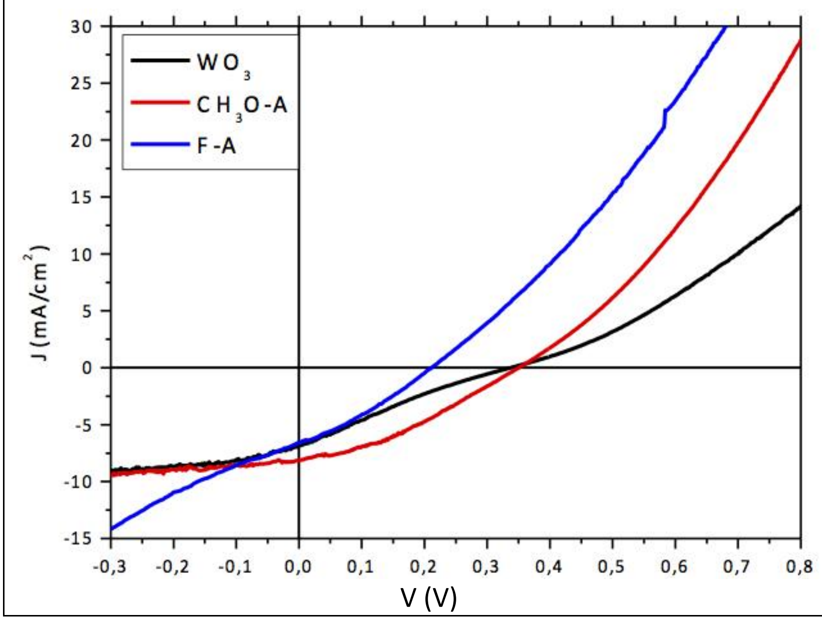
Mariem Ben Youssef[1,2], Jean-Yves Piquemal[1], Fayçal Kouki[2] , Mahamadou Seydou [1] Philippe Lang[1*]

[1]ITODYS UMR CNRS 7086, Université Paris Diderot 75205 Paris Cedex 13, France *lang@univ-paris-diderot.fr

[2]Laboratoire des Matériaux Avancés et Phénomènes Quantiques Département de Physique, Faculté des Sciences de Tunis, Université Tunis El-Manar 2092 Tunis, Tunisie

## Abstract:

The insertion of very thin metal-oxide (MOx) semi-conducting (SC) layers at the interface between the conductive electrodes (FTO/ITO, Metals) and the active layer (polymer, perovskite) has given an efficient solution to improve the separation and collection of free carriers at electrodes and the performances of organic and hybrid photovoltaic devices. In order to avoid the energy losses, carrier's recombination and to promote the good structuration of organic active blend P3HT: PCBM, the MOx layers have been functionalized by adequately oriented dipolar self-assembled monolayers (SAMs). By choosing two Y-PP-COOH (Y=OCH3, F) molecules grafted onto n-type and p-type SC MOx layers and having opposed dipolar moment, we exhibit clearly the dipole effect on the Voc (open circuit potential) via the variation of Work functions of oxide layers . The SAM may also influence the surface energy of MOx layers and so the wetting/organization of the active layer. In these both effects the chemical nature and the orientation of the grafted molecules appear as the key parameters of the solar cells improvements



Current density versus bias J (V) for solar cells FTO/WO3-**SAM**/P3HT: PCBM/ZnO/Al/ under AM1.5 G illumination

----- Without SAMs $WO_3$

----- CH3O-PP-COOH

----- F-PP-COOH

9th International Conference on Molecular Electronics
Paris, France
December, 17-20th 2018

# Electronic properties of few layer tungsten oxide WO3 on gold (111) surface modified by tetraphenyl porphyrin and grafted dipolar molecules studied by STM and spectroscopy

Rishav HARSH[1], Jerome Lagoute[1*], Mariem Ben Youssef[2], Cyril CHACON[1], Vincent REPAIN[1],
Sylvie ROUSSET[1] , jean Yves Piquemal[2], Mahamadou Seydou[2] and Philippe Lang[2*]

[1] Laboratoire Matériaux et Phénomènes Quantiques, Université Paris Diderot, CNRS UMR 7162;
*jerome.lagoute@univ-paris-diderot.fr

[2]ITODYS UMR CNRS 7086, Université Paris Diderot, France* lang@univ-paris-diderot.fr

## Abstract:

Tungsten oxide WO3 is used in organic and hybrid/inorganic electronics as p-type semiconductor and hole transport layer (HTL). The WO3 which may be inserted between the conductive electrodes (FTO/ITO, Metals) and the active layer (molecule, polymer, perovskite) has given an efficient solution to improve the separation and collection of free carriers at electrodes and the performances of organic and hybrid photovoltaic devices. Our goal is to study the properties of mono or few layers of $WO_3$ as a promising candidate for photoharvesting, electronic interaction with molecules -such as porphyrin and dipolar molecules- and charge transfer processes.

WO3 shows tendency to form 1D structures (amorphous), 2D periodic monolayers and 3D islands. I-V spectra reveal diode type behavior for 2D periodic islands and 3D islands whereas 1D structures show metallic I-V characteristic. As example , dI/dV spectra of porphyrin molecule on 1D structures shows an increase in the band gap (~ 0.8 eV).

