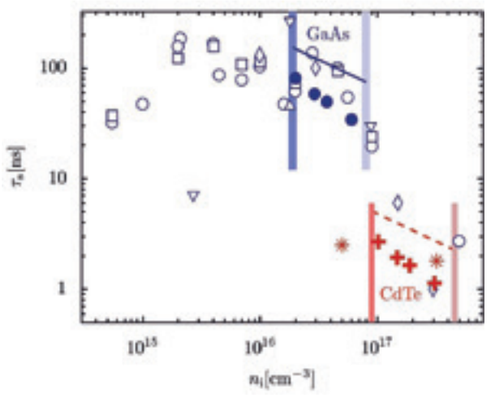


Lifetime of spin excitations as a function of the dopant density. Solid lines and filled symbols depict our prediction for the regime between the metal-insulator transition and the hybridyzation of the impurity band with the conduction band (vertical lines). Open symbols represent experimental results from the literature (see (1) for details). Blue data and results are for GaAs, red ones for CdTe. The figure is taken from our publication (1).

Spin Relaxation near the Metal-Insulator Transition: Dominance of the Dresselhaus Spin-Orbit Coupling, Guido A. Intronati, Pablo I. Tamborenea, Dietmar Weinmann, and Rodolfo A. Jalabert, *Phys. Rev. Lett.* ***108***, 016601 (2012).

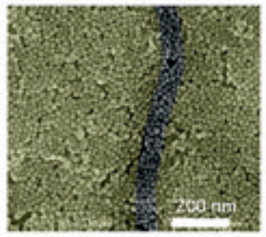
Contact: Dietmar.Weinmann@ipcms.unistra.fr

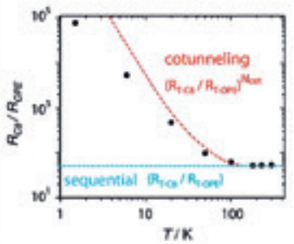
This work was performed within a french-argentinian collaboration, involving a Ph.D. Student in co-tutelle between the universities of Strasbourg and Buenos Aires, and supported by ECOS-Sud.

◆ Amplifying with co-tunneling

Metal Nanoparticles Networks are ideal model materials for studying the charge transport properties of Quantum Dots Networks. We designed electrical interconnects addressing sub-micron 'slices' of nanoparticles assemblies, typically 80 nm long, and several tens of microns wide. These provide access to electrical properties with a finite number of interparticle tunneling events N, in the range 1-7 by design. The usual device resistance results from a sequential interparticles tunneling process, with a resulting device resistance proportional to N.R_T, where R_T is the interparticle resistance value. Metal nanoparticles can also behave as Coulomb Island where strong electron-electron repulsion prohibits sequential charge transfer. At sufficient low temperatures, a coherent process can take place, where adding a charge to one nanoparticle requires a simultaneous charge leaving the island leading to a co-tunneling process. The resulting device resistance is then strongly enhanced by becoming proportional to R_T^N.

In a first experiment, [1] researchers at IPCMS led by B. Doudin and S. Bégin-Colin, in collaboration with D. Golubev of the Karlsruhe Institute of Technology (Germany), demonstrated the existence of co-tunneling in magnetic Nanoparticles Networks. Taking advantage of the spin dependence of the tunneling resistance R_T, they used an external magnetic field to modify R_T. This way they reached magnetoresistance values beyond those possible for fully spin polarized particles. In a second experiment [2], in collaboration with the KIT and the group of S.J van der Molen of Leiden University (The Netherland), the authors used chemical exchange for chemically varying R_T by 1 to 2 orders of magnitude. At low temperatures, when co-tunneling becomes predominant, the device resistive sensibility is dramatically amplified by 60^N, reaching 10^5 !
These two experiments demonstrate the opportunity given by co-tunneling processes in nanoparticles networks to realise innovative amplifying devices in electrical transport, open to multiple physical or chemical excitations. These devices could pave the way for creating multifunctional molecular devices with enhancing properties. ■





(Left) SEM image of a magnetic-nanoparticle multilayer deposited over a nanotrench (the filled nanotrench is darker in color, from [1]) (Right) Resistance ratio of identical networks with different molecular spacers as a function of temperature. A dramatic increase from an initial value of 50 in sequential regime up to 10^5 upon entering the co-tunneling regime is reported. (from [2]).

J.-B. Beaufrand, B. P. Pichon B. Doudin and S. Bégin-Colin, *Small*, ***8***, (2012),108–115.

