Synthesis, separation, and isomer-dependent packing in two dimensions—detected by scanning tunnelling microscopy—of a TTF derivative

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The synthesis, isolation and STM imaging on graphite of the *cis* and *trans* isomers of a TTF reveal isomer-dependent packing, and constitutes a way to study the non-covalent interactions at play in these systems.

The packing of molecules in three dimensions has profound influences on their properties,[1] and the design and control of the arrangement of molecules in solids is an important and challenging area of research.[2] In principle, control over the packing of molecules in two dimensions is simpler.[3] This challenge is particularly motivating when considering the importance of molecules and nanometre-scale aggregates of them in the area of molecular electronics.[4] In this respect, we are interested in the self-assembly of derivatives of tetrathiafulvalene (TTF) on graphite, their visualization by scanning tunnelling microscopy (STM),[5] and the effects of the substitution of these compounds on the interactions between them. Here, we report synthesis and separation of the *cis* and *trans* isomers of **1** (Figure 1) and show that the use of one or the other leads to very different two-dimensional packing because of the substitution pattern on the TTF moiety.

Synthesis of **1** was achieved through the route shown in Scheme 1. Starting from the known bis(2-cyanoethyl)-1,3-dithiol-2-one (**2**)[6] and using the mono-deprotection strategy established by Becher and colleagues,[7] followed by alkylation of the intermediate caesium salt[8] with octadecyl bromide, the thione **3** was isolated. After conversion of this compound to the corresponding ketone **4** and coupling in trimethyl phosphite the mixture of isomers of **1** was isolated. The chromatographic separation of this type of *cis/trans* isomers of TTFs is not at all trivial,[9] but on this occasion we were able to isolate the two by flash column chromatography on silica gel. Great care has to be taken with the solvents to avoid any traces of acid that can catalyse isomerisation.[10] The isomers were clearly distinguished by NMR spectroscopy, although they give the same number of resonances because of their C_{2v} and C_{2h} symmetries (Fig. 1), while other spectroscopic characteristics are identical for the two compounds. Their assignment was made appealing
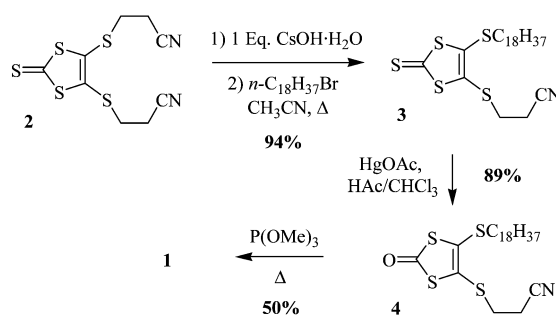
Scheme 1 Synthesis of the mixture of isomers of **1**.

to polarity arguments, the first-eluted material from the column was therefore supposed to be the *trans* isomer. STM experiments support this assignment. Prior to imaging, *trans*-**1** and *cis*-**1** were dissolved in 1-octanol or 1-phenyloctane (Aldrich, 99%), and a drop of solution was placed on freshly-cleaved graphite. STM images were acquired in the variable current mode (constant height) under ambient conditions. In the STM images, white corresponds to the highest and black to the lowest tunnelling current.‡

A monolayer of *trans*-**1** in 1-octanol spontaneously physisorbs at the liquid–graphite interface (Fig. 2a–c) as STM imaging reveals. Two polymorphs are observed, nominated α and β, and in both the molecules are organized in a lamellar (or tape-like) structure. The TTF moieties (cores) in the middle of the lamellae (red arrows in 2a) appear as bright bands corresponding to high tunneling current, in accord with their π-electron rich nature. Packing analysis of the α polymorph indicates that the cores are lying flat on the surface, forming an angle of 31 ± 1° with respect to the lamellar axis. The octadecyl chains appear with a darker contrast than the TTF moieties and form an angle of 60 ± 2° with respect to the lamellar axis. The difference in contrast observed for the octadecyl chains located on the left and those located on the right of the TTF moieties is a scanning artefact. The intermolecular distance within lamellae is 8.3 ± 0.2 Å and the distance between equivalent points in abutting lamellae is 36 ± 1 Å. The β polymorph (Fig. 2b and c) has the molecules organized in alternating double-core (red arrows) single-core (yellow arrows) lamellae. In addition, the octadecyl chains are perpendicular with respect to the lamellar axes and are interdigitating. The TTF cores form an angle of 27 ± 2° with respect to the lamellar axis. The intermolecular distance between equivalent molecules in a lamella is 15.2 ± 0.9 Å and the distance between equivalent points on two equivalent lamellae is 84 ± 2 Å. The intermolecular distance did not change (within the experimental error) for molecules in a double-core or a single-core lamella. The alternation between double and single rows can be explained as a result of the constraints imposed by the alkyl chains in order to form a dense 2D packing
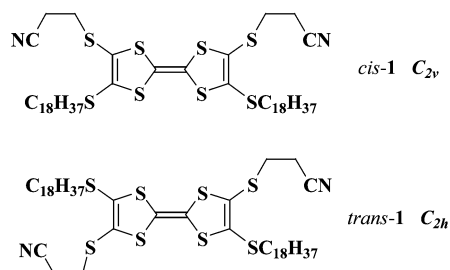

Fig. 1 The isomers of **1** and their symmetries.

