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Noncovalent Control for Bottom-Up Assembly of Functional Supramolecular Wires

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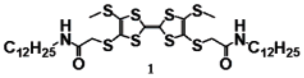
The creation of circuits at the nanoscale is important for miniaturization of electronic devices.[1] Candidate components for the wires in the circuits are generally considered to be conventional metals[2] or carbon nanotubes.[3] We report here preparation of supramolecular wires[4] using a bottom-up[5] and conceptual alternative to these strategies, using organic molecules which are self-assembled[6] at a surface under ambient conditions in a liquid. The wire-like system shows a small experimental conductance gap, and quantum-chemical calculations predict favorable charge transport along the π-electron-rich cores.

To emulate at the nanoscale the stacks of organic molecules that can behave as conductors and superconductors in a crystalline environment,[7] we chose tetrathiafulvalene (TTF) as the functional component. These π-electron-rich units stack flat on the graphite surface in absence of strong intermolecular interactions.[8] We have introduced amide functional groups in the structure to generate hydrogen bonded chains[9] to modify the molecular orientation and create one-dimensional assemblies. Scanning tunneling microscopy (STM) was used to image the molecules at the graphite−liquid interface, and scanning tunneling spectroscopy (STS) was used to probe the electronic behavior of the system.

The STM images of physisorbed layers of compound **1** (see Supporting Information) show equally spaced continuous lines of high tunneling current, indicative of the formation of supramolecular fibers at the surface (Figure 1). Distances between fibers are 4.65 ± 0.15 nm, approximately the length of one extended molecule of **1** (4.5 nm). The repeat distance between TTF units within a fiber was found to be approximately 0.44 ± 0.03 nm, in good accord with an X-ray structure of a related molecule with one amide group.[10] On occasions, as in the lower image in Figure 1, the alkyl chains are visualized. Their long axis forms an angle of 17(±1)° to the π-electron-rich core.[11] These observations indicate that the planes of the TTF moieties are not parallel to the HOPG surface, but are tilted up with stacking between them at a high angle to the plane.

Molecular modeling of several columnar stacks of **1** with molecular mechanics (MM) shows that, among the stable structures found, those in which both π−π interactions and hydrogen bonding are both operative give rise to straight, regular stacks with the TTF units parallel to each other. To address the issue of the molecule−molecule versus molecule−substrate interactions, two different types of stacks on the graphite surface were modeled, examining their behavior in time at room temperature with molecular dynamics (MD; see Supporting Information).



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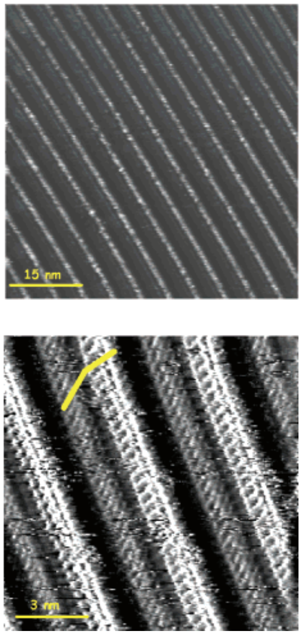

Figure 1. STM images of **1** at the HOPG−octanoic acid interface (top, $I_{\text{set}} = 0.45$ nA, $V_{\text{bias}} = -0.463$ V; bottom, $I_{\text{set}} = 1.5$ nA, $V_{\text{bias}} = -0.322$ V, where the lines indicate the angle formed between alkyl and TTF moieties).

A stack of the unsubstituted TTFs, that is, without amide groups, breaks up, and the molecules are spread on the surface, adsorbed flat because of the strong interaction of the TTF with the π-system of graphite. In contrast, amide-substituted TTF stacks are stable: the planes of TTF units remain perpendicular to the surface and parallel to each other, and the hydrogen bonding pattern between the amide groups is preserved. This shows that hydrogen bonding is required to maintain the TTF units in a π-stacking configuration.

Two hydrogen bonds are necessary (and sufficient) to maintain π-stacking.[12] A model for two parallel stacks of **1** on the surface (Figure 2) has an orientation (quasi perpendicular to the surface) and intermolecular distance in good agreement with that measured in the STM images (0.44 nm, dashed line and solid line parallel to stacks in Figure 2), as is that corresponding to the distance between stacks (4.4 nm, dashed line perpendicular to stacks in Figure 2).