[2] *Enhancing the Molecular Signature in Molecule-Nanoparticle Networks via Inelastic Cotunneling,* J.-F. Dayen, E. Devid, M.V. Kamalakar, D. Golubev, C. Guédon, V. Faramarzi, B. Doudin and S. J. van der Molen, *Advanced Materials*, (2012) doi: 10.1002/adma.201201550

Contact: jean-francois.dayen@ipcms.unistra.fr

IPCMS *News*

- **Publisher:** Marc Drillon - **Coordination:** Charles Hirlimann
- **Redaction committee:** Jean-Yves Bigot, Yves Galerne, Stefan Haacke, Jean-Paul Kappler, Geneviève Pourroy, Wolfgang Weber

➜ **To subscribe, contact** Charles.Hirlimann@ipcms.u-strasbg.fr

I.P.C.M.S
23 rue du Loess - B.P. 43
F-67034 Strasbourg cedex 2, France
Tél: +33 38-810-7141
Fax: +33 38-810-7250

Design atelierc.com

IPCMS *News*
International Newsletter
September 2012
No. 14

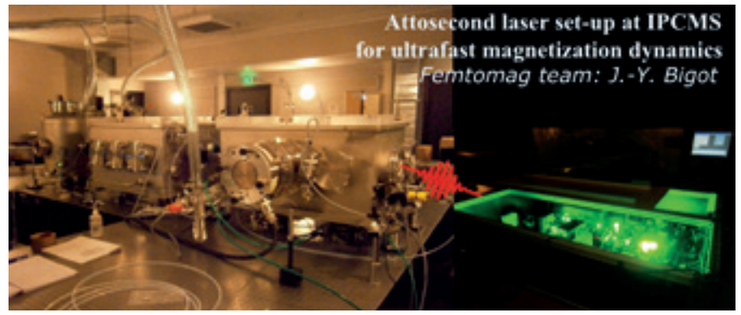
Summary

www-ipcms.u-strasbg.fr

Editorial

The delay that occurred since the previous issue of IPCMS News has been fully fulfilled by working out new projects in reaction to the French "Investments for the Future" initiative aimed at strengthening the country research landscape and capacities. IPCMS has been very successful in that competition. It was first awarded significant funding as a lab of excellence (LabEx), involving ISIS and ICS teams in Strasbourg, to be competitive with the best international laboratories. The associated project deals with nanostructures in interaction with their environment and will address the two following issues:

- *Controlling Light-Matter interactions in Nanostructures,*
- *Manipulating and controlling spins: from molecules to nanostructures.*



Second, IPCMS teams have succeeded in having two equipments of excellence (EquipEx) projects passing the highly competitive selection and insuring funding of new equipments aimed at enhancing the impact of our research. The project UTEM (Ultrafast Transmission Electron Microscopy) proposes the acquisition and the setting up of a transmission electron microscope with ultrahigh temporal resolution. This is a new technique with an enormous potential in the study of nanosystems which behavior at short time scales has hardly been accessible to observation yet. While the project UNION (Ultrafast Optics, Nanophotonics and Plasmonics), in collaboration with ISIS, aims at developing a new experimental platform focusing on the study of the temporal and spatial properties of magnetic and plasmonic nanostructures. The methods of investigation are the ultrafast magnetization dynamics using femtosecond and attosecond optical pulses as well as nanophotonics at the sub-wavelength scale.

It is to be noticed that IPCMS is the only one laboratory for which two EquipEx projects have been selected.

As it has now become a tradition, this issue of our international news reports on some of the most impacting results that have been reported in literature by the researchers at IPCMS.

Marc Drillon, *Director*

• A robust Zirconium-Carbene complex for the polymerisation of lactide.

N-heterocyclic carbenes (NHCs) have been recognized as forming a "privileged" class of ancillary ligands for coordination to late transition metal complexes and subsequent applications as homogeneous catalysts that often feature increased activity and/or selectivity.

We have shown that zirconium(IV) complexes may be stabilized by N-heterocyclic carbene ligands. These novel species act as an effective initiator for the ring opening polymerization of *rac*-lactide under mild conditions giving poly(lactic acid) PLA in a controlled and highly stereoselective manner (pdi< 1.1 and level of heterotacticity> 95%) *(see figure 1)*.

In addition, the resulting lactide monomer does not require purification to remove protic impurities such as lactic acid, indicating an excellent stability of the zirconium NHC complexes used as a catalyst.