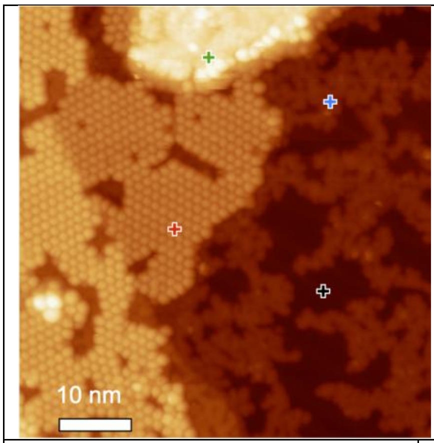


Figure-1a: STM image showing different structures of $WO_3$ at 10 pA and 1.5 V

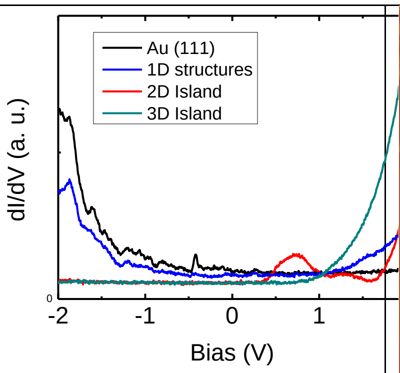


Figure-1b: dI/dV spectra for points marked in fig-1a

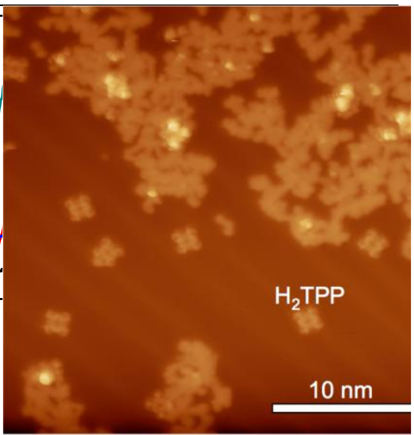


Figure-2: STM image showing porphyrin molecules on Au and on $WO_3$ 10 pA and 1.5

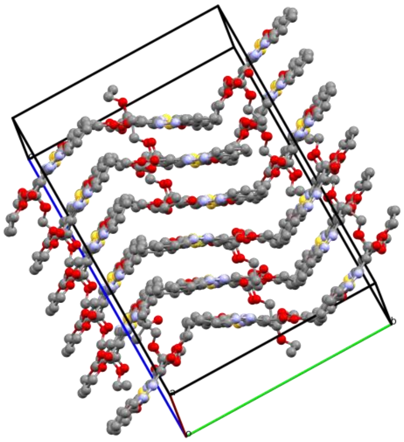
# Modulating Fluorescence with Supramolecular Contacts

Marie-Hélène Tremblay[a] and W. G. Skene[a]

[a]*Department of Chemistry, Université de Montréal, cp 6128, Centre-Ville, Montréal, QC, H3C 3J7, Canada.*
*Email:w.skene@umontreal.ca*

Abstract:

Although azomethines have the benefit of being easily prepared, their properties can be limited. This is the case for their photoemission where their quantum yields are limited. In fact, the imine bond undergoes both photoisomerization and photoinduced electron transfer. These deactivation pathways can efficiently quench the fluorescence of otherwise instrisic fluorescence fluorophores. Therefore, azomethine incorporation in conjugated organic fluorophores leads to substantial fluorescence quenching. These deactivation modes can be mitigated by intermolecular contacts,[1] especially in terms of aggregation induced emission.[2] A red colored conjugated azomethine was prepared having urea end-groups. These were to promote hydrogen mediated emission enhancement by intermolecular hydrogen bonding. It will be demonstrated that emission enhancement is possible both in protic solvents and when aggregated. It will be demonstrated that the prepared compound is further electroactive, undergoing electrochemically mediated color changes.



*X-ray crystal structure of the conjugated azomethine showing the intermolecular hydrogen bonding and supramolecular network, in part responsible for the emission enhancement.*

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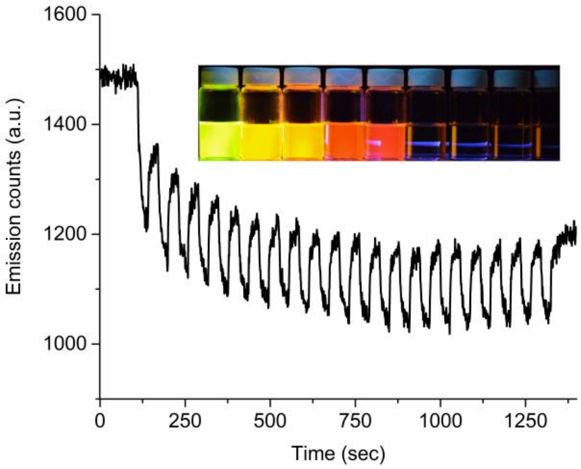
# Towards An Electrofluorescent Switch

Chengzhang Yao,[a] Hu Lei,[a] Mathieu Frémont,[a] Laurie Walach,[a] Georges Turner,[a] W. G. Skene[a]

[a]*Department of Chemistry, Université de Montréal, cp 6128, Centre-Ville, Montréal, QC, H3C 3J7, Canada.*
*Email:w.skene@umontreal.ca*

## Abstract:

Visible conjugated organic fluorophores have found uses in many applications, including organic electronics, probes, and sensors among many others.[1] Pushing the emission envelop into the NIR region has many advantages for both organic electronics[2] applications and biological imaging.[3] Extending the emission to the NIR can in part be done by incorporating complementary strong electron donors and acceptors into the fluorophore. While -$NO_2$ and -$NR_2$ substituents are typically used as complementary electronic donor-acceptor groups, respectively, the nitro group can lead to undesired limitations such as quenched fluorescence, solvent interactions, and instability. We therefore explored –CN as an alternative functionality for electronic *push-pull* fluorophores. Electroactivity can additionally be incorporated into the fluorophore when the –$NR_2$ substituent is triphenylamine. The oxidized intermediate of the triphenylamine that can be produced electrochemically can quench the intrinsic fluorophore emission. This leads to an electrochemically mediated fluorescence switch. The photophysical and electrochemical properties of the electrofluorescent switch will be presented, including the spectroelectrochemical and spectroelectrofluorescent properties of the fluorescence switch.



