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Supporting Information

Biaxial aromatics with face-on/edge-on stacking adaptability: an STM/STS study of 1D nanowires assembled via rotatable ethynyls

Shern-Long Lee,[†,§] Hung-Jen Wu,[†] Yu-Ju Hsu,[†] Hsiu-Hui Chen,[‡,§]
Hsiu-Fu Hsu,[‡,*] and Chun-hsien Chen[†,*]

[†] Department of Chemistry and Centre for Emerging Material and Advanced Devices, National Taiwan University, Taipei, Taiwan, 10617

[‡] Department of Chemistry, Tamkang University, Tamsui, Taiwan 25137

[§] Current address: Dr. S.-L. Lee, Department of Chemistry, Division of Molecular Imaging and Photonics, KU Leuven-University of Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium; Professor H.-H. Chen, Department of Chemistry, National Kaohsiung Normal University, Kaohsiung, Taiwan 82446

Corresponding authors: hhsu@mail.tku.edu.tw (H.-F.H.); chhchen@ntu.edu.tw (C.-h.C.)

Content of Supporting Information:

Experimental Section:

Molecular synthesis. The synthesis procedures of **1** are reported as follows.

*Synthesis of 1,2,4,5-tetrakis(4'-alkyl-biphenyl-4-ethynyl)benzene (**1**)*: To a mixture of *trans*-dichlorobis(triphenylphosphine)palladium (II) (50 mg, 0.29 mmol), copper iodide (30 mg, 0.14 mmol), triphenylphosphine (40 mg, 0.14 mmol), and 1,2,4,5-tetrabromobenzene (270 mg, 0.69 mmol) in triethylamine (10 mL) was added 4-dodecyl-4'-ethynyl-1,1'-biphenyl (2.39 g, 6.90 mmol) in 10 mL triethylamine dropwise at room temperature (25—26°C). The solution was allowed to stir to reflux for 17 hrs and then dichloromethane (100 mL) was added. The reaction mixture was washed with NH_4Cl(*aq*) (100 mL x 3), H_2O (100 mL x 3), and dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography (SiO_2, *n*-hexane/dichloromethane 6:1) to yield **1**.

*1,2,4,5-tetrakis((4'-dodecyl-[1,1'-biphenyl]-4-yl)ethynyl)benzene (**1**)*: a yellow solid (yield: 73%). ^{1}H NMR (CD_2Cl_2, 600 MHz): δ 7.82 (s, 2H), 7.69 (d, *J* = 7.8 Hz, 8H), 7.64 (d, *J* = 7.5 Hz, 8H), 7.57 (d, *J* = 8.4 Hz, 8H), 7.30 (d, *J* = 7.8 Hz, 8H), 2.70 (t, *J* = 7.8 Hz, 8H), 1.60~1.70 (m, 8H), 1.20~1.50 (m, 72H), 0.93 (t, *J* = 6.9 Hz, 12H). ^{13}C NMR (CD_2Cl_2, 150 MHz): δ 142.9 (4C), 141.4 (4C), 137.3 (4C), 134.8 (2C), 132.2 (8C), 128.9 (8C), 126.8 (8C), 126.7 (8C), 125.4 (4C), 121.5 (4C), 95.6 (4C), 88.1 (4C), 35.6 (4C), 31.9 (4C), 31.4 (4C), 29.7 (8C), 29.6 (4C), 29.5 (8C), 29.35 (4C), 29.33 (4C), 22.7 (4C), 13.8 (4C). HRMS (FAB+) m/z calcd for $C_{110}H_{134}$ 1455.0486, found 1455.0470. Anal. Calcd for $C_{110}H_{134}$ (1455.05): C 90.73, H 9.27; found: C 90.70, H 9.31.

STM experiments. STM imaging was performed at the liquid-solid interface at room temperature by using a Multimode Nanoscope IIIa (Bruker). The solvent, hexadecane from TCI, were used as received. HOPG (highly orientated pyrolytic graphite) was purchased from Advanced Ceramics (ZYH grade). The STM probes were mechanically cut Pt/Ir tips. Imaging parameters of E_{bias} and $i_{tunnelling}$ ranged from −0.10 to −1.00 V and from 10 to 500 pA, respectively. Lattice parameters were calibrated by employing the corresponding unit-cell vector of the underlying HOPG. WSxM 5.0 was used to prepare STM images.

