Electronic Supplementary information

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

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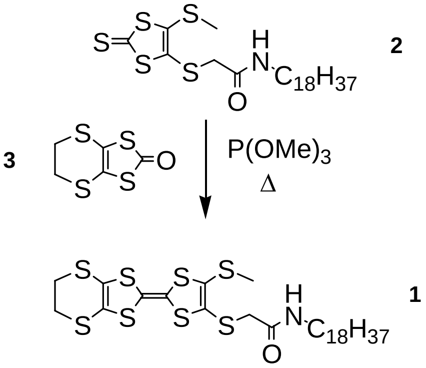
1. **Synthesis and characterisation of 1.**

Compound **1** was prepared by the coupling of equimolar amounts (0.57 mmol) of thione **2** (J. Puigmartí-Luis *et al.*, *Chem. Eur. J.*, **2006**, *12*, 9161-9175) and oxo-derivative **3** (J. Becher *et al.*, *J. Chem. Soc.*, *Chem. Commun.*, **1994**, 2715, N. Svenstrup and J. Becher, *Synthesis*, **1995**, 215) in boiling and pre-dried (over sodium) trimethylphosphite (6 ml), under an atmosphere of argon for 12 hours. The solvent was removed and the residue was purified by column chromatography (silica, CH_2Cl_2/EtOAc 95:5) to give 114 mg (29%) of the product as an orange solid.



The compound was characterised as before (*Angew. Chem. Int. Ed.*, **2006**, *46*, 238-241), details are given here for convenience: mp 104.4 ºC (DSC). LDI-TOF/MS m/z (%): 681.1 (M+, 100); FT-IR (KBr): 3301 (m, NH), 2916 (f), 2849 (s), 1645 (s, CONH), 1551 (m, CONH), 1471 (w), 1410 (w), 1289 (w), 1145 (w), 885 (w), 772 (w), 718 (w), 648 (w, NH) cm^{-1}; ^{1}H-NMR (250 MHz, $CDCl_3$): 6.74 (s, 1H, -$SCH_2CON\underline{H}$-), 3.49 (s, 2H, -$SC\underline{H}_2CONH$-), 3.30-3.23 (m, 6H, -$C\underline{H}_2(CH_2)_{16}CH_3$, -$SC\underline{H}_2C\underline{H}_2S$-), 2.46 (s, 3H, $SC\underline{H}_3$), 1.30-1.20 (m, 32H, -CONH $CH_2(C\underline{H}_2)_{16}CH_3$), 0.88 (t, J = 5.9 Hz, 3H, -$CH_2(CH_2)_{16}C\underline{H}_3$) ppm. ^{13}C-NMR- (62.8 MHz, $CDCl_3$): 166.5 (-CONH-), 113.7, 111.7 (C=C), 40.1 (-SCH_2CONH), 39.3 (-SCH_2-), 31.9, 30.2, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 29.3, 27.0, 22.7 (-$NH(CH_2)_{17}CH_3$), 19.4 (-SCH_3), 14.1 (-$NH(CH_2)_{17}CH_3$) ppm. Elemental analysis for $C_{29}H_{47}NOS_8$ Calc: C. 51.06; H. 6.94; N. 2.05. Found: C. 50.95, H. 6.88, N. 1.96.

2. STM imaging

For STM measurements compound **1** was disolved in octanoic acid with a concentration of about 1 mg/ml or 0.02 mg/ml; 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.

3. Molecular modeling

Molecular modeling calculations were performed using the molecular code package TINKER 4.2 with a force-field based on MM3(2000). All the molecular dynamics (MD) simulations were performed in the NVT ensemble at room temperature (RT), considering trajectories 100ps long (with time steps of 1 fs). MD frames were recorded each 0.5 ps (500 steps) and used to perform statistics. The first 25 ps were considered as equilibration time and the corresponding data were discarded from the statistical analysis. Two-dimensional periodic boundary conditions (2D PBC) were applied to the molecular layers adsorbed on the graphite surface.

Two monolayers that differ in terms of the alkyl chain orientation with respect to the lamella axis, which are called tilted and extended model respectively, were considered. Two adjacent lamellae of 20 molecules each have been included in the model. It is important to point out that this difference in the orientation of the alkyl chains affects the inter-lamellae distance. Figure S1 shows the tilted model (a) and the extended one (b).

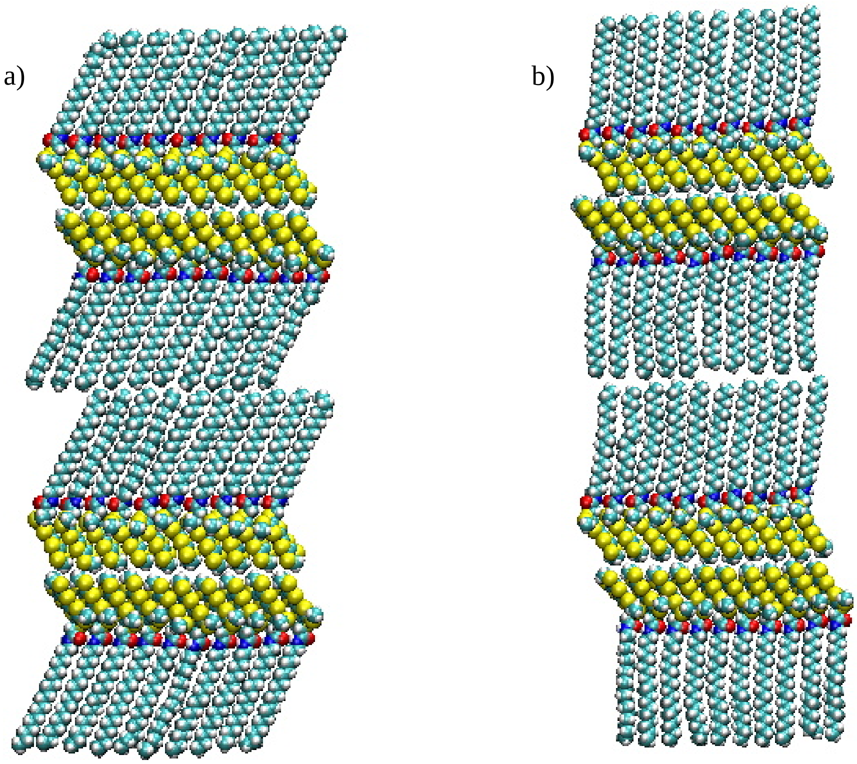


Figure S1. Tilted (a) and extended (b) model. The two models differ in terms of the orientation of the alkyl chains: in (a) they are tilted while in (b) they are orthogonal to the lamella axis.

For each couple of equivalent molecules in the two lamellae we have calculated the inter-lamellae distance for both models, obtaining a value of 7.23 nm for the tilted model and 7.83 ± 0.02 nm for the extended one, which is in good agreement with experiment. The stability of the monolayer is expressed in terms of intermolecular energy for the molecules in the assembly. Molecular dynamics calculations show that both models are almost equally stable.