*Emission change of an electrofluorescent switch with applied potential. Inset: range of emissions possible with an electrofluorescent switch as a function of solvent.*

## References:

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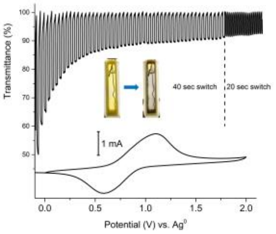
# Photoimmobilization of Electrochromic Layers

Monika Wałęsa-Chorab[a,b] and W. G. Skene[a]

[a]*Department of Chemistry, Université de Montréal, cp 6128, Centre-Ville, Montréal, QC, H3C 3J7, Canada.*
*Email:w.skene@umontreal.ca*
[b]*Current address: Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b, 61614 Poznań, Poland*

## Abstract:

Conjugated azomethines have garnered much attention owing to their ease of preparation. They are also advantageous for property modification that is possible by the judicious choice of their arylamines and aldehydes used in their preparation. While small molecules of azomethines are beneficial for accurate structure-property studies, their high solubility is common organic solvents is problematic. This is particularly the case when using them in electrochromic applications. In such devices that undergo reversible color change with applied potential, the low molecular weight azomethines cannot sustain repeated oxidation/neutralization cycles. This limits the device performance and ultimately results in device failure. Although performant electrochromic devices are possible with azomethine polymers,[1-8] it is challenging to selectively pattern the electrode surface of the device. We therefore explored the immobilization of low molecular weight azomethines by photochemical means. In fact, standard photolithography could be used to selectively immobilize an electroactive azomethine on the electrode. It will be shown that the immobilization of the layer could be successfully done photochemically. Also, it will be illustrated that the layer was electrochromic and that it was capable of resisting upwards of 80 min of switching.



*Top: electrochromism of a triphenylamine azomethine immobilized on an ITO electrode, monitored at 700 nm with applied potentials between 100 and 1100 mV in acetonitrile for given switching times. Middle: colors of the immobilized film in the neutral (left) and (right) states with electrochemical switching. Bottom: cyclic voltammogram of the immobilized film at 100 mV/sec.*

## References:

(1) Ma, X.; Niu, H.; Wen, H.; Wang, S.; Lian, Y.; Jiang, X.; Wang, C.; Bai, X.; Wang, W. *J. Mater. Chem. C,* **2015**, *3*, 3482.
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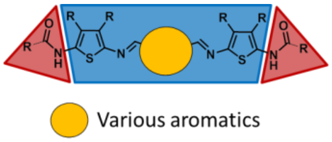
# Unravelling the Structural Requirements of Conjugated Azomethines for Electrochromics

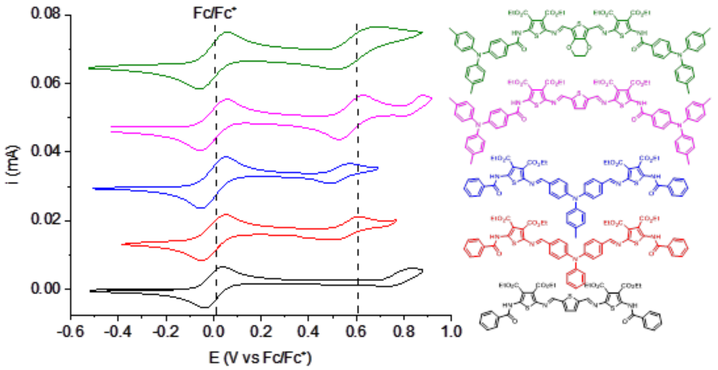
Yohan Gautier[a] and W. G. Skene[a]

[a]*Department of Chemistry, Université de Montréal, cp 6128, Centre-Ville, Montréal, QC, H3C 3J7, Canada.*
*Email:w.skene@umontreal.ca*

## Abstract:

Azomethines have been successfully used as functional materials in a wide range of applications such as organic light-emitting diodes,[1] organic photovoltaics,[2] memory devices,[3] and pH sensors.[4] Their versatility is in part owing to the properties that can be tailored through the selection of aryl aldehydes and amines used for their preparation. Despite this, knowledge regarding the effect of structural effects on the electrochemical and optical properties remains under explored. This knowledge would be beneficial for designing and preparing conjugated azomethines having targeted colors along with reversible oxidation. These are key properties for use in electrochromics, being the reversible color switching with applied potential. Within this context, extensive structure-property studies of the conjugated azomethine (see Figure) were undertaken. This was to understand the key structural requirements for achieving reversible color changes with applied potential and reversible oxidation. The effect of structure of these key electrochemical and spectroscopic properties will be presented.





*Cyclic voltammograms illustrating the variation in oxidation potential contingent on azomethine structure, while maintaining reversible oxidation.*

## References:

(1) Khalid, N.; Bibi, A.; Akhtar, K.; Mustafa, K.; Khan, M.; Saeed, N. *Polym. Plast. Technol. Eng,*. **2018**, 1.
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# Organic push-pull compounds for the sensitization of p-type oxides. Inverted Grätzel Solar cell and Photocathode for hydrogen evolution

R. Brisse,[a] V. Mafféis,[a,b] T. Gustavsson,[b] B. Geffroy,[a,c] and B. Jousselme[a]

*[a]LICSEN, CEA Saclay, DSM/IRAMIS/NIMBE (UMR 3685), F-91191 Gif sur Yvette, France.*
*Email: bruno.jousselme@cea.fr*
*[b]LIDYL, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France.*
*[c]LPICM, CNRS, Ecole Polytechnique, F-91128 Palaiseau, France.*

## Abstract:

With theoretical PCE reaching 40%, Tandem Dye Sensitized Solar Cells (T-DSSCs), which are composed of two dye-sensitized photoelectrodes, a photocathode and a photoanode, sandwiching a redox electrolyte, could represent a cost-effective and promising alternative to silicon based solar cells.[1] This poster will report different works done for the development of p-type electrode:

- The synthesis of p-type mesoporous NiO films through ink-jet printing of a sol-gel ink. Multilayer NiO films were formed and different morphologies could be obtained by playing on the interlayer thermal treatment. The different morphologies and thicknesses of the NiO films were correlated to their performance in a p-DSSC configuration. [2]
- The design, synthesis and physical property characterization of four new triphenylamine–bithiophene push–pull dyes with acceptors of increasing electronic affinity, in order to shift their absorption to the red region of the visible spectrum. The dyes were tested in a p-type DSSC configuration with 850 nm NiO ink-jet printed photocathodes and their performances were compared with that of the reference dye P1.[3]
- Time-resolved fluorescence study of a triphenylamine–bithiophene–naphthalimide dye in four solvents of varying polarity using fluorescence upconversion. After photoexcitation, the directly populated state (S1/FC) evolves toward a relaxed charge transfer state (S1/CT). This S1/CT state is characterized by a lower radiative transition moment and a higher nonradiative quenching. The fast dynamic shift of the fluorescence band is well described by solvation dynamics in polar solvents, but less so in nonpolar solvents, hinting that the excited-state relaxation process occurs on a free energy surface whose topology is strongly governed by the solvent polarity. This study underlines the influence of the environment on the intramolecular charge transfer (ICT) process, and the necessity to analyze time-resolved data in detail when solvation and ICT occur simultaneously.[4]
- The molecular assembly of a push–pull organic dye and a cobalt diimine–dioxime catalyst co-grafted on a p-type NiO electrode substrate realized at the CEA Grenoble (V. Artero's Team). (Photo)electrochemical measurements allowed characterization of electron transfer processes within such an assembly and to demonstrate for the first time that a CoI species is formed as the entry into the light-driven H2 evolution mechanism of a dye-sensitized photocathode.[5]