STS experiments. STS experiments were also carried out at the solid-liquid interface after well-defined molecularly resolved STM images were obtained. Prior to switching to the STS mode, the parameters for STM imaging were $E_{bias} = -0.75$ V and $i_{tunnelling} = 100$ pA, which determined the tip-surface spacing. The voltage was ramped from 1.5 to −1.5 V with a ramping rate of 1.74 Hz. The I-V curves were accepted for the subsequent analysis provided that (1) before and after spectroscopy recording, the STM images were stable and remained essentially the same and that (2) the reversed and forward traces (velocity: 9.85 V/s) of STS overlapped perfectly and passed through the set-point of bias and current parameters. Roughly 15 % of the curves were discarded because of transitory noise. Note that to reduce thermal drift, prior to STS recording we first scanned a large-area surface and then zoomed-in on a small area (as showed in Figure 3 in the main text) for STS measurements. Figure S3 shows that such protocol allows us to obtain STS data with higher reliability and reproducibility.[S1]

STS spectra were obtained by the software equipped with NanoScope IIIa (Bruker). Upon switching from imaging mode to STS mode, the feedback loop was turned off and the tip was positioned at the centre of the imaged area. Accordingly, to acquire STS spectra over a specific feature, the feature was translated to the centre of the image and the scan sizes were reduced gradually from one frame to another to minimise the effect of thermal drift. For example, the images of Fig. 3 were zoomed down to the size of 2.8×2.8 nm^2. The magnification improved the tip positioning. To obtain representative STS spectra of the linear and mesh-like assemblies of **1**, STS measurements were carried out on the positions indicated by the red and blue dots in Fig. 3.

Panels 1e and f in the main text were cartoons which are prepared to better visualise the morphological features of STM images (Panels 1a~d). Compound **1** and hexadecane were constructed by Gaussian 03. The relative positions of the molecules in the image frames were placed based on Panels 1a and b.

