Face-on vs edge-on: tuning the structure of tetrathiafulvalene monolayers with solvent

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1. Additional STM images

**Fig. S1** STM images of TTFAm18 self-assembly at the TCB / HOPG interface before (a) and after annealing at 70°C for 5mins (b-c). A general tunneling condition: $I_{\text{set}} = 200-300$ pA, $V_{\text{bias}} = -550$ mV.

**Fig. S2** (Multi)layers of TTFAm18 formed by drop-casting on HOPG a 1 mM solution in octanoic acid. (a) STM image of TTFAm18 monolayer composed of 3.5nm-wide short-range ordered lamellae. $I_{\text{set}} = 250$ pA, $V_{\text{bias}} = -550$ mV. (b) STM image of TTFAm18 multilayers (1-2 layers). $I_{\text{set}} = 280$ pA, $V_{\text{bias}} = -550$ mV.

**Fig. S3** STM images of TTFAm18 films at the octanoic acid (0.1 mM)/HOPG interface annealed at 110 °C for 2 mins. $I_{\text{set}} = 280$ pA, $V_{\text{bias}} = -650$ mV.
2. Additional AFM images

Fig. S4 Dry film of TTFAm18 solution (0.1mM) in chlorobenzene spin-casted onto HOPG substrate. AFM images at large scale (a) and zoom-in area (b) with corresponding height-profile (bottom).
3. Molecular models and DFT calculations

**Model a**

![Model a](image)

**Model b**

![Model b](image)

**Fig. S5** Two alternative models with face-on adsorption, considered for the packing of TTFAm18 at TCB/HOPG interface. **Model a** (UC: $a = 0.96$ nm, $b = 3.8$ nm, $\alpha = 80.4^\circ$) with interdigitated alkyl chains and **Model b** (UC: $a = 1.3$ nm, $b = 3.3$ nm, $\alpha = 81.7^\circ$) with interdigitated TTF cores. Both models show much shorter lamellar spacing than the experimental one (6.5 nm, Fig. 1a) and were rejected in favor of the edge-on model (Fig. 1c).

**Fig. S6** Gas phase structure of TTFAm18 in *trans*- and *cis*-conformations, optimized by DFT calculations (M06-2x/6-31G(d,p)). The trans-conformer (a-1) is 1.48 kcal/mol more stable than cis-conformer (b-1) and both conformers reveal a slight boat-like deformation of the TTF core. The frequency check (a-2, b-2) shows only positive frequencies, confirming the optimized structures are the minima.
**Fig. S7** Two views of two π-stacked TTFAm18 molecules in the edge-on arrangement.
4. Synthesis procedures and spectrum characterization

A solution of tetrathiafulvalene (0.500 g, 2.45 mmol) in dry ether (40 mL) was stirred at -78 °C in N₂ atmosphere when LDA (1.35 mL, 2.0 M in hexane, 2.70 mmol) was added dropwise. When the reaction mixture was stirred at -78 °C for 45 mins, dry ice powder (1.0 g) was added. The reaction mixture was stirred at -78 °C for another 1 h and then warmed up to room temperature gradually overnight. The solvent was evaporated and water was added. The aqueous solution was filtered to remove unreacted tetrathiafulvalene, and the filtrate was acidified by 1M HCl. Red precipitates was formed and collected, affording tetrathiafulvalene-2-carboxylic acid as a red solid (0.76 g, 64%).

\[ ^1H \text{ NMR (δ, DMSO-d}_6\text{): 13.57 (1H, br s), 7.68 (1H, s), 6.76 (2H, s).} \]

A solution of tetrathiafulvalene-2-carboxylic acid (0.300 g, 1.2 mmol) in dry THF (60 mL) was stirred under N₂ flow while oxalyl chloride (0.6 mL, 7.09 mmol) and pyridine (0.1 mL) were added dropwise. The reaction mixture went from red to brown purple. After stirring at room temperature for 1.5 h, the solvent was removed under vacuum, affording tetrathiafulvalene-2-carbonyl chloride as a brown purple solid. This was redissolved in dry THF (50 mL) a solution of octadecylamine (0.60 g, 2.22 mmol) in dry THF (30 mL) was added dropwise, followed by triethylamine (0.3 mL, 2.2 mmol). Yellow precipitate is formed immediately upon addition. The reaction mixture was stirred at room temperature for 5 h. The precipitate was filtered out, and the filtrate was evaporated under a reduced pressure. The crude product was purified by passing through a silica plug in ethyl acetate, affording the pure TTFAm18 as an orange red solid (0.538 g, 98%).

\[ ^1H \text{ NMR (δ, DMSO-d}_6\text{): 8.39 (1H, t, J = 8 Hz), 7.45 (1H, s), 6.74 (2H, s), 3.12 (2H, q, J = 8 Hz), 1.44 (2H, br.m), 1.26 (30H, br.s), 0.86 (3H, t, J = 8 Hz).} \]

\[ ^13C \text{ NMR (δ, DMSO-d}_6\text{): 159.14, 134.35, 124.78, 120.69, 120.43, 112.19, 106.91, 31.77, 29.51, 29.49, 29.47, 29.41, 29.38, 29.26, 29.18, 29.12, 26.78, 22.57, 14.43.} \]
$^1$H NMR spectrum of [2,2'-bi(1,3-dithiolylidene)]-4-carboxylic acid
$^1$H NMR spectrum of N-octadecyl-[2,2'-bi(1,3-dithiolylidene)]-4-carboxamide

$^{13}$C NMR spectrum of N-octadecyl-[2,2'-bi(1,3-dithiolylidene)]-4-carboxamide