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# Seebeck coefficient of AuGe thin films for thermoelectric applications in organic nanoscale devices

Chloé Salhani, Philippe Lafarge, and Maria-Luisa Della Rocca

*Laboratoire MPQ, Université Paris-Diderot, Sorbonne Paris Cité, UMR 7162, CNRS. 10, rue Alice Domon et Léonie Duquet, 75205 Paris Cedex 13, France*

We experimentally study the thermoelectric properties of $Au_xGe_{1-x}$ thin film alloys close to the metal-insulator transition with the goal of obtaining an element with good thermal sensor properties for integration into nanoscale organic devices.

Based on finite element simulations and by taking into account all spurious thermoelectric effects, we have revealed a Seebeck coefficient of the thin film very close to that of Au thin films. Simultaneously we have observed good electrical properties of the thin film allowing its use as a high-resolution thermometer.

As a proof of principle, we have demonstrated the possibility to integrate such an element as the top electrode of a large-area vertical molecular junction, embedding thin (5-15 nm) molecular layers and producing devices in which the AuGe film simultaneously fulfills the functions of a local heater and thermometer.

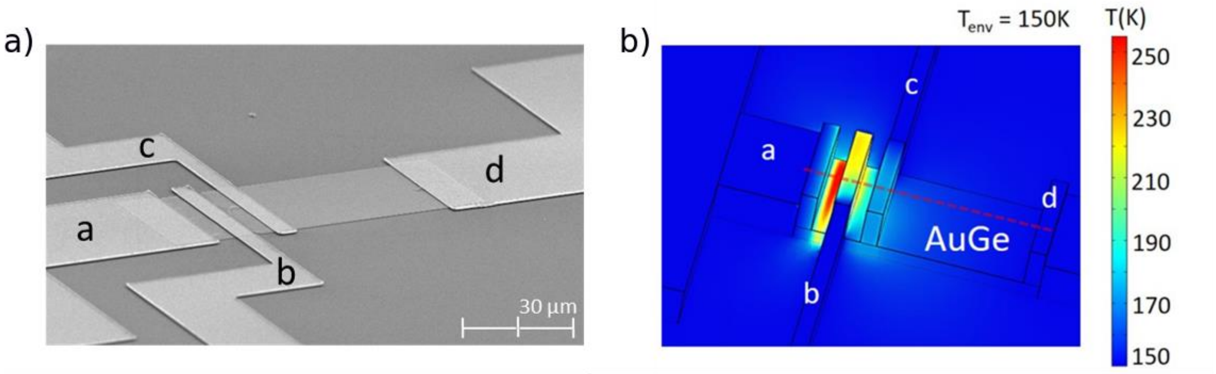


***Figure 1****: a) SEM image of a device intended to measure the Seebeck coefficient of an AuGe thin film alloy. b) Simulated three-dimensional plot of the temperature in said sample for an applied voltage $V_{ab}$ of 2V between the a and b contacts at a temperature T=150K of the environment.*

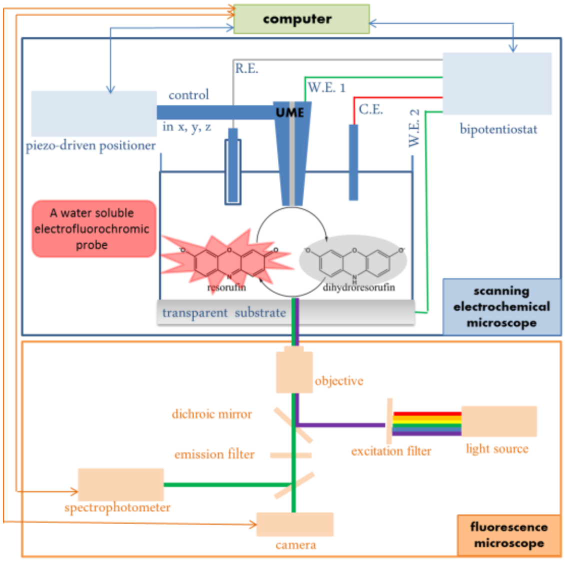
# Combined SECM and fluorescence microscopy using a water-soluble electrofluorochromic dye as the redox mediator

Laetitia Guerret,[a] Jean-Frédéric Audibert,[a] Galina V. Dubacheva,[a] Fabien Miomandre

[a] *PPSM, ENS Cachan, 61 avenue du Président Wilson 94230 Cachan, France.*
*Email:laetitia.legras@ens-cachan.fr*

## Abstract:

The combination of electrochemical and fluorescence techniques has been the subject of a growing interest from the beginning of the 1990s, moving gradually towards more advanced configurations allowing spatio-temporal resolved measurements. However examples where fluorescence microscopy and SECM are combined are scarce in the literature [1-3]. We recently reported the use of an electrofluochromic probe both as redox mediator and fluorophore in a combined SECM-fluorescence microscopy experiment [4]. The SECM tip was polarized in order to convert the fluorophore into a non-emissive form and thus switch off luminescence locally and reversibly. The resulting fluorescence intensity modulation was studied by fluorescence imaging and emission spectroscopy. Our first study was however restricted to organic media. We got interested in extending the concept to a water-soluble electrofluorochromic redox mediator, resorufin, under conditions compatible with biological experiments [5]. The tip potential, the tip-substrate distance, the substrate nature and potential (for a conducting substrate) are the parameters that are likely to control the modulation amplitude. Their influence in the positive and negative feedback as well as generation-collection SECM configurations is investigated in detail.