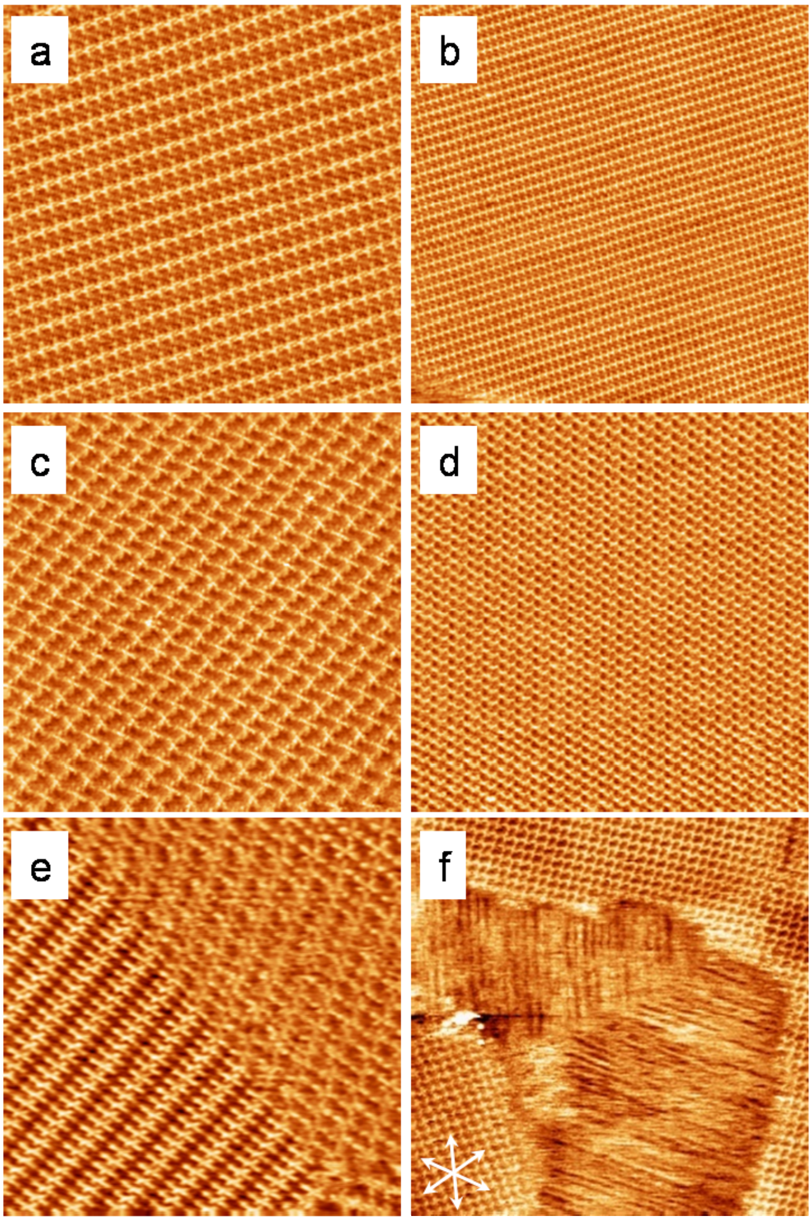

Figure S1. Concentration-dependent polymorphs of **1** self-assembled at the hexadecane/HOPG interface. The Panels display typical STM images of (a,b) linear structure at high concentrations (0.32 mM), (c,d) mesh motif at low concentrations (3.2 μM), (e) co-presence of linear (lower left) and mesh motifs at an intermediate level (32.0 μM), and (f) co-presence of mesh structure of **1** and hexadecane solvent molecules at a further diluted level (0.32 μM). The central portion of Panel f shows domains of striped solvent molecules. The 120° angle between the stripes is consistent with 3-fold symmetry of the underlying HOPG. The stripes align in parallel to the unit cell vectors of HOPG substrate (white arrows). Conditions: concentrations of **1**: a,b) 0.32 mM, c,d) 3.2 μM e) 32.0 μM, f) 0.32 μM; image sizes: a,c) 50 × 50 nm^2, b,d) 100 × 100 nm^2**,** e) 40 × 40 nm^2, f) 85 × 85 nm^2; imaging parameters: E_{bias}, –0.85 V; $i_{tunnelling}$, 50 pA.

