# C'NONO 2018 THE NANOSCIENCE MEETING

December, 11, 12 and 13 Palais des Congrès Neptune

Club nanoMétralagie



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#### Biography

Dominique Vuillaume is an Electronics Engineer from the Institut Supérieur d'Electronique du Nord (Lille, France). He received his PhD degree and Habilitation Diploma in solid-state physics, from the University of Lille in 1984 and 1992, respectively. He is now Research Director at CNRS. From 1982 to 1992, his research interests covered physics and characterization of point defects in semiconductors and MIS devices, physics and reliability of thin insulating films, hot-carrier effects in MOSFET's. Since 1992, he has been engaged in the field of Molecular and Organic Electronics. His current research concerns: i) design and characterization of molecular and nanoscale electronic devices, ii) elucidation of fundamental electronic properties of these molecular and nanoscale devices, iii) study of functional molecular devices and integrated molecular systems, iv) exploration of new computing paradigms using molecules and nanostructures. He was scientific advisor for industrial companies (Bull R&D center) on advanced CMOS technology reliability (1988-1990) and for the CEA in the frame of the "Chimtronique" (Chemistry for nanoelectronics) research program (2006-2013).

#### **MOLECULAR NANOSTRUCTURES IN A NANOELECTRONICS PERSPECTIVE**

In this presentation, I will present the properties of molecular junctions fabricated on a large array of sub-10 nm single crystal Au nanodot electrodes, each junction being made of less than one hundred molecules<sup>1,2</sup>. Thanks to this approach, I will discuss some pending issues in molecular electronic: effects of mechanical strain<sup>3</sup> on the conductance of molecular junctions, determination of inter-molecular interactions from the conductance histograms of molecular junctions<sup>4</sup>, demonstration of molecular electronic devices for high-frequency operation with a molecular diode working in the microwave regime up to 18 GHz<sup>5</sup>. I will discuss implications of these results to devices in organic electronics.

Then, towards more practical devices at the molecular scale, I will discuss new molecular switches designed, synthesized, and used to form self-assembled monolayers (SAM) on gold as well as Nano-Particle Self-Assembled Networks (NPSANs) with high ON/OFF conductance ratios<sup>6,7</sup> and plasmon assisted isomerization<sup>8.</sup> I will also present how we used these NSPANs to demonstrate an optically-driven reconfigurable logic molecular circuit and a high-order harmonic generator for neuromorphic "reservoir computing"<sup>9</sup>. These approaches, without direct analogs in semiconductor devices, would open new perspectives to molecular electronics in unconventional computing as an example of the Evolution-in-Materio concept<sup>10</sup>.

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**Keywords:** Molecular electronics, electron transport, interaction energy, microwave, conducting-AFM, scanning microwave microscope, molecular switch, neuromorphic devices.

# C'NOO 2018 THE NANOSCIENCE MEETING TOULON December, 11, 12 and 13 Palais des Congrès Neptune

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Nicolas Bergeal

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#### Biography

Nicolas Bergeal received a PhD from Pierre & Marie Curie University in 2005 for his dissertation thesis on Josephson effect in high-Tc superconductors. During these three years, he developed several methods to fabricate nanostructures (junctions, nanowires) with oxide superconductors both for fundamental and applied perspectives. After his Phd, he joined D. Roditchev team at the Institute for NanoSciences in Paris as a Postdoc to carry out researches on graphite intercalated compounds with low-temperature Scanning Tunneling Microscopy and Spectroscopy techniques. Nicolas completed his professional experience by a Postdoc in M. Devoret Lab at Yale University, where he developed a quantum-limited microwave amplifier suitable to perform quantum non-demolition measurements of superconducting Qubits.

In 2008, Nicolas Bergeal joined the Laboratory of Physics and Materials Study (LPEM) at ESPCI in Paris. His research activities are shared between the exploration of the fundamental electronic properties of superconducting materials, and the realization of functional superconducting circuits.

#### Two-dimensional electron gas at LaAlO<sub>3</sub>/SrTiO<sub>3</sub> interfaces

Perovskites-based structures, including transition metal oxides, have attracted much attention in recent decades for the richness of their phase diagrams that include a wide variety of electronic properties ranging from high-Tc superconductivity to colossal magnetoresistance. The achievement of high-quality epitaxial interfaces involving such materials gives a unique opportunity to engineer artificial materials where new electronic phases take place. The discovery of a high mobility two-dimensional electron gas (2-DEG) confined in a quantum well at the interface between two insulating oxides such as LaAlO<sub>3</sub> and SrTiO<sub>3</sub>, is probably one of the most striking examples in the field. Unlike more conventional semiconductor based quantum wells, conducting electrons at LaAlO<sub>3</sub>/SrTiO<sub>3</sub> fill 3d-bands, which gives a favourable ground for the emergence of complex electronic phases. In particular, two-dimensional superconductivity, magnetism and strong spin orbit coupling have been reported in such interfaces.