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10.1021/ja0640288 CCC: $33.50

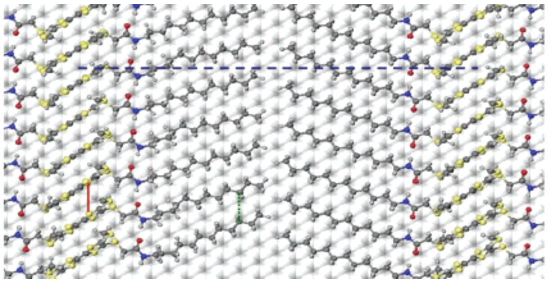

Figure 2. A model of two parallel stacks of **1** on HOPG, after MD/MM simulation.

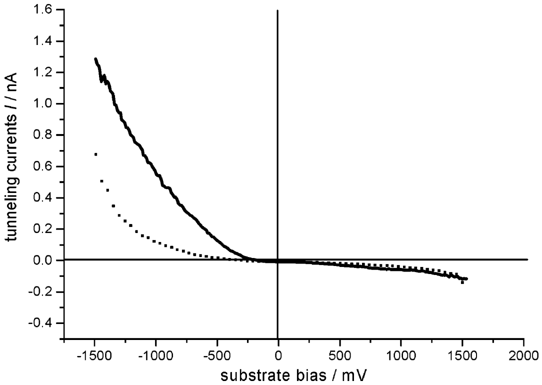

Figure 3. An STS curve of **1** at the 1-octanoic acid−HOPG interface (solid line, average of 56 spectra recorded with the tip located above the TTF moieties in the regular lamellae with set-point value $I_{\mathrm{set}} = 0.5$ nA, $V_{\mathrm{bias}} = -1.03$ V). The dotted line shows a curve recorded in the solvent alone.

Quantum-chemical calculations were performed to quantify the electronic coupling between two adjacent molecules in the stack (see Supporting Information). The transfer integral for the HOMO, which is related to the capacity for hole transport,[13] was computed to be 134 meV, and for the LUMO, which is related to electron transport, it was 111 meV. This indicates a strong interaction between the π-systems of the molecules. According to Hückel theory, for an infinite one-dimensional stack, the width of the valence band and conduction band is equal to 4 times the transfer integral associated with the HOMO and LUMO levels, respectively, that is, 0.54 and 0.44 eV. These large bandwidths show that those TTF stacks can act as molecular wires for both hole and electron transport.[14]

The electronic properties of the aggregates of **1** at the interface of HOPG and 1-octanoic acid were probed by STS (see Supporting Information), an established approach for probing local electronic behavior in physisorbed systems.[15] Although the method does not probe transport laterally, it proves increased density through π-stacking systems[16] and thus wire-like character. Current−voltage sweeps were performed with the feedback loop open, with the STM tip located either over the TTF moieties of **1** in fibers or in areas of the layer where the alkyl chains are present. An averaged $I(V)$ curve obtained above the TTF moieties is shown in Figure 3. The curve shows a clear rectifying effect: The current at negative potentials is approximately 10 times that at positive ones for a bias of 1 V. A small experimental conductance gap—the horizontal part of the curve around zero potential—is observed. In conjunction with the theoretical results,[17] the STM data indicate that the fibers are capable of acting as supramolecular wires because the small experimental conductance gap is in line with the theoretical calculations which reveal strong π-interactions and large bandwidths (see above).

Compound **1** forms monolayer domains in which the TTF units form a thermodynamically stable wire-type supramolecular structure, without the need for external reagents or manipulation. The parallel arrangement of the TTF moieties leads to a small experimental conductance gap, an observation which bodes well for their use as a connecting organic electronic fiber in atmospheric conditions. The molecule thus proves itself a useful component for bottom-up nanofabrication and shows that self-assembly of molecules to form supramolecular wires is a viable way for preparing nanometer scale circuits.

Acknowledgment. We thank W. Mamdouh for help with STM and STS, V. Lemaur, D. da Silva Filho and J.-L. Brédas for their help in the quantum-chemical calculations. This work was supported by the PGC-DGI (Spain, BQU2003-00760), DGR, Catalonia (2001SGR00362 and JPL grant associated with Fundacio ICN), 6FP NAIMO Integrated Project (NMP4-CT-2004-500355), the Marie Curie RTN CHEXTAN (MRTN-CT-2004-512161), FNRS, FWO, and PAI-V-03 (Belgium). JC in an FNRS fellow.

Supporting Information Available: Synthesis and characterization of **1**, STM and STS measurements, and molecular modeling. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0640288