

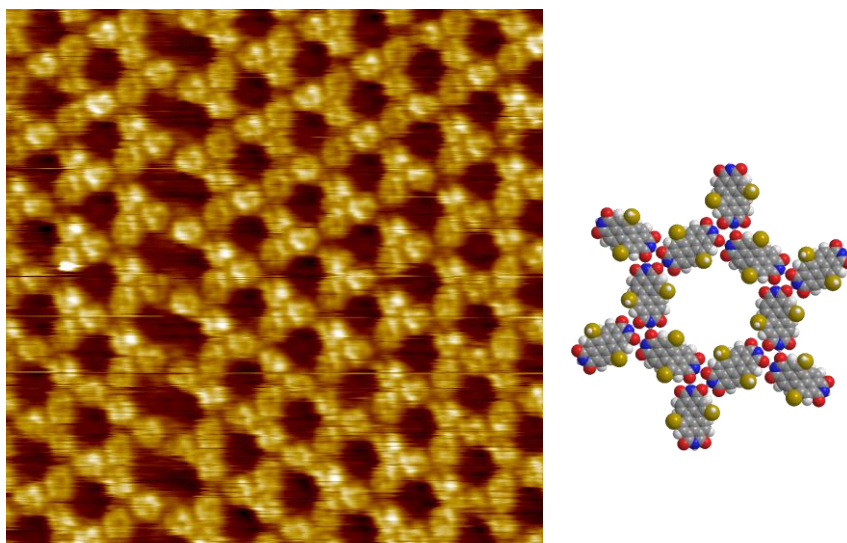
Supporting Information

Bi-component H-bonded porous molecular networks at the liquid-solid interface: what is the influence of pre-organization in solution?

