ELECTRONIC SUPPORTING INFORMATION FOR

SELF-ASSEMBLY OF SUPRAMOLECULAR WIRES AND CROSS-JUNCTIONS AND EFFICIENT ELECTRON TUNNELLING ACROSS THEM

by Josep Puigmartí-Luis,[a,b] Andrea Minoia,[c] Shengbin Lei,[b] Victor Geskin,[c] Bing Li,[b] Roberto Lazzaroni,[c*] Steven De Feyter[b*] and David B. Amabilino[a*]

[a] Institut de Ciència de Materials de Barcelona (CSIC), Campus Universitari de Bellaterra, 08193 Cerdanyola del Vallès, Catalonia, Spain, E-mail: amabilino@icmab.es

[b] Katholieke Universiteit Leuven, Laboratory of Photochemistry and Spectroscopy, and INPAC-Institute for Nanoscale Physics and Chemistry, Celestijnenlaan 200-F, 3001 Heverlee, Belgium, E-mail: steven.defeyter@chem.kuleuven.be

[c] Service de Chimie des Matériaux Nouveaux, Université de Mons, 20, Place du Parc, B-7000 Mons, Belgium, E-mail: roberto.lazzaroni@umons.ac.be

Materials

The isomers of **1** were prepared and separated as reported previously (J. Puigmartí-Luis, A. Minoia, A. Pérez del Pino, G. Ujaque, C. Rovira, A. Lledós, R. Lazzaroni and D.B. Amabilino, *Chem. Eur. J.*, 2006, **12**, 9161-9175). The ester derivative **2** was prepared using a similar route, although the isomers were not separable by silica gel chromatography.

Scanning tunnelling microscopy and Scanning tunnelling spectroscopy methods

To study the assembly of the molecules on the surface, the compounds were dissolved in octanoic acid, and a drop of the solution was placed on freshly-cleaved highly oriented pyrolitic graphite (HOPG). Scanning tunnelling microscopy (STM) was performed by lowering the tip into the solution until the system formed a tunnelling junction and then imaging by scanning at the liquid/solid interface. The presented STM images were acquired with three different STM devices all them under ambient conditions: (a) In the variable current mode (constant height) by using a Discoverer scanning tunnelling microscope (Topometrix Inc. Santa Barbara, CA) with a typical frame acquisition time of 7s, along with an external pulse/function generator (model HP 8111 A). (b) with a a PicoSPM (Agilent) and (c) with Nanoscope IV (Digital Instruments, Santa Barbara, USA) both of them working in the variable height mode (constant current).

Some of the tips were etched electrochemically from Pt/Ir wire (80%/20%, diameter 0.2 mm) in a 2N KOH/6N NaCN solution in water and others were cute mechanically, with no apparent difference in the results. The experiments were repeated in several sessions using different tips to check for reproducibility and to avoid artefacts. Note that during the experiments, the STM tip is immersed in the supernatant solution. Different settings for tunnelling current and the bias voltage were used during the imaging, ranging from 0.7 nA to 1.5 nA and +1.2 to -1.0 V. All STM images contain raw data and are not subjected to any manipulation or image processing.

The Scanning tunnelling spectroscopy (STS) measurements presented were performed using either a Multimode Nanoscope IV (Digital Instruments, Santa Barbara, USA) or a PicoSPM (Agilent). Current-voltage sweeps were acquired with the feedback loop open with the STM tip located over the crossing points of 1 at the multilayers. The curves were measured in stable layers when the drift between the tip and the sample was negligible. Each curve was recorded using anodic and cathodic sweeps, and only those which produce the best signal-to-noise ratio and the ones which we could obtain clear STM images again after the STS measurement where considered for the analysis.