*Set-up combining SECM (upper part) and epifluorescence microscope (lower part).*

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# Long distance electron transfer between redox partner proteins through the aqueous solution

Anna Lagunas[a,b], Alejandra Guerra-Castellano[c], Alba Nin-Hill[d], Irene Díaz-Moreno[c],
Miguel A. De la Rosa[c], Josep Samitier[b,a,e], Carme Rovira,[d,f] Pau Gorostiza.[b,a,f,*]

*[a]Networking Biomedical Research Center (CIBER), Madrid 28029 Spain.*
*[b]Institute for Bioengineering of Catalonia (IBEC), The Barcelona Institute of Science and Technology (BIST), Barcelona 08028 Spain.*
*[c]Institute of Chemical Research (IIQ) – Centre of Scientific Research Isla de la Cartuja 9 (cicCartuja), University of Sevilla - CSIC, Sevilla 41092 Spain.*
*[d]Inorganic and Organic Chemistry Department & Institute of Theoretical and Computational Chemistry (IQTCUB), University of Barcelona (UB), Barcelona 08028 12 Spain.*
*[e]Department of Electronics and Biomedical Engineering, University of Barcelona (UB), 14 Barcelona 08028 Spain.*
*[f]Catalan Institution for Research and Advanced Studies (ICREA), Barcelona 08010 Spain.*

*Email: alagunas@ibecbarcelona.eu*

Abstract:

Despite the importance of electron transfer (ET) between redox proteins in photosynthesis and respiration, the inter-protein ET rate between redox partner proteins has never been measured as a function of their separation in aqueous solution. Here we use electrochemical tunneling spectroscopy (ECTS) to show that the current between two protein partners decays along more than 10 nm in the solution. Molecular dynamics simulations reveal a reduced ionic density and extended electric field in the volume confined between the proteins. The distance decay factor and the calculated local barrier for ET are regulated by the electrochemical potential applied to the proteins. Redox partners could use electrochemically gated, long distance ET through the solution to conciliate high ET specificity with weak binding, thus keeping high turnover rates in the crowded environment of cells.

# Electrical properties by CAFM of photo-switchable SAMs grafted on ferromagnetic substrates

Louis THOMAS, David GUÉRIN, Dominique DERESMES, Thierry MÉLIN, Dominique VUILLAUME, Stéphane LENFANT

*Institute of Electronics, Microelectronics and Nanotechnology, CNRS, University of Lille, 59652 Villeneuve d'Ascq, France. Email: stephane.lenfant@univ-lille.fr*

Molecular spintronics aims at developing nanoscale devices with improved performances or new functionalities by using molecules to conduct spin-polarized carriers. A promising approach is to graft these molecules by a self-assembling process to form SAM on a ferromagnetic electrode (FM). Until now, only molecules acting as a tunnel barrier have been studied [1]. Here we use functional molecules (photochromic) whose the conformation and the electrical conductance can change, reversibly, under light stimuli. Based on theoretical work [2], this study has the objective to investigate the relationship between spin-polarized carriers transport and molecular conformations.

Two systems are considered: (i) diarylethene derivative (DDA) SAM (Fig 1A) grafted on lanthanum strontium manganite (LSMO) surface, and (ii) azobenzene derivative (AzBT) SAM (Fig 1B) on cobalt surface. These systems are electrically characterized by CAFM at ambient temperature for the both configurations, in air for LSMO system and under ultra-high vacuum for Co system to avoid the oxidation.

These analyses show a variation of the electrical resistance of the LSMO surface without SAM up to 1200 (Fig. 1C) due to a stoichiometry modification caused by the tip pressure and electrical field [3;4]. For the naked cobalt a similar behavior was observed with a ratio ~ 933 (Fig. 1D) attributed to the oxidation of Co. These effects are strongly reduced with the SAM covering the FM electrode (Figs. 1C-D). However, these features impede the detection of the open/closed weak conductance change of ~5 for DDA, while a clear cis/trans conductance change of about 20 is observed for the AzBT/Co junctions (Fig 1E).

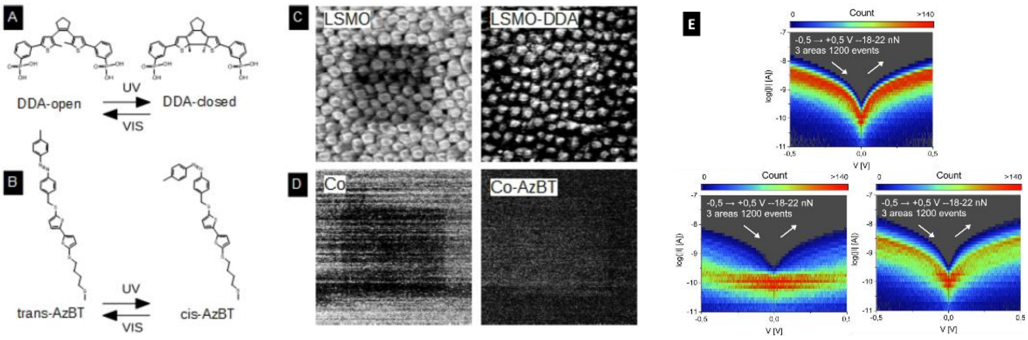

*Figure 1: Molecule of DDA (A) and AzBT (B). (C) Image of currents of the naked LSMO showing the lower conductance in the center (dark area) induced by a previous scan (1×1 µm², F=30 nN, ΔV=0.1V, I from 1pA to 1nA) and with DDA SAM (1×1 µm², F=30 nN, ΔV=0.3V, I from 1pA to 1nA); (D) Idem without SAM on Co (1.5×1.5 µm², F=20 nN, ΔV=0.2V, I from 1nA to 10µA) and with AzBT SAM (1.5×1.5 µm², F=20 nN, ΔV=0.1V, I from 100pA to 100nA). (E) 2d Current-voltage histograms for the AzBT/Co junctions (pristine,* cis *and* trans *states).*

Acknowledgements. We thank P. Seneor and R. Mattana (UMPhy CNRS/Thales) for supplying the LSMO, and the financial support from ANR "spinfun" project.