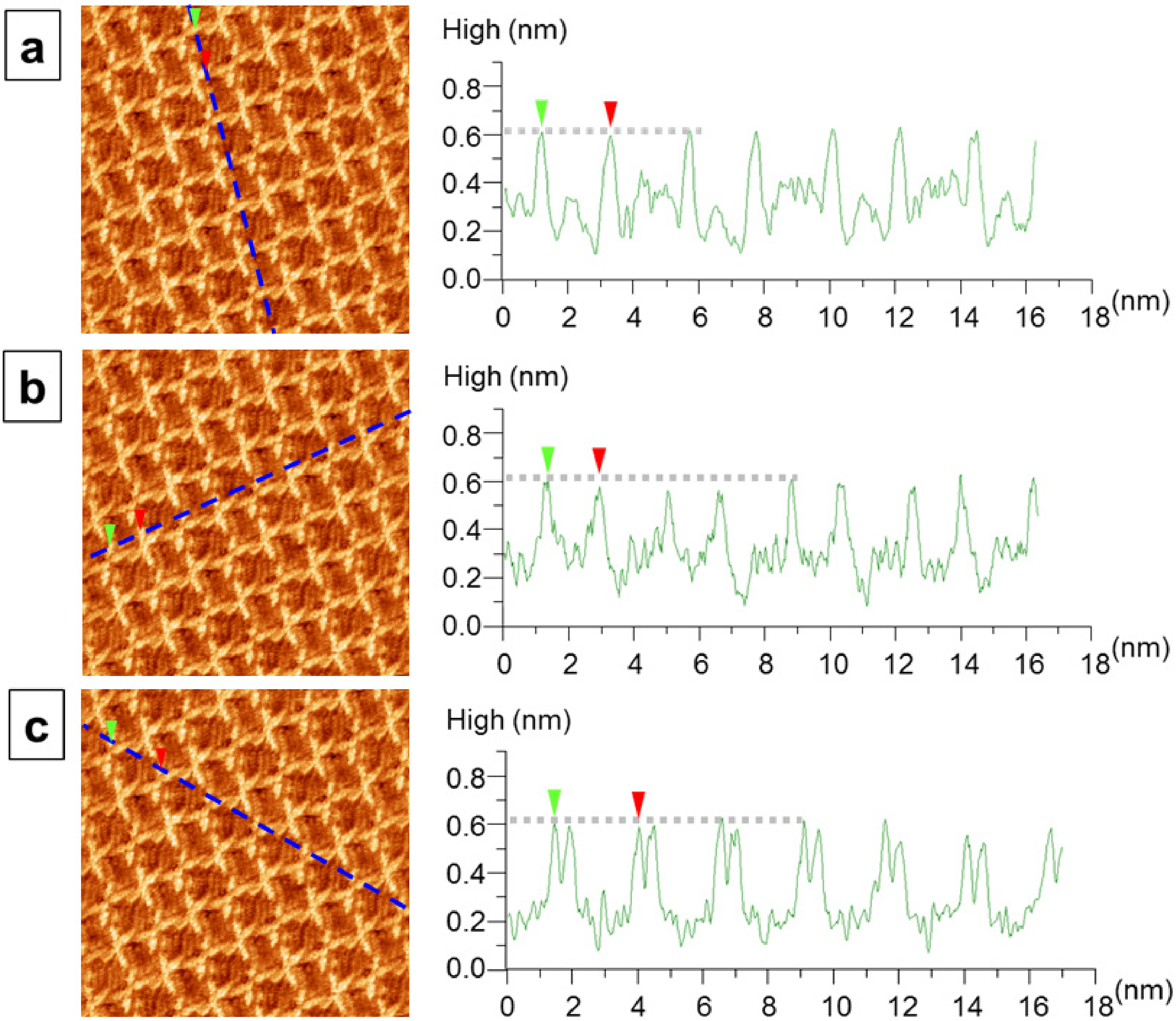

Figure S2. Section-profile analyses of the topography of the mesh-like motif of **1**. Three section profiles of the topography show no apparently height difference among biphenyls. The analyses indicate that all the biphenyls of the mesh-like structure adopt face-on configuration on HOPG, distinct from that of the linear motif (Fig. 2a). Imaging parameters: E_{bias}, –0.85 V; $i_{tunnelling}$, 50 pA.

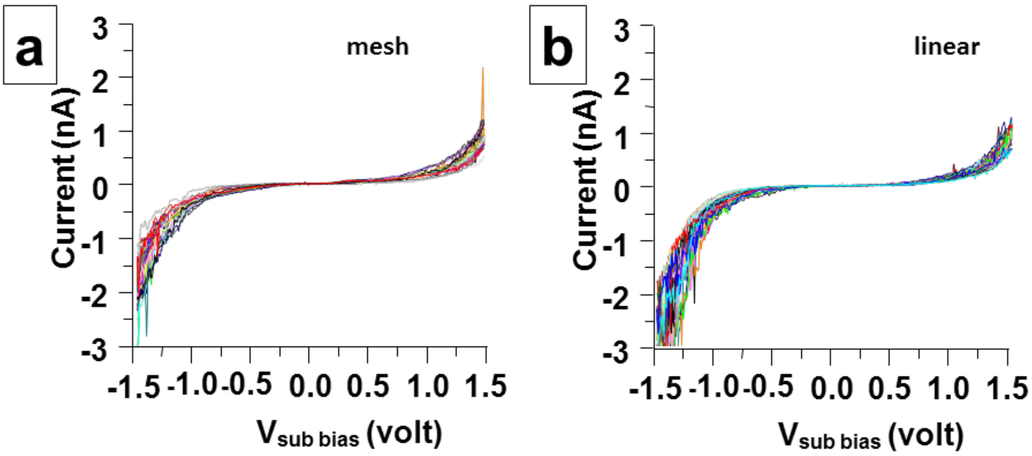

Figure S3. Reproducibility of STS traces. Overlaid STS spectra were acquired successively for the evaluation of the reproducibility of I-V traces. The traces (consecutive 24 and 29 I-V curves from one experimental session) were obtained at locations of (a) mesh-like and (b) linear motif of **1**. In the main text, the red and blue I-V traces were averaged from 3 experimental sessions. Parameters for STS measurements: E_{bias}, −0.75 V; $i_{\text{tunnelling}}$, 100 pA.