Atomic force microscopy

AFM samples were prepared by drop-casting method. Briefly, a drop of TTF solution dissolved in octanoic acid with a concentration of 1.0×10^{-8} M was applied to a freshly cleaved HOPG surface. After keeping in a sealed glass vial overnight, the samples were heated dry at 70 °C on a hotplate for 3 hours. The AFM measurements were carried out by using a Multi-mode SPM (DI) with an E scanner. All the images were obtained in tapping mode in ambient air condition.

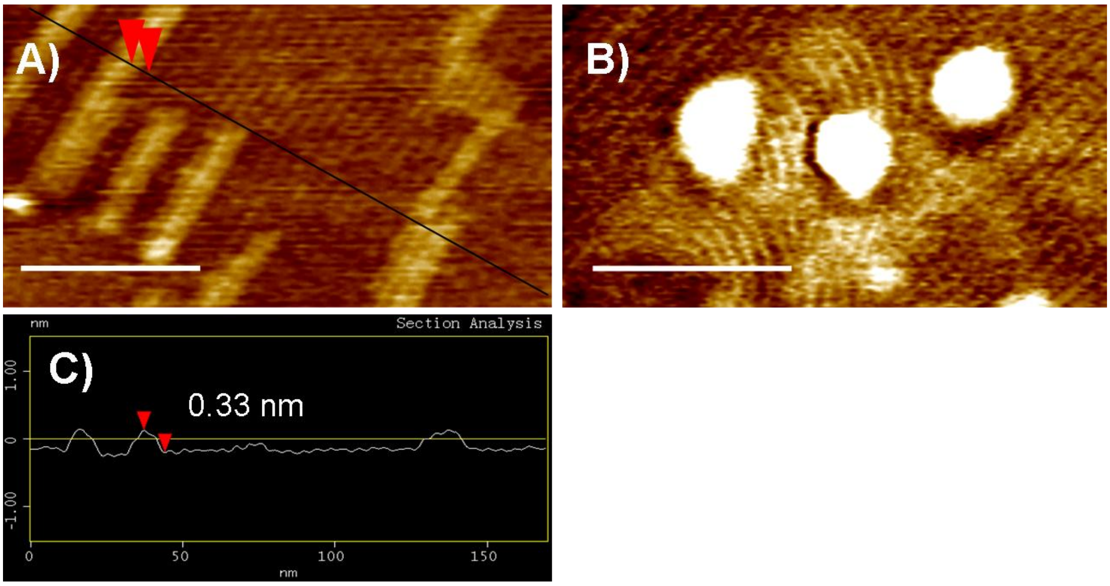

Figure 1. AFM height images of self-assembled cis-1 monolayer and multilayer on HOPG surface. A) The multilayer cis-1 lamella runs co-parallel on top of the monolayer. B) Multilayer cis-1 lamella crossings on top of the monolayer. C) Height profile measured along the line in Figure 1A. The height difference between the monolayer and the center of the multilayer is 0.33 nm. Scale bars: *50 nm.*

Modelling

The force field calculations have been carried out using the molecular modeling package TINKER 4.2, [Tinker molecular modeling package: http://dasher.wustl.edu/tinker/.] using the Tinker implementation of Allinger's MM3 force field.[B. Y. Ma, J. H. Lii, and N. L. Allinger, *J. Comput. Chem.*, 2000, **21,** 813–825.] Periodic boundary conditions have been applied to the orthorhombic simulation cell. The size of the simulation box has been tuned on the size of the substrate, in order to represent an infinite surface of graphite, avoiding edge effects. The cut-off for the non-bonded interactions has been set at 1.2 nm and a Particle Mesh Ewald method has been used to treat the electrostatic interactions. To keep the computational effort to a tractable level, the substrate has been frozen, i.e., all the atoms of the surface have fixed position throughout the simulation runs. This is a reasonable assumption since the molecular physisorption is not expected to affect the substrate surface. All simulations have been carried out in the NVT ensemble. The system was maintained at constant, room temperature with an Andersen thermostat (a coupling constant of 0.5ps^{-1} was used).