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# Study of the adsorption mechanisms of oriented dipoles of carborane-thiol molecules on a flat gold surface

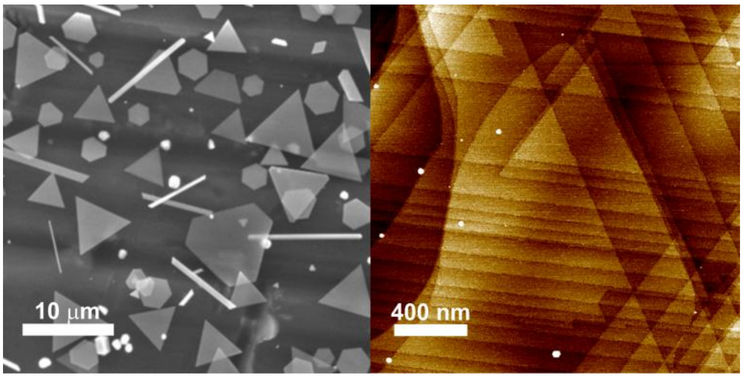
Aliaksei Vetushka,[a] Martin Müller,[a] Martin Hladík,[a] Martin Ledinský,[a] Antonín Fejfar,[a] Jan Macháček,[b] Tomáš Baše.[b]

[a] *Institute of Physics CAS, Thin films and nanostructures, Prague 8, Czechia. Email:vetushka@fzu.cz*
[b] *Institute of Inorganic Chemistry CAS, Department of Syntheses, 250 64 Husinec-Řež, č.p. 1001, Czechia.*

## Abstract:

The surface work-function (WF) of a (semi-)conductor is the key parameter which determines the amount of electrons that can be emitted from its surface and thus it defines the electronic parameters of the electrical junctions which, in turn, define the final characteristics of various electronic devices. One of the possible ways to tune the noble metal WF is the use of Self-Assembled Monolayers (SAMs) of oriented dipoles [1]. However, the applicability of SAMs is limited by relatively low thermal stabilities of organic molecules. In this regard, SAMs of carboranes with exceptionally high thermal stability represent promising candidates and it was shown that silver work-function can be tuned very precisely over a range of 1 eV by using a mixture of oppositely oriented carborane-thiol dipoles [2].

In this work we show the formation of SAMs of carborane-thiols molecules ($1,2-(HS)_2-1,2-C_2B_{10}H_{10}$ and $9,12-(HS)_2-1,2-C_2B_{10}H_{10}$) on the smooth gold surfaces of well-defined gold single-crystals [3] using ambient conditions AFM. The detailed comparison of high-resolution topography maps obtained under different deposition conditions will be presented and their physisorption and chemisorption will be discussed.



*SEM image (left) of gold microplate crystals with flat surfaces. AFM topography (right) of a gold microplate showing atomic layers (Z-scale: 2 nm)*

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# Molecular Isomerization and self-assemblies from Ditopic Molecules with variable central bridges

Xinlei Yao,[a] Xiaonan Sun,[a] Denis Frath,[a] Gilles Lemercier,[b] Frédéric Lafolet,[a] François Maurel, [a] Jean-Christophe Lacroix,[a]

*[a] Univ. Paris Diderot, Sorbonne Paris Cité, ITODYS, CNRS UMR 7086-15, rue Jean-Antoine de Baïf, 75205 Paris Cedex 13, France. Email:yxlei676@gmail.com*

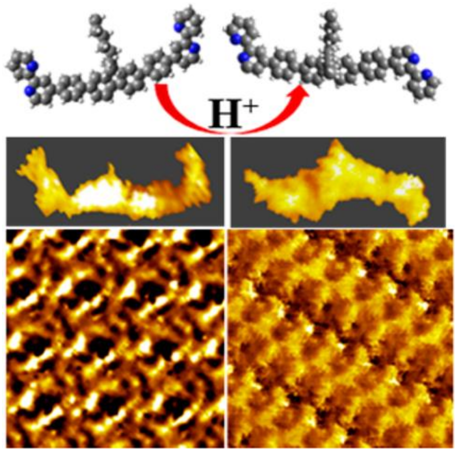
*[b] Univ. Reims Champagne-Ardenne, Institut Chimie Moléculaire de Reims, UMR 7312 CNRS, BP1039, 51687 Reims Cedex 2, France.*

## Abstract:

Series of molecules with a format of **Bpy-X-Bpy** (Bpy is presenting Bipyridine) are synthesized and are investigated by Scanning Tunneling Microscopy (STM) at the solid liquid interface. The bipyridine moitie is employed as molecular terminal groups due to its active capabilities to form selective hydrogen bonds. The central X bridges can vary so as to involve different molecular functionalities.

Molecules **Bpy-F-Bpy** (F is presenting a fluorecene center) are observed to form variable two dimensional (2D) supramolecular networks. Highly ordered gear chains organizations are observed at the none-acid/HOPG interface where Bpy-F-Bpy molecule shows a cis-like conformation. The organizations are stabilized with intermolecular CH-N hydrogen bonds. When involving acid solvents, the surface organizations turn into a 2D linear stripe organization with the Bpy-F-Bpy molecule in trans-like conformation. The intermolecular interaction has been modified to stronger NH-N hydrogen bonds simultaneously. The $H^+$ protonation induced Bpy-F-Bpy cis-to-trans isomerization is therefore a multi-scale switch which involves a change from weak to strong hydrogen bonds, and a structural phase transformation of gear chains into a stripe-like organization.

Molecules **Bpy-PE2P-Bpy** (where PE2P is presenting a biEDOT center) can self-assemble into various ordered organizations on surfaces. The molecule shows a same cis-to-trans isomerization behavior from the bipyridine protonation, whereas the biEDOT central bridge is always locked in its trans conformation thanks to the intramolecular sulfur–oxygen interactions. The cis-bpy-PE2P-bpy conformers form linear supramolecular stripe and herringbone structures. The trans-bpy-PE2P-bpy conformers form both a zigzag structure and supramolecular wires of variable width. In the various supramolecular organizations, the intermolecular hydrogen bonds between the bipyridine units vary, whereas the biEDOT moieties are always aligned with the same organization and the intermolecular biEDOT interactions remain identical as a dominating force for the supramolecular self-assembly.