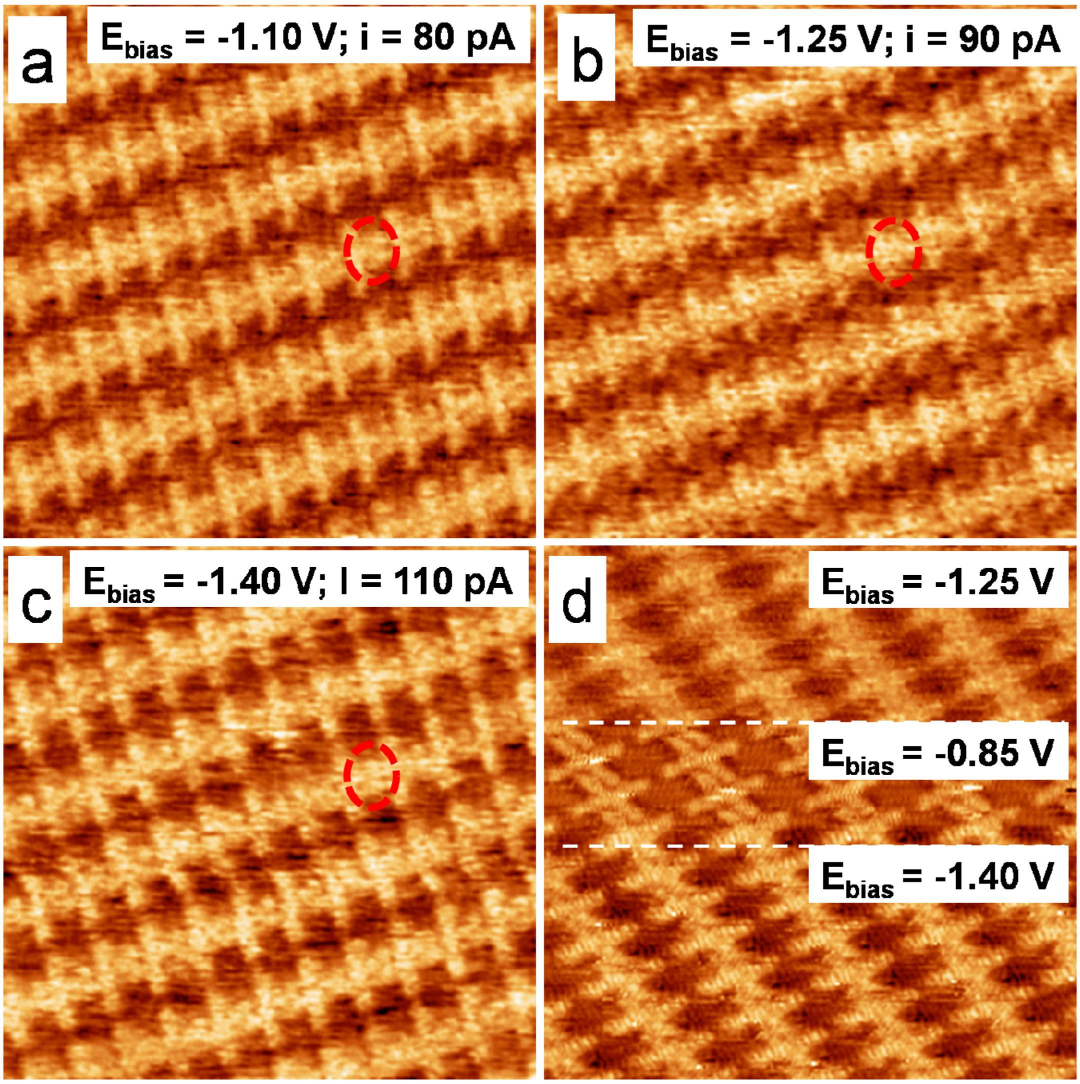

Figure S4. Bias-dependent STM images of the linear motif of **1**. (a-c) By using higher imaging bias, the electronic clouds between the neighbouring tilted biphenyls of **1** appear overlapped, indicative of the existence of intermolecular interactions. (d) STM image was obtained by instantaneously changing imaging bias under a constant tunnelling current (50 pA). The results suggest the electronic coupling between the edge-on biphenyls and demonstrate the reversibility of image varieties upon bias modulations. Image sizes: 17 × 17 nm^2.

