

Bottom-up assembly of high density molecular nanowire cross junctions at a solid/liquid interface†

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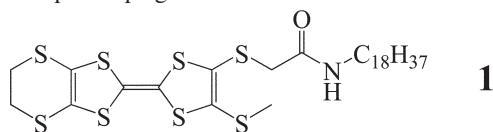
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A monoalkylated tetrathiafulvalene derivative forms multilayer structures at the solid–liquid interface, with high density of cross junctions, which are interesting for molecular electronic circuit self-assembly.

The self-assembly of organic molecules is an attractive approach for the formation of supramolecular systems with possible exploitation as electronic devices.¹ The preparation of fibres of molecules to give supramolecular columns has been proven in the past, with various systems displaying these kinds of one dimensional stacks.² Tetrathiafulvalene (TTF) derivatives are very relevant in this respect, because of their proven function in systems displaying efficient electrical transport. One such derivative self-assembles at a liquid–graphite interface giving fibres,³ instead of a ‘flat-on’ arrangement of the TTF moieties on the surface, thanks to the formation of two amide intermolecular hydrogen bonds on both ends of the π -functional unit. This situation results in significant intrastack intermolecular interactions. However, it is far more challenging to find systems that will assemble beyond this first dimension. If this can be done, the way is paved for the bottom-up assembly of molecular circuits.⁴

In this work we investigate the assembly of the TTF derivative **1**, with only one side-chain containing an amido group.⁵ We will show, *via* an STM study, that this compound adsorbs in a head-to-head and tail-to-tail manner, and with the aid of intermolecular hydrogen bonds, the TTF moieties are also tilted at a high angle from the surface forming π -stacks. More interestingly, polymorphous multilayer adsorption is observed and high density cross junctions of the supramolecular fibres are formed reproducibly. These results are interesting regarding the organisation of the compound, which gels organic solvents and gives conducting nanofibres upon doping.⁵



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Almost immediately after deposition of a solution of **1** in octanoic acid onto highly oriented pyrolytic graphite (HOPG), STM† images were obtained at the solid–solvent interface. Lamellar structures were observed in large areas for both the original (1 mg ml⁻¹) and diluted (0.02 mg ml⁻¹) solutions (Fig. 1a). These lamellae—composed of bright bands and dark troughs—extend most frequently along the three symmetry-related directions

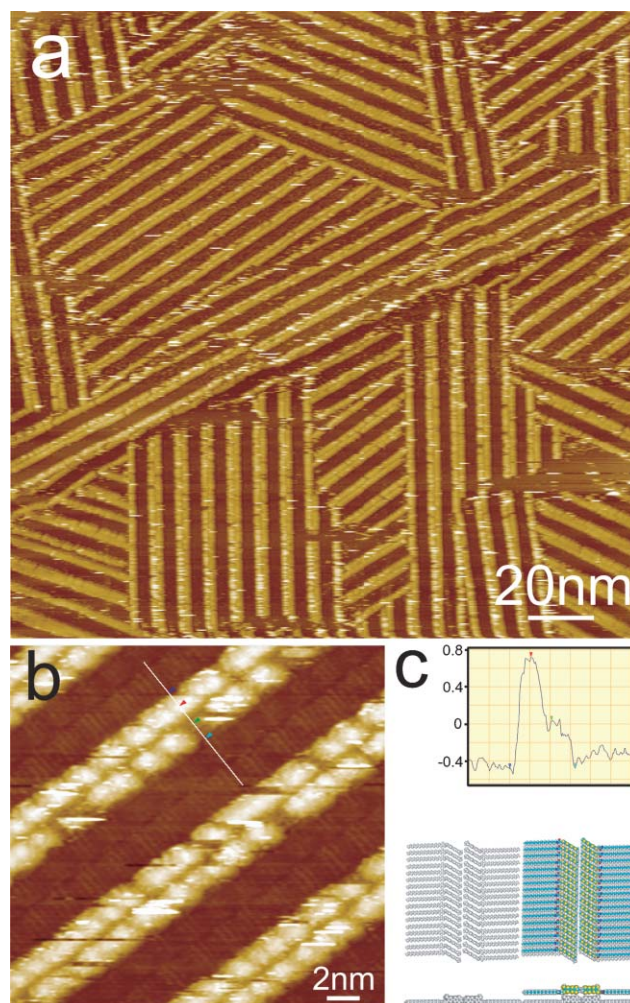


Fig. 1 STM images (–1.30 V, 356 pA for (a) and –1.30 V, 79 pA for (b)) of the TTF derivative **1** obtained at the octanoic acid–HOPG interface. The cross section profile (c, upper part) along the line marked in image b clearly indicates multilayer formation. A tentative model for the assembly is shown in the lower part of (c).

of the substrate, *i.e.* the $\langle -1\ 1\ 0\ 0 \rangle$ direction. The interlamellar distance is measured to be about 8 nm, with the bright bands estimated to be 3.6 nm and the dark troughs 4.4 nm in width. Taking into account the length of the TTF units (1.3 nm) and the aliphatic tail (2.6 nm), the bright band is attributed to a double row of TTF moieties, with the molecules packed head-to-head and tail-to-tail. The alkyl chains are observed to orientate nearly perpendicularly to the lamellae axes and the distance between adjacent TTF moieties is estimated to be 0.45 nm.³ This distance indicates that the TTF moieties are strongly tilted away from the surface of the basal plane of HOPG (0001), *i.e.*, they are in an 'edge-on' arrangement.