A key feature of these electronic systems lies in the possibility to control the 2-DEG properties, including superconductivity and spin-orbit coupling, by electric-field effect. This gate-tunability associated with the very unique combination of properties in the same two-dimensional electronic system opens new avenues to address fundamental questions in condensed matter physics but also to develop new functional devices. In this talk, I will review several field-effect experiments performed on LaAIO<sub>3</sub>/SrTiO<sub>3</sub> interfaces of different crystal orientations, both in back-gate and top-gate geometry. In particular, the superconducting phase diagram of this system, obtained by plotting the superconducting critical temperature as a function of gate voltage, will be introduced and discussed based on dc and microwave transport experiment. In this multiband system, both the emergence of superconductivity at a certain doping and the strength of spin-orbit coupling are intimately related to the filling of specific bands in the interfacial quantum well. Finally, I will discuss the realization of mesoscopic devices by various fabrication techniques (lithography, AFM...) whose physical properties, including superconductivity and Rashba spin-orbit coupling, can be manipulated at the nanoscale by electrostatic doping. The fascinating LaAIO<sub>3</sub>/SrTiO<sub>3</sub> interfaces emerge as a promising platform for the manipulation of spin, charge and orbital degrees of freedom.

Keywords: interfaces, superconductivity, LaAlO<sub>3</sub>/SrTiO<sub>3</sub>, spin-orbit coupling, field-effect, oxides



#### 11, 12 & 13 septembre

Session : Nanoelectronics

Keywords: Organic bioelectronics, Flexible Electronics, Soft Lithography, Impedance, Cells proliferation.

## Top-down fabrication of micro & nanostructured conducting polymers: advantageous platform to interface with the Living world.

#### Mohammed ElMahmoudy<sup>1</sup>, Anne M. Charrier<sup>2</sup>, R. O'Connor<sup>1</sup>, George M. Malliaras<sup>3</sup>, <u>Sébastien Sanaur</u><sup>4</sup>

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Surgeons and physicians need more and more efficient medical tools. In particular the need for electrodes, for both *in vivo* and *in vitro*, for recording and/or stimulation of high quality electronic signal is indispensable. Much of these devices are planar biocompatible substrates and do not provide close contact with cells, resulting in higher electrical impedance at those interfaces.

This talk will present about a new, facile top-down method for a 3D micro and nanopatterning of conducting polymers. Its benefit over others methods such as nanoimprint lithography (NIL) and capillary force lithography (CFL) will be here presented and discussed.

That method is using an epoxy supporting layer to facilitate the transfer of nanopatterns from a polydimethylsiloxane (PDMS) mold to rigid or flexible substrates (Figure 1). A supporting layer, as such UV-curable epoxy, advantageously allows i) a dry release of the patterned polymer layer and/or gold layer and ii) the sticking of a such stack to a substrate.

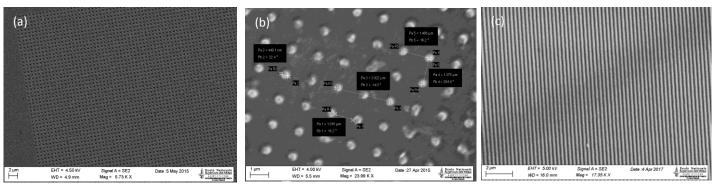


Figure 1 – SEM pictures of micro/ nano holes (a), pillars (b) and grooves (c)



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Finally, Electrochemical Impedance Spectroscopy (EIS) measurements show how such micro/ nanostructures are a benefit to lower their impedance, as instance for electrophysiological applications, where the reduction in size of the electrodes is required.



**11, 12 & 13 decembre** Session (ex : Nanoélectronique) Keywords: SAMs, lipids, organic, dielectrics.

# Ultrathin supported lipids monolayer onto P3HT with unprecedented mechanical and dielectric properties

#### Volkan Kilinc<sup>1</sup>, Tin Nguy<sup>4</sup>, Sébastien Lamant<sup>1</sup>, Frédéric Brunel<sup>1</sup>, Catherine Henry-de-Villeneuve<sup>2</sup>, Guillaume Monier<sup>3</sup>, Matthieu Petit<sup>1</sup>, Yutaka Wakayama<sup>4</sup>, Anne Charrier<sup>1</sup>, Jean-Manuel Raimundo<sup>1</sup>

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The development of ultrathin dielectrics for low power electronics operations, flexible and printed electronics, and field-effect-transistor-based sensors is still a challenge. Herein, monolayers of engineered lipids supported both on Si or P3HT are reported presenting exceptional mechanical and dielectrics properties. The lipid monolayers are stabilized using a simple procedure based on a two-stage reticulation process in both their internal aliphatic chains and their head-group. With a thickness lower than 3 nm, such layers are demonstrated to offer exceptional mechanical and dielectric strength. Surprisingly, the mechanical and dielectric pressures required to rupture/breakdown the monolayers are shown to be similar. These results suggest the presence of a strong correlation between mechanical and dielectric properties, as well as between the mechanisms of rupture and breakdown. Such reticulated layers with a thickness of 3 nm only have a direct dielectric breakdown occurring at ~30 MV/cm, i.e. much higher than for a silicon oxide layer of similar thickness.

