SUPPORTING INFORMATION

Transformation of self-assembly of a TTF Derivative at 1-phenyloctane/HOPG Interface Studied by STM—from Nanoporous Network to Linear Structure

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1. A cross-sectional profile of TCDB1-EDTTF-PO

A cross-sectional profile (Figure S1.b) corresponding to Figure S1.a shows that the height of the bright spots is higher than the traditional TCDB network and the hollow hexagonal cavity.

Figure S1. (a) Coexistence of traditional TCDB self-assembly (I) and TTF-Loose pattern (II). Tunneling condition: \( I_{set}=299.1\text{pA}, V_{bias}=599.1\text{mV} \). (b) Cross-sectional profile corresponding to the white solid line in (a).
2. STM investigation of TCDB-EDTTF-OA system

Control experiments have been carried out to ensure that 1-phenyloctane take part in the TCDB/EDTTF system. We introduced another solvent octanoic acid (OA) as the counterpart into TCDB/EDTTF system. However, we could only observe the final EDTTF-Tight pattern (Figure S2) instead of the hexagonal network. The measured unit cell is superimposed on the STM image with \(a=3.44\pm0.1\text{nm}, b=2.19\pm0.1\text{nm}\) and \(\alpha_1=72.1\pm2^\circ\).

**Figure S2.** STM image of TTF-TCDB-OA system. Tunneling condition: \(I_{\text{set}}=299.1\text{pA}, V_{\text{bias}}=599.1\text{mV}\). A unit cell was superimposed on the packing pattern.
3. Suggested molecular model of TCDB1

In this suggested fully-extended TCDB1 model, every TCDB molecule could interact with three TCDB molecules via hydrogen bonding through the terminal carboxylic groups (marked by red dashed circle). However, we could not observe the pure hexagonal pattern of this TCDB framework since the total energy per unit area is only -0.077 kcal mol\(^{-1}\) Å\(^{-2}\), which is much higher than that of the traditional packing TCDB.

Figure S3. Calculated molecular model of the fully-extended TCDB1.
4. Unit cells

(1) Unit cell of TCDB

Figure S4.1. The calculated structure in the unit cell of TCDB assembly. The calculated unit cell parameters were: $a = 3.80$ nm, $b = 2.25$ nm, $\alpha = 73.00^\circ$.

(2) Unit cell of TCDB1

Figure S4.2. The calculated structure in the unit cell of TCDB1 assembly. The calculated unit cell parameters were: $a = b = 6.08$ nm, $\alpha = 60.00^\circ$. 
(3) Unit cell of TCDB1-EDTTF

Figure S4.3. The calculated structure in the unit cell of TCDB1-EDTTF assembly. The calculated unit cell parameters were: $a = b = 6.08$ nm, $\alpha = 60.00^\circ$.

(4) Unit cell of TCDB1-EDTTF-PO

Figure S4.4. The calculated structure in the unit cell of TCDB1-EDTTF assembly. The calculated unit cell parameters were: $a = b = 6.08$ nm, $\alpha = 60.00^\circ$. 
Figure S4.5. The calculated structure in the unit cell of TCDB assembly. The calculated unit cell parameters were: $a = 3.59$ nm, $b=2.28$nm, $\alpha = 69.00^\circ$.

Figure S4.6. The calculated structure in the unit cell of TCDB assembly. The calculated unit cell parameters were: $a = 3.59$ nm, $b=2.28$nm, $\alpha = 69.00^\circ$. 