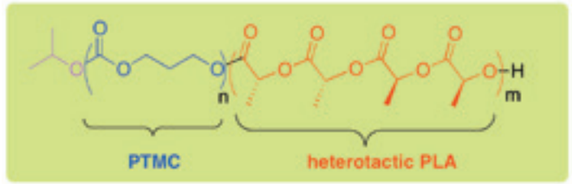


Figure 2

Furthermore we synthesized novel stereoregular co-polymeric biomaterials of potential interest, such as well-defined (heterotactic)PLA-PTMC block co-polymers (PTMC = poly-trimethylene carbonate)*(see figure 2)*.

This class of biomaterials has recently received attention as they may be more flexible and acid-resistant materials than isotactic PLA. In our case, after a controlled ring opening polymerisation of trimethylene carbonate, subsequent addition of *rac*-lactide yielded the formation of well-defined, molecular-weight controlled and high stereoregular (heterotactic)PLA-PTMC.

The use and application of these zirconium catalysts have been patented worldwide (WO 2012076140, CNRS-Clariant Int. Ltd). This work has been carried out in collaboration with Samuel Dagorne (UMR7177, Institut de Chimie) and Clariant (Basel, Switzerland). ■

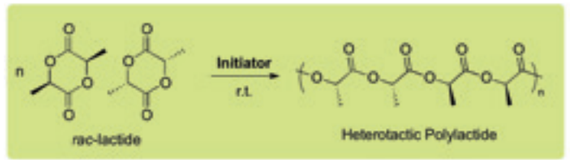
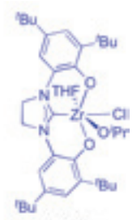


Figure 1

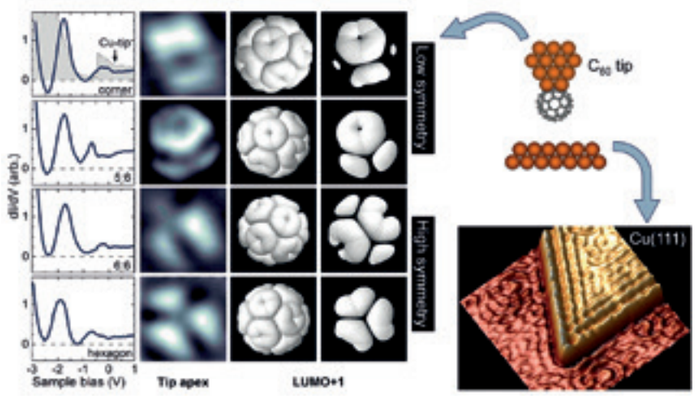


A robust zirconium N-heterocyclic carbene complex for the living and highly stereoselective ring-opening polymerization of rac-lactide, C. Romain, B. Heinrich, S. Bellemin-Laponnaz and S.Dagorne, *Chem Commun*, 2012, ***48***, 2213-2215

Contact: bellemin@unistra.fr

• Engineering Negative Differential Conductance with the Cu(111) surface state

Important advances have been made over the past decades in molecular electronics. Among these is the demonstration that molecules can perform controllable functions such as negative differential resistance or conductance (NDC). First discovered in the Esaki diode, NDC leads to regions in the I-V curve where the current I decreases (increases) with increasing (decreasing) voltage V. Early atomic-scale observations of NDC by scanning tunneling microscopy (STM) have been attributed to narrow energy states in tip and sample, in analogy with the resonant tunneling leading to NDC in semiconductors. In principle, resonant tunneling via molecular orbitals also leads to NDC in single molecules, but progress in this direction has been hindered by the lack of microscopic control over electrode and molecule status.



Measurements are carried out with a C_{60} tip positioned above a pristine Cu(111) surface. Tip status is monitored through "counter images" of the tip apex, which allow determining the exact orientation of the C_{60} molecule. An NDC is observed below the LUMO+1 resonance of C_{60}. High-symmetry orientations inhibit NDC occurrence contrary to the low-symmetry orientations.