The pattern shown in Fig. 1 is in fact a double layer in which the double-strand lamellae of the second layer are exactly on top of and coparallel with the bottom one. The cross section of the image in Fig. 1b, where a few molecules in the top layer have been removed by the scanning tip, shows clearly this double layer characteristic (Fig. 1c). The apparent height of the TTF moiety in the double layer and monolayer is estimated to be 1.2 and 0.5 nm, respectively, in this image. The height corresponding to a monolayer of π -stacked TTF moieties within a fibre could vary in the range from 0.3 to 0.6 nm, depending on the imaging conditions, leading to an average value of 0.4 ± 0.1 nm. The width of individual TTF strands is estimated to be 1.8 and 1.5 nm for the double and monolayer, respectively. Defects in the TTF strands (holes) are attributed to the STM-tip induced removal of molecules.

Of particular interest for the assembly of this TTF derivative is the high density of lamellae cross junctions, indicating clearly that the self-assembly process favours multilayer rather than monolayer formation. This situation leads to relatively complicated multilayers which are imaged with various contrast levels (Fig. 2 and 3). In these particular images four different contrast levels can be distinguished, which is supported by the profile across the lines marked in Fig. 2 and 3. The difference in the apparent height between the contrast or height levels is 0.4 to 0.5 nm, in agreement with the apparent height of the tilted TTF moieties measured from Fig. 1. This observation indicates clearly that the bright double-stranded features with different contrast observed in the images should be attributed to tilted TTF moieties in different layers. Assuming that the lowest contrast features observed in these images are the alkyl chains in the bottom layer, at least three layers of tilted TTF strands are imaged.

Careful inspection reveals two main categories of TTF strand orientations with respect to the layer underneath: parallel and cross junctions. In the parallel category, the top lamellae of TTF double strands either run side by side with the TTF strands underneath, or half overlap the one underneath (as indicated in Fig. 2a as A and B). In the cross junctions category, in most cases the top TTF strands cross the layer underneath at an angle of $60/120^\circ$, an observation accounted for by the three fold symmetry of the substrate and the preferred adsorption of the alkyl chains along the main lattice axes $\langle 1\ 1\ -2\ 0 \rangle$ of HOPG.⁶ This orientation indicates that overlaying fibres are able to propagate over domain boundaries through the formation of hydrogen bonds and collaborating non-covalent interactions in the chain, rather like a directionally growing supramolecular polymer. However, in some other cases the top TTF strands cross the layer underneath at angles deviating by 8° to 30° from the substrate induced typical

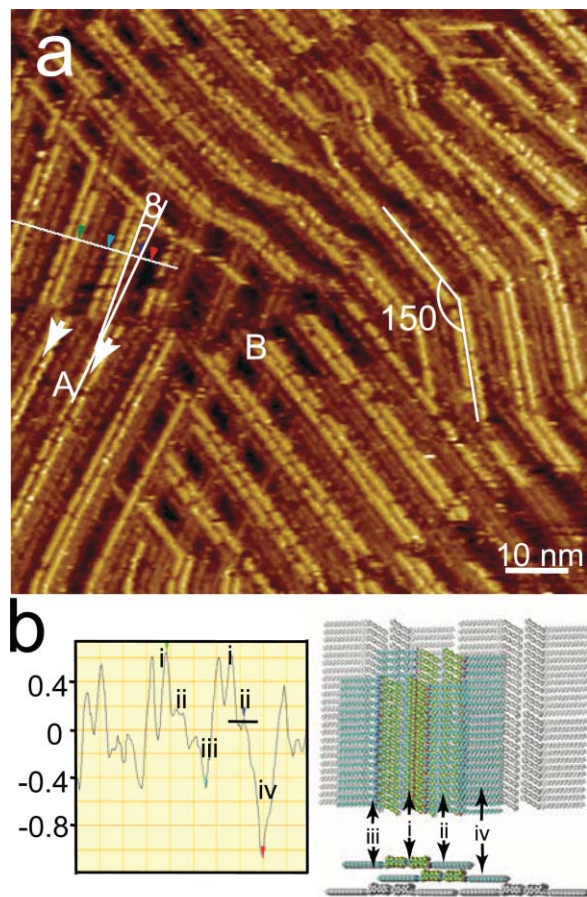


Fig. 2 An STM image showing TTF multilayer formation. Four different contrast levels are observed in the image, appreciated more clearly in the section profile shown in (b). The alignment of the TTF strands with respect to the layer underneath can be classified into two categories: Parallel and cross junctions, as marked in the image as A and B. The two white arrows mark two TTF double-strands aligned with slightly different distance with respect to the one in the layer underneath. A simplified tentative model of the parallel multilayer structure is shown in the lower part of (b). Imaging conditions: -1.02 V, 356 pA.

crossing angles. Moreover, double-strand lamellae even split into single strands (upper half Fig. 2a): This feature highlights the weakness of the van der Waals interactions between the two head-to-head TTF strands.