*The cis to-trans isomerization in the supramolecular network of bpy-F-bpy molecules*

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# Double functional switching from photochromic molecules on surface

Imen Hnid, Xiaonan Sun, Frédéric Lafolet, Denis Frath, Jean Christophe Lacroix

*Univ. Paris Diderot, Sorbonne Paris Cité, ITODYS, CNRS UMR 7086 - 15, rue Jean-Antoine de Baïf,*
*75205 Paris Cedex 13, France. Email: lacroix@univ-paris-diderot.fr*

## Abstract:

Molecules can be switched between different states by different stimulis, including heating, light, and pH. Among these molecules, aromatic azobenzenes are excellent candidates as photochromic molecular switches since they can exist in two forms, the AZO-cis and the AZO-trans isomers [1]. We introduce here two different molecules incorporating an azobenzene group as a central photochromic unit bridging two different terminal groups: bipyridine for the first [Bipy-Azo-Bipy] and terpyridine for the second [Tpy-Azo-Tpy]. The organizations of these molecules on a surface have been investigated by Scanning Tunneling Microscopy (STM). Both molecule self-assemble on surfaces and various supramolecular networks can be observed with a sub-molecular resolution, thanks to the intermolecular interactions of the terminals moieties.

Hence, we studied by STM the different phase transitions induced by the protonation of the bipyridine terminal moities or by the photo-switching of the photochromic central bridge. Indeed, a multiscale irreversible phase transition upon protonation was already observed on similar molecules consisting of a central bifluorene bridge and bipyridine terminal groups [Bipy-Fl-Bipy] [2]. Using [Bipy-Azo-Bipy], A similar, protonation induced, phase transition involving the switching from a cis-like to a trans like isomers is also observed as depicted in Figure 1. Next we studied the effect of irradiation on the system. The photos-witching transition from the Azo-trans bridge (the stable state) to the Azo-cis can be triggered by UV light and reversed back to its initial state by visible light [3]. The photo-effect on the central photochromes was firstly confirmed in solution by UV-visible absorption spectroscopy and the organisation of the the Azo-cis isomers on surfaces will be presented.

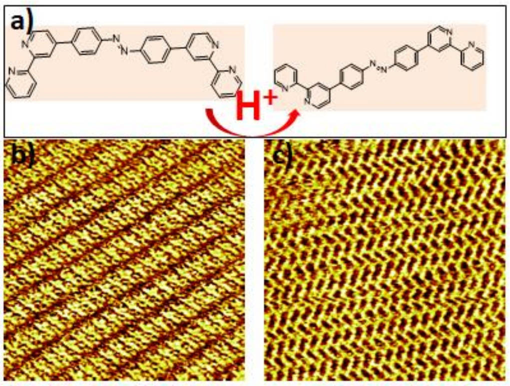

*Figure1. a) Transition cis to trans. b),c) STM images 25x25 nm$^2$ of b) cis Bipy -Azo-Bipy structure at 1-octanol/HOPG interface and c) trans Bipy -Azo-Bipy structure at acid/1-octanol/HOPG interface.*

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# ELECMOL$^9$
# List of participants

Elecmol$^{9}$
December, 17-20 2018
Paris, France

| | | | |
|---|---|---|---|
| ADAM | Catherine | Moltech-Anjou | France |
| AHOULOU | Samuel | LCPME-Nancy | France |
| AKAI-KASAYA | Megumi | Osaka University | Japan |
| AL-ZOHBI | Fatima | PCM2E University of Tours | France |
| ANNADATA | Harshini | National University of Singapore | Singapore |
| AO | Zitong | Chungbuk National University | republic of Korea |
| AOYAMA | Tetsuya | Riken | Japan |
| ARDESI | Yuri | Politecnico Di Torino | Italy |
| ATTIAS | Andre-Jean | UMI 2B-Fuel CNRS-Sorbonne | France |
| AUDEBERT | Pierre | PPSM ENS Paris-Saclay | France |
| AVRILLER | Rémi | LOMA - University of Bordeaux | France |
| BARRAUD | Clément | MPQ Paris Diderot University | France |
| BARRETEAU | Cyrille | Cea CNRS Paris Saclay University | France |
| BARTH | Johannes | Technical University Munich | Germany |
| BATTAGLINI | Nicolas | ITODYS - Paris Diderot University | France |
| BEN YOUSSEF | Mariem | ITODYS - Paris Diderot University | France |
| BERGGREN | Magnus | Linköping University | Sweden |
| BETERMIER | FANNY | University of Evry | France |
| BLIEN | Stefan | University of Regensburg | Germany |
| BOCQUET | Marie-Laure | ENS-CNRS UMR Pasteur Paris | France |
| BOUDON | Corinne | University of Strasbourg | France |
| BROWN | Anton | K.U. Leuven | Belgium |
| BRUNEL | Damien | Aix-Marseille University | France |
| BUCINSKAS | Audrius | Kaunas University of Technology | Lithuania |
| CHEN | Zhijin | Osaka University | Japan |
| CHOI | Yoonseuk | Hanbat National University | republic of Korea |
| CICEK | Aydan | Montanuniversitaet Leoben | Austria |
| COPPEDÈ | Nicola | IMEM CNR Parma | Italy |
| CORAUX | Johann | Institut Néel | France |
| CRANNEY | Marion | CNRS IS2M | France |
| CREDI | Alberto | Universita' Di Bologna | Italy |
| CULLY | John | University of Oxford | United Kingdom |
| DALLA FRANCESCA | Kevin | MPQ Paris Diderot University | France |
| DAPPE | Yannick | Paris Saclay University | France |
| De FEYTER | Steven | KU Leuven Belgium | Belgium |
| DEDIU | Valentin Alek | ISMN-CNR | Italy |
| DEKKICHE | Herve | Durham University | United Kingdom |
| DELLA ROCCA | Maria Luisa | MPQ Paris Diderot University | France |
| DENHOLME | Saleem | Communications Physics Nature Research | United Kingdom |
| DUBACHEVA | Galina | PPSM ENS Paris-Saclay | France |
| DUCHÉ | David | IM2NP Aix Marseille University | France |
| DULIC | Diana | University of Chile | Chile |
| EGUCHI | Keitaro | Technical University of Munich | Germany |
| EL ABBASSI | Maria | T.U. Delft | Netherlands |
| ESCOUBAS | Ludovic | IM2NP Aix Marseille University | France |
| FARQUHAR | Anna | University of Alberta | Canada |
| FERNANDEZ | Maxence | ISCR | France |
| FONTAINE | Olivier | ICGM - University of Montpellier | France |
| FORGE | Vincent | CEA Grenoble | France |
| FRISBIE | Dan | University of Minnesota | France |
| GAM DEROUICH | Sarra | ITODYS - Paris Diderot University | France |
| GIMENO | Lea | Nantes University | France |