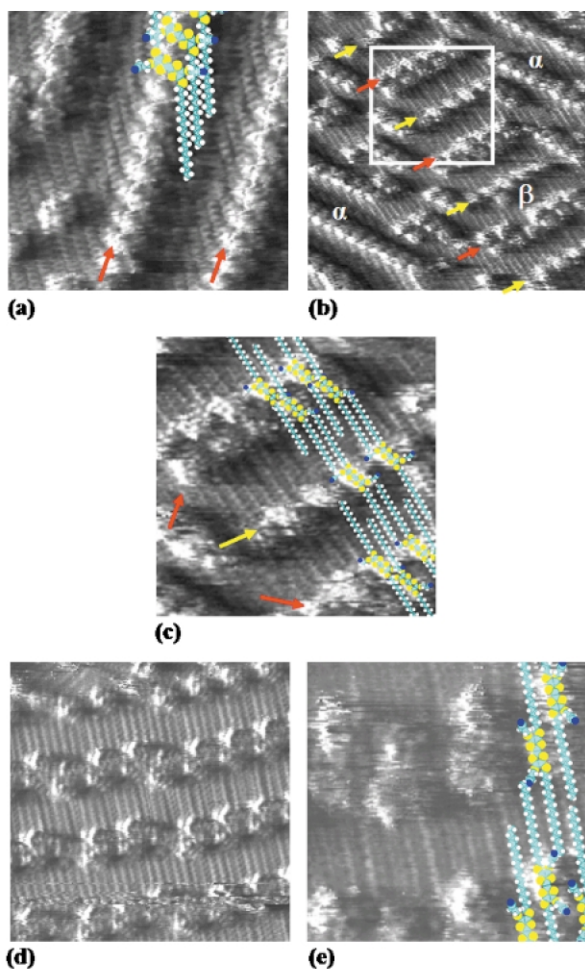† These authors contributed equally to the work described in this paper.

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Fig. 2 STM images at the liquid–graphite interface. (**a**) A monolayer of α *trans*-**1** deposited from 1-octanol. (10×10 nm². $I_{set} = 0.5$ nA, $V_+ = -0.226$ V), (**b**) the same, but 19.5×19.5 nm² ($I_{set} = 0.5$ nA, $V_{set} = -0.294$ V) showing the two different polymorphs. Red arrows indicate double-core lamellae, while yellow arrows indicate single-core lamellae. (**c**) Zoom-in on the area indicated in (**b**). Red and yellow arrows indicate double-core and single-lamellae respectively. Nine molecules are superimposed on the image for clarity (9×9 nm². $I_{set} = 0.5$ nA, $V_+ = -0.294$ V). (**d**) A monolayer of *cis*-**1** (13.8×13.8 nm². $I_+ = 0.9$ nA, $V_- = -0.31$ V). No single-core lamellae are observed. Alkyl chains are interdigitating. (**e**) Monolayer of *cis*-**1** with superimposed molecules for clarity. (6.9×6.9 nm². $I_{set} = 0.8$ nA, $V_{set} = -0.288$ V).

with optimised van der Waals interactions between the alkyl chains. In a double-core lamella (as is the case with the first polymorph) the cyanoethyl groups cannot fully adsorb on the surface. Solvent molecules are probably coadsorbed in the empty spaces available in between the molecules especially in the case of single-core lamella. Thus the solvent is expected to have a strong impact on the formation of the monolayer. When 1-phenyloctane is used as a solvent, no monolayers were observed by STM at the liquid–solid interface. This observation supports the aforementioned assumption of solvent effect.

Upon applying a drop of *cis*-**1** in either 1-octanol or 1-phenyloctane a monolayer is spontaneously formed at the liquid–solid interface (Fig. 2d). A lamellar structure is evident. Images—with similar contrast to the *trans* isomer—are again submolecularly resolved, allowing the identification of the different parts of the molecules. The alkyl chains are perpendicular to the lamella axis and are interdigitating. No single-core lamellae were observed for monolayers of *cis*-**1**. Fig. 2e shows an image of a monolayer of *cis*-**1**, where the cores and the alkyl chains can be clearly distinguished. The intermolecular distance between equivalent molecules in a lamella is 17.8 ± 0.9 Å and

the distance between equivalent points in abutting lamellae is 34.6 ± 1.5 Å. Modelling shows that in the case of the *trans* isomer, if the molecules pack in abutting double rows (as in case of the *cis* isomer) the distance between such double rows would be larger compared to that of the *cis* isomer packing, which would lead to less optimised van der Waals interactions between the alkyl chains. It must be stressed that for both isomers, the alkyl chains observed in the STM images have a 1 : 1 ratio with respect to the number of cores. Thus, all the alkyl chains are fully adsorbed onto the graphite surface in a fully extended *anti* conformation.

The separation of *cis* and *trans* isomers of **1** has allowed their definitive identification at the liquid–solid interface by their characteristic packing patterns. While TTFs in crystals have packing dominated by π–π stacking and S···S side-on interactions,[11] on the surface of graphite, the former is ruled out because of the preferential π–π stacking of the TTF moieties with the π system of the substrate, aided and abetted by C–H–π interactions between the aliphatic substituents and graphite's aromatic rings. The solvent plays an important role in stabilizing the monolayers. We also note the interest in modifying the cyanoethyl protecting group to incorporate hydrogen bonding moieties which could help in the organisation at the surface. The information obtained from this study will be important in the design of related systems for molecular electronics.

Notes and references

‡ STM experiments were performed as described in ref. 5, with negative sample bias. Different settings for the tunneling current and the bias voltage were used. The experiments were repeated in several sessions using different tips to check for reproducibility and to avoid artifacts. All STM images contain raw data and are not subjected to any manipulation or image processing.

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