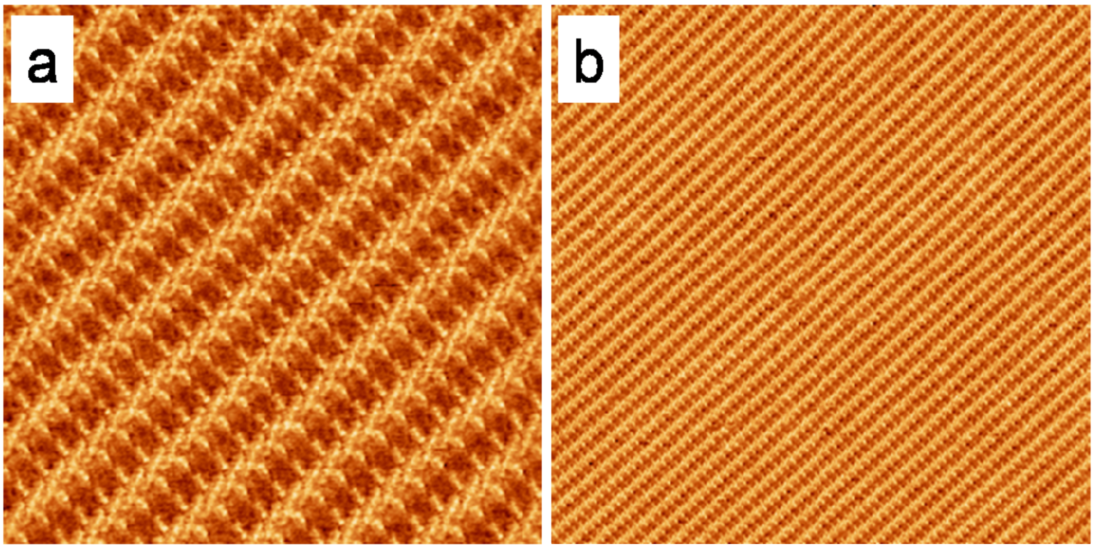

Figure S5. Stability of the linear motif of **1**. The STM images were acquired at 36 hrs or longer after the sample was prepared. The linear motifs did not undergo observable change or phase transition, demonstrating the high stability of the linear motif. Image sizes: a) 28 × 28 nm^2; b) 100 × 100 nm^2. Imaging parameters: E_{bias}, –0.85 V; $i_{tunnelling}$, 50 pA.

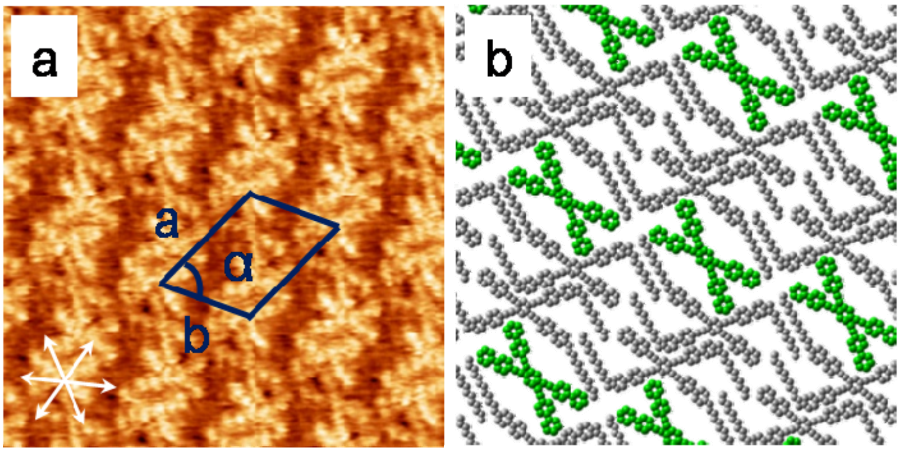

Figure S6. STM image of 0.32-mM **1** assembled at the 1-phenyloctane/graphite interface. This packing structure is distinct from those in hexadecane reported in the main text. No co-adsorbed 1-phenyloctane was found, attributed to the weak adsorption of 1-phenyloctane on graphite. A lower concentration of 3.2 μM also yielded the same assembly. These results, along with those with hexadecane solvent reported in the main text, demonstrate that the assembling is strongly affected by solvent co-adsorption. The competition between the solvent and adsorbate for the available sites determines the resulted packing structure. Unit cell parameters of $|\vec{a}|$, $|\vec{b}|$, and α: 4.7 (± 0.2) nm, 3.5 (± 0.3) nm, 72° (± 3°); the packing density is 0.19 **1**/nm^2; sizes: 16 × 16 nm^2; imaging parameters: E_{bias}, –0.80 V; $i_{\mathrm{tunnelling}}$, 80 pA.

Reference:

(S1) S.-L. Lee, Z. Yuan, L. Chen, K. S. Mali, K. Müllen and S. De Feyter, *J. Am. Chem. Soc.*, 2014, **136**, 4117-4120.