J. Phys. Chem. B 116, 7190-7195 (2012). J. Mat. Chem. B 1, 443-446 (2013). Biosens. Bioelect. 54, 571-577 (2014). Anal. Chem. (88) 3804-3809 (2016). Patent: PCT/EP2016/074569. Adv. Func. Mat. (2018) 28, 1801024.



#### 11, 12 & 13 decembre

Nanoelectronics Keywords: quantum transport, quantum thermodynamics, molecular optoelectronics

### Time-dependent energy dynamics in molecular circuits

### Fabienne Michelini<sup>1</sup>, Katawoura Beltako<sup>1</sup> Nicolas Cavassilas<sup>1</sup>, Marc Bescond<sup>2</sup>, and Laurent Raymond<sup>3</sup>

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How energy is controlled at the nanometer scale is gaining more and more interests due to its implications in particular in the construction of quantum thermodynamics, the efficient production of energy, and the deeper understanding of nanosystems. In this context, we theoretically derive and analyze time-resolved charge and energy currents induced by femtosecond laser pulses inside a loop made of molecules in contact with two thermal reservoirs.

We first provide a definition for the energy current operator used to derive the expression of time-dependent energy current by means of non-equilibrium Green's functions (NEGF). We thus develop a methodology based on lattice Hamiltonian that enables us to investigate energy dynamics on ultimate time and size scales.

These formal developments are then numerically implemented to study a molecular circuit which includes a loop made of two donors interacting with femtosecond laser pulses and connected to the same acceptor group. We investigate the time-dependent energy dynamics at donor-acceptor interfaces in the loop, from the energy currents we calculated using the NEGF-based wave function technique [1]. The photocurrent exhibits characteristic frequencies that are correlated to both the internal structure of the nanocircuit [2], as well as the features of the excitation. In particular, we explore this dynamics in asymmetric configurations, when the two donors cannot exchange their role inside the circuit loop working.

#### References

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[2] K. Beltako, et al., J. Chem. Phys. 148, 104301 (2018).



Session (Nanoelectronics, Biomaterials)

Keywords: 'Redox Enzymes, Carbon Nanotubes, SAMs, Electrochemistry, Bioelectronics, Biofuel cells'

### Enzymatic electrocatalysis: From functional Orientation of redox enzymes on Carbon Nanotubes to dynamic behavior on Self-Assembled-Monolayers

# Vivek P. HITAISHI<sup>1</sup>, I. MAZURENKO<sup>1</sup>, David Duché,<sup>2</sup> M. ILBERT<sup>1</sup>, A. de POULPIQUET<sup>1</sup> and E. LOJOU<sup>1</sup>

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Redox enzymes such as bilirubin oxidase (BOD) are envisioned as biocatalysts in biotechnological devices such as enzymatic fuel cells<sup>1</sup>. By modulation of the pH of adsorption of BOD on functionalized carbon nanotubes (CNT), we previously demonstrated that electrostatic interactions were the main processes controlling the orientation of the enzyme for fast electron transfer<sup>2</sup>. In this work, we aim to make a clear correlation between enzyme activity on SAM-modified gold electrode and on CNTs. SAMs allow to be rid of the influence of the nanostructuration induced by the CNTs, and to put forward the key parameters required for stable and fast electron transfer. We initiated our work exploring the interaction between SAM-gold electrode surface and Myrothecium verrucaria BOD by modifying both the pH of enzyme adsorption and the pH of the electrochemical assays. This modulation of pH modifies i) the electrode surface charge as a function of the type of SAM chemical functions, ii) the enzyme surface charge, and iii) the intrinsic enzyme activity. Using electrochemistry at negatively charged SAMs, supported by ellipsometry and SPR, we proposed a model of functional enzyme immobilization, in which electrostatic interactions between the enzyme global charge and the SAMs drive the loading of enzymes, while the charge around the copper site acting as the entry point of electrons drives the enzyme orientation, hence the electron transfer rate. We then extended the study to positively charged SAM to further validate our electrostatic model. Importantly, we clearly demonstrated by electrochemistry and modeling pH zones where changes in orientation of the enzyme controls the catalytic process. We will finally discuss how molecular basis acquired on SAM-gold electrodes should be used for proper orientation of enzymes in a porous material<sup>3</sup>.

<sup>&</sup>lt;sup>1</sup> Hitaishi, Vivek, et al. Catalysts 8.5 (2018): 192 ; Mano and De Poulpiquet, Chemical reviews 118.5 (2017).

<sup>&</sup>lt;sup>2</sup> Mazurenko, levgen, et al. ACS applied materials & interfaces 8.35 (2016).

<sup>&</sup>lt;sup>3</sup> Hitaishi, Vivek, et al. Submitted.