We also noticed that even in the parallel configuration, the lateral distance between the TTF strands in the top and lower layers could vary slightly (Fig. 2a, indicated by white arrows). The perpendicular orientation of the alkyl chains with respect to the long axis of the TTF moiety—as observed in Fig. 1b—is probably not the only possible situation. TTF derivatives containing an amide functionality on both sides have their alkyl chains tilted with respect to the stacking direction.³ Molecular dynamics simulations indicate that assemblies with tilted or perpendicular orientations of the alkyl chains are both stable and the energy difference between the two situations is not significant for TTF derivative 1.† Therefore, small differences in the lateral distance between TTF strands in the top and underneath layers probably reflect different orientations of the alkyl chains with respect to the stack axis.

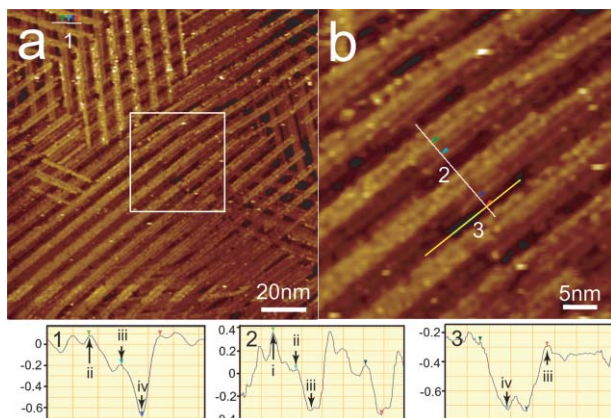


Fig. 3 Cross structures observed upon assembly of **1**. Image b is a zoom-in of the marked area in the image a. Below the images are section profiles along the lines marked 1 (in a), and 2 and 3 (in b). Different levels of contrast can be seen in the image indicating the formation of multilayers. Image condition: -1.05 V, 258 pA.

These layers are dynamic too: cross junctions are observed with very high density at the initial stage of the assembly process, while parallel configurations are more frequently observed afterwards. The interactions between the molecules in different layers are considered to be mainly van der Waals. These interactions include the interactions between aliphatic chains, between aliphatic chains and TTF moieties, and between TTF moieties in the same or different layers. Solid state studies of TTF derivatives and their salts indicate that S \cdots S interactions between the TTF moieties in different layers in crystals is a significantly attractive force,^{7–9} and this interaction is important for conductivity in many of the compounds. This relatively strong interaction favours the parallel configuration of the π -stacked TTF fibres with those in the layer underneath, and may explain the observed dynamic process at the interface. Even so, cross junctions can still be observed several hours after deposition.

It is interesting that the interaction between supramolecular fibres governs the formation of the multilayer structure. We are only aware of one other type of molecule which display this property: squaraine dyes, where the electrostatic interaction between the betainic units is surely important in the formation of the multilayers.¹⁰ In the present case, the much weaker interaction between sulfur atoms is apparently enough to promote the growth of ordered multilayers.

In summary, the monoalkylated TTF derivative **1** forms multilayer structures at the 1-octanoic acid–graphite interface. One single amide functionality is sufficient to force π -stacking of the TTF moieties *via* intermolecular hydrogen bonding and to overcome the intrinsic tendency of TTF moieties to adsorb flat on the graphite substrate. This side-on interaction between the TTF moieties is of prime importance to encourage hierarchical growth. Once initiated in the over-layer, the fibres are able to propagate over the domain boundaries of the underlayer, showing characteristics of a supramolecular polymer. The system reported here is one of the very rare cases of directional multilayer growth at a dynamic solution–solid interface. The joining and separation of the fibres next to each other and on top of each other may provide a

very accurate molecular level model of the crossing of fibres in the gel state,⁵ and in our opinion is of interest in the design of supramolecular electronic systems.

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Notes and references

‡ For STM measurements compound **1** was dissolved in octanoic acid with a concentration of about 1 mg ml⁻¹ or 0.02 mg ml⁻¹; STM characterization of the surface confined self-assembled TTF structures was carried out by applying a drop of the above solution on a freshly cleaved graphite substrate (HOPG, grade ZYB, Advanced Ceramics Inc., Cleveland, USA) using a PicoSPM (Agilent) operating in constant current mode at room temperature. Pt–Ir (80 : 20) tips were prepared by mechanical cutting.

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