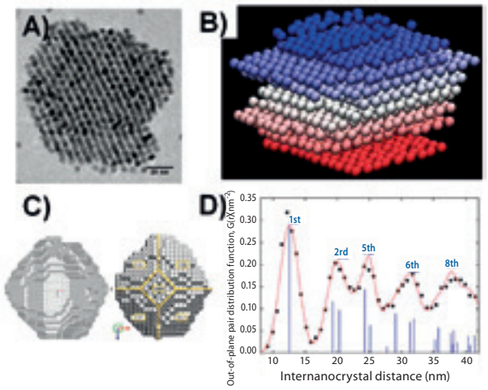
In this study, we report the occurrence of single-molecule NDC with a C_{60}-terminated tip (see figure). By attaching a molecule to the tip of a low-temperature STM (4.6 K) an increased control is gained over the entire tunnel junction. This method allows exploring the NDC occurrence with well-defined pristine metal surfaces serving as a counter-electrode. We have demonstrated that NDC can be produced by electron tunneling between a molecular orbital of the tip and a two-dimensional electron gas hosted by the copper surface—the Shockley surface states of Cu(111). In this calibrated setup, NDC may be tuned by varying the barrier thickness or by changing the C_{60} orientation up to complete extinction. Our study demonstrates that molecular orbitals act as angular momentum filters to the tunneling process, leading, in particular, to NDC if accurately matched with the local orbital symmetry of the surface states. These findings should simplify NDC engineering at the atomic scale. ■

B. W. Heinrich, M. V. Rastei, D.-J. Choi, T. Frederiksen, L. Limot, *Phys. Rev. Lett.* ***107***, 246801 (2011)

Contact : limot@ipcms.unistra.fr

• Electron tomography analysis of Pt nanoparticle superlattices

This work focuses on the 3D spontaneous arrangement of individual platinum nanocrystals having a size of about 5 nm as superlattices. 3D information in the real space on these structures has been obtained using electron tomography. Performing tomography in the bright-field TEM mode allowed investigating the short and long-range ordering of the nanoparticles packed as self-organized supercrystals. Systematic fcc pilings were observed with a mean lattice parameter measured to be 19.5 nm, the nature of the arrangement being controlled by the truncated octahedral morphology of the platinum nanocrystals and the associated steric effect. A numerical 3D quantitative analysis of the ordering characteristics of the superlattice with a one nanometer resolution has been performed that, for the first time, showed a direct correlation between single entities' characteristics and their ordering as periodic arrays. Using a precise PDF analysis, it has been shown that the lattice parameter is different in two orthogonal directions of the fcc structure, which indicates the presence of a slightly compressed superlattice. Inside the superstructure, vacancies and axial defects were observed that do blur the occurrence of potential collective effects from the supercrystals. Our findings strongly underline the benefit and the uniqueness of this kind of multiscale analysis for the characterization of self-assembled systems, where the morphology of the constitutive entities governs their periodic arrangement. ■



Schematic representation of the 3D analysis. A) Classical TEM image. B) 3D image of the Pt superlattice obtained using tomographic reconstruction. C) Nanoparticle faceting deduced from high resolution tomography combined with molecular dynamics simulations. D) Out-of-plane pair distribution function calculated from the tomographic reconstruction.

3D Quantitative Analysis of Platinum Nanocrystal Superlattices by Electron Tomography, I. Florea, A. Demortière, C. Petit, H. Bulou, C. Hirlimann and O. Ersen, *ACS Nano* ***6*** (3) 2574–2581 (2012).

Contacts:
lenuta.florea@ipcms.unistra.fr
ovidiu.ersen@ipcms.unistra.fr

• Spin relaxation near the metal-insulator transition: dominance of the Dresselhaus spin-orbit coupling

The experimentally observed spin relaxation times in n-doped semiconductors are maximal close to the doping-driven metal-insulator transition in the impurity band, reaching hundreds of nanoseconds. Such long times are not only interesting from the fundamental point of view, but also for applications in spintronics and quantum information devices.

In our work, we focus on the metallic side of the transition, with dopant densities just above the critical value, but low enough to keep the impurity band separated from the conduction band. In this regime, the Dyakonov-Perel mechanism relating spin- and momentum relaxation cannot be used to calculate the spin relaxation, such that the long observed lifetimes have remained unexplained during several decades.

We use a model based on electron states localized on the impurities, connected by hopping matrix elements. The presence of spin-orbit coupling leads to hopping matrix elements with and without spin-flip. Based on analytical and numerical approaches, we identify the Dresselhaus spin-orbit coupling as the dominant source of spin relaxation on the metallic side of the metal-insulator transition in the impurity band. The resulting spin lifetimes agree with experimentally observed values for different semi-conductors with zinc-blende structure (see figure p.4). ■