

NEAR FIELD INVESTIGATIONS OF MODEL MATERIALS FOR ORGANIC AND MOLECULAR ELECTRONICS

*B. Grévin*¹

and in alphabetical order M. Brun², R. Demadrille¹, M. Dubois¹, S. Latil³, P. Rannou¹, A. Rubio⁴, L. Scifo¹

¹ UMR5819-SPrAM (CEA-CNRS-UJF) DRFMC CEA-Grenoble, 17 rue des Martyrs 38054 Grenoble Cedex 9 – France. ²CEA/LETI/DIHS, 17 rue des Martyrs 38054 Grenoble Cedex 9, France. ³Laboratoire de Physique du Solide, FUNDP, 61 rue de Bruxelles, B-5000 Namur, Belgium ⁴Dpto. Física de Materiales, Facultad de Químicas, Universidad del País Vasco, Centro Mixto CSIC-UPV/EHU and Donostia International Physics Center (DIPC), 20018 San Sebastian, Spain

benjamin.grevin@cea.fr

Controlling the self-organization and electronic properties of molecular and macromolecular systems on surfaces is amongst the most challenging quests of molecular and organic electronics. To date, scanning tunneling microscopy and its spectroscopic modes (STM/STS), and atomic force microscopy (AFM), have been major tools for local investigations on various π -conjugated molecular and organic systems.

These past years, π -conjugated macromolecular systems have also emerged as a new class of materials which can present both self-assembly and novel electronic features, at the interface between organic and molecular electronics. Especially, some self-organized semi-conducting polymers constitute now model systems, for the realization of π -conjugated molecular nanowires and for fundamental STM investigations on surfaces.

In that frame, we have used regio-regular poly(3-alkylthiophene)s (P3ATs) and related materials for STM and STS investigations of the local electronic properties of self-organized π -conjugated polymer chains. P3ATs sub-monolayer films indeed self-organize into 2D polycrystals on HOPG, where chains are fully packed within mono-domains following a three-fold symmetry, and connected by regular, 60° and 120° folds due to the epitaxy of lateral alkyl groups on graphite. This allows studying the local structure and electronic properties of π -conjugated chains on reference samples where the polymer adopts well defined conformations.

In this communication, STM experiments on new self-organized π -conjugated liquid crystalline macro-monomers and related region-regular alternate copolymers designed with specific molecular and macromolecular engineering considerations will be presented. In comparison with the case of P3ATs 2D crystals self-organized on HOPG, the STM images obtained on the alternate copolymer PDOBTF demonstrate that the incorporation of fluorenone sub-units improve significantly the nanostructure by preventing the chain folding process.

On poly(3-alkylthiophene)s (P3ATs) 2D crystals, we have directly investigated the polymer local electronic states, by performing two dimensional STS imaging at the single chain scale, with the support of theoretical calculations combining *ab initio* with semi-empirical approaches. Simulated spectra in very good agreement with the experimental data have been obtained by a method combining *ab initio* and semi-empirical approaches, which allows a careful discussion of the polymer electronic states. From the experimental data, with the support of modeling, we will show that the STS spectra give a direct access to the polymer semi-conducting bandgap without noticeable charge transfer effects from the substrate. The effective gap reduction displayed by the STS conductance spectra, arises from extrinsic charge screening effects in the tunnelling junction. By performing 2D spectroscopic images at

the single chain scale, it becomes possible to scrutinize the electronic consequences of chain folds and π -stacking effects through spectroscopic contrasts. While chain folds do not locally increase the polymer bandgap more than a few tens of meV, a striking widening of the STS conductance gap is observed in case of electronic tunneling through two interacting polymer layers. Scenarios based on non planar configuration of thiophene cycles within the second layer or variations of the charge screening effects are proposed to explain this phenomenon.

Last, our efforts for developing SPM techniques for new investigations on π -conjugated materials will be described. Especially, a frequency modulation atomic force microscopy (FM-AFM) study using rigid tuning fork on polymer thin film will be presented. The ability of high spring constant tuning fork AFM to image polymeric material and to perform 2D dynamic force spectroscopy will be demonstrated on microphase separated block (PS-*b*-PMMA) copolymer films used in this case as reference samples.

References:

- [1] B. Grévin, P. Rannou, R. Payerne, A. Pron and J.P. Travers *J. Chem Phys* **118** (2003) 7097 [2] B. Grévin, P. Rannou, R. Payerne, A. Pron and J.P. Travers, *Adv. Materials*, **15** (2003) 881 [3] M. Brun, R. Deamdrille, P. Rannou, A. Pron, J.P. Travers and B. Grévin *Advanced Materials*, **16** (2004) 2087 [4] M. Brun, S. Decossas, F. Triozon, P. Rannou and B. Grévin *Appl. Phys. Lett.* **87** (2005) 133101

Figures:

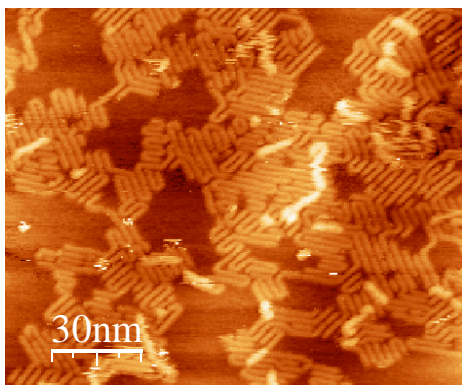


Fig 1. LC-STM image (UHV, 300K) of a sub-monolayer self-organized P3DDT film on HOPG

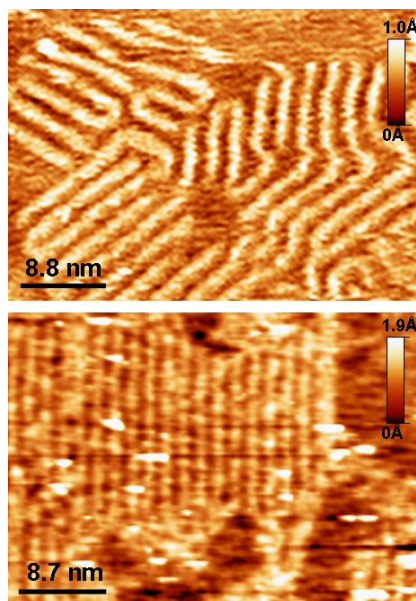


Fig 2. LC-STM images (ambient) of sub-monolayer self-organized P3DDT (top) and PDOBTF (bottom) films on HOPG at the same scale.

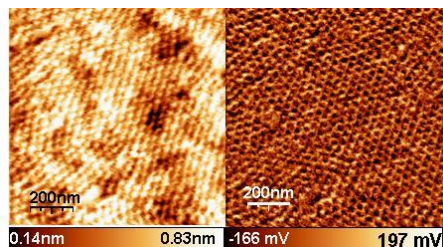


Fig 3. TF-AFM images (HV, 300K) of a PS:PMMA copolymer. Left : topography. Right : dissipation.