| | | | |
|---|---|---|---|
| GLUKHOVA | Yana | Saint-Petersburg State Institute of Technology | Russia |
| GOHIER | Frederic | Moltech-Anjou Angers | France |
| GRAZULEVICIUS | Juozas Vidas | Kaunas University of Technology | Lithuania |
| GROSS | Andrew | CNRS - University Grenoble Alpes | France |
| GRUZAUSKAITE | Justina | Vilnius University Life | Lithuania |
| GRYN'OVA | Ganna | EPFL | Switzerland |
| GU | Mong-Wen | National Taiwan University | Taiwan |
| GUDEIKA | Dalius | University of Latvia | Latvia |
| GUO | Hongbo | Chungbuk National University | republic of Korea |
| HAGFELDT | Anders | EPFL | Switzerland |
| HAMAI | Takamasa | University of Tokyo | Japan |
| HAN | Yingmei | National University of Singapore | Singapore |
| HARASHIMA | Takanori | Tokyo Institute of Technology | Japan |
| HIROKI | Kazauki | National Institute of Technology | Japan |
| HLADÍK | Martin | Institute of Physics of The Czech | Czech republic |
| HNID | Imen | ITODYS - Paris Diderot University | France |
| HOLZINGER | Michael | CNRS - University Grenoble Alpes | France |
| HUC | Vincent | University of Paris-Sud | France |
| HÜTTEL | Andreas K. | University of Regensburg | Germany |
| JOUSSELME | Bruno | CEA Saclay | France |
| KAAFARANI | Bilal | American University of Beirut | Lebanon |
| KIM | Byeonggwan | Sorbonne University | France |
| KIM | Do-Kyung | Kyungpook National University | republic of Korea |
| KIM | Han-Sang | Chungbuk National University | republic of Korea |
| KOCH | Norbert | Humboldt-Universität & H.Z.B | Germany |
| KULAPICHITR | Pakapol | The University of Manchester | United Kingdom |
| LACROIX | Jean Christophe | ITODYS - Paris Diderot University | France |
| LAFARGE | Philippe | MPQ - Paris Diderot University | France |
| LAFOLET | Frederic | ITODYS - Paris Diderot University | France |
| LAGOUTE | Jérôme | MPQ - Paris Diderot University | France |
| LAGUNAS | Anna | IBEC | Spain |
| LANG | Philippe | ITODYS - Paris Diderot University | France |
| LAUNAY | Jean-Pierre | CEMES-CNRS | France |
| LE GOFF | Alan | CNRS - University Grenoble Alpes | France |
| LEBON | Florian | LICSEN - CEA Saclay | France |
| LEE | Seungjoo | Tokyo Institute of Technology | Japan |
| LENFANT | Stéphane | IEMN - University of Lille | France |
| LIESS | Andreas | University of Wuerzburg | Germany |
| LIN | Chih-Hsun | National Taiwan University | Taiwan |
| LIU | Mingyang | ITODYS - Paris Diderot University | France |
| LMIMOUNI | Kamal | IEMN University of Lille | France |
| LUCAS | Fabien | Institut Des Sciences Chimique De Rennes | France |
| MAILLEY | Pascal | CEA - Leti | France |
| MARCHI | Valerie | Institut Des Sciences Chimiques De Rennes | France |
| MARCUS | Rudolph | California Institute of Technology | USA |
| MARLETTA | Giovanni | University of Catania | Italy |
| MARTIN | Pascal | ITODYS - Paris Diderot University | France |
| MATTANA | Giorgio | ITODYS - Paris Diderot University | France |
| MATTERA | Michele | IPCM Sorbonne University | France |
| MAUREL | Francois | ITODYS - Paris Diderot University | France |
| MAURO | Matteo | IPCMS - University of Strasbourg | France |
| MAYNE | Andrew | ISMO - CNRS | France |

| | | | |
|---|---|---|---|
| MCCORMAC | Tim | Dundalk Institute of Technology | Ireland |
| MCCREERY | Richard | University of Alberta | Canada |
| MEDINA RIVERO | Samara | University of Malaga | Spain |
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| PIRO | Benoit | ITODYS - Paris Diderot University | France |
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| RABAH | Jad | UVSQ - Paris Saclay | France |
| RANNOU | Patrice | CNRS/UMR 5819 Symmes | France |
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| REISBERG | Steeve | ITODYS - Paris Diderot University | France |
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| SALLES | Raphaël | IPCM - Sorbonne University | France |
| SANVITO | Stefano | Trinity College Dublin | Ireland |
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| SUN | Xiaonan | ITODYS - Paris Diderot University | France |
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| VAN DER ZANT | Herre | Delft University of Technology | Netherlands |
| VASILIJEVIĆ | Sandra | ITODYS - Paris Diderot University | France |
| VETUSHKA | Aliaksei | Institute of Physics Czech | Czech republic |
| VIDELOT-ACKERMANN | Christine | CINAM - UMR 7325 | France |
| VILA | Neus | LCPME | France |
| VOLATRON | Florence | IPCM - Sorbonne University | France |
| VOLYNIUK | Dmytro | Kaunas University of Technology | Lithuania |
| VUILLAUME | Dominique | IEMN - UMR 8520 | France |
| WEISS | Jean | CNRS Strasbourg | France |
| WENZEL | Wolfgang | Karlsruhe Institute of Technology | Germany |
| WOO | Han Young | Korea University | republic of Korea |
| XU | Wenjun | University of Oxford | United Kingdom |
| YAO | Xinlei | ITODYS - Paris Diderot University | France |
| YONGFENG | Tong | MPQ - Paris Diderot University | France |
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