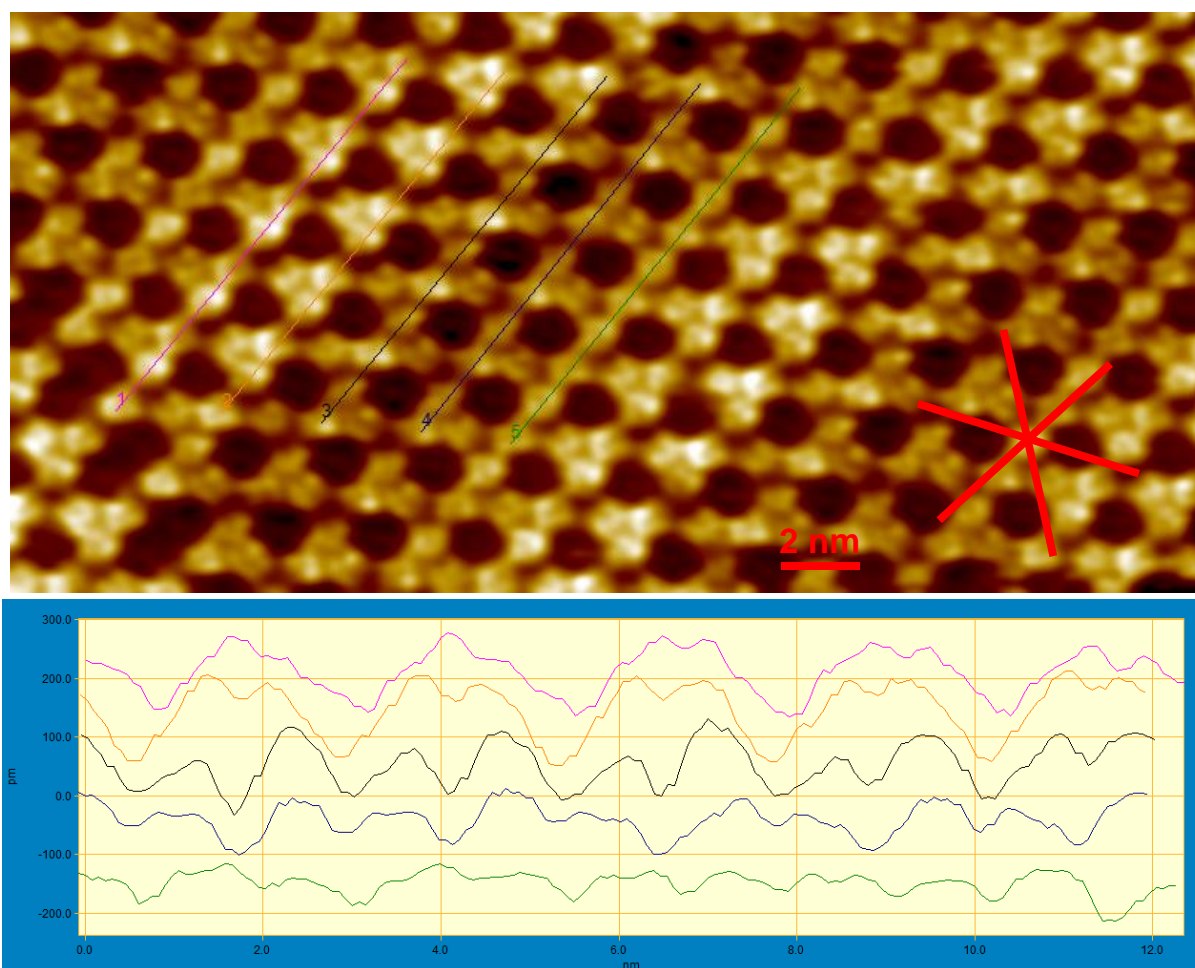
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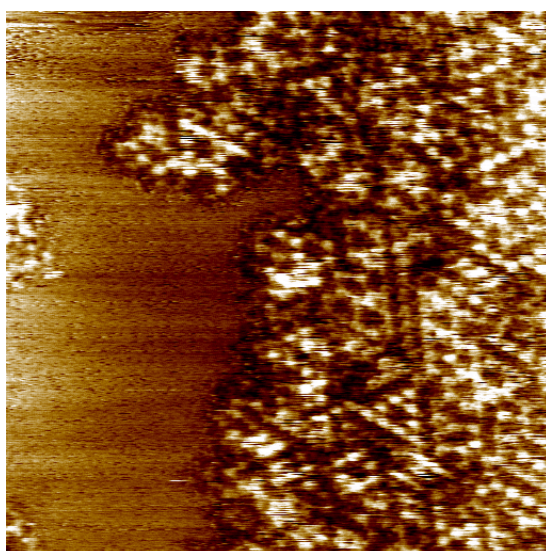
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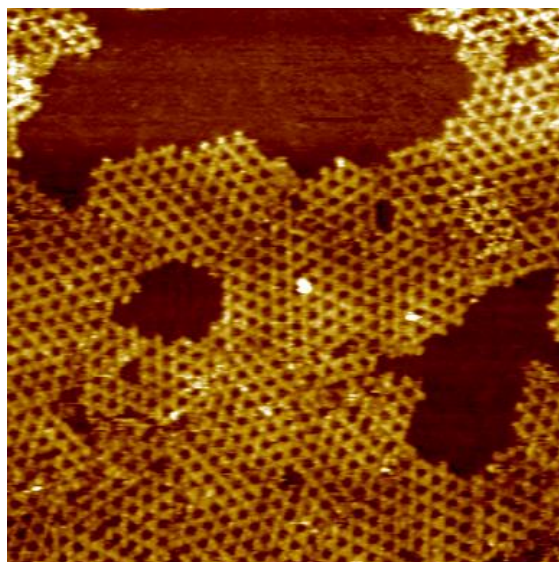
Supporting Figure 1. STM image and molecular model of self-assembly of PTCDI-SC6 at TCB/HOPG interface $V_T = 473$ mV, $i_T = 22$ pA, 20.6×20.6 nm².



Supporting Figure 2. STM height images with the series of cross-sections of the P3 porous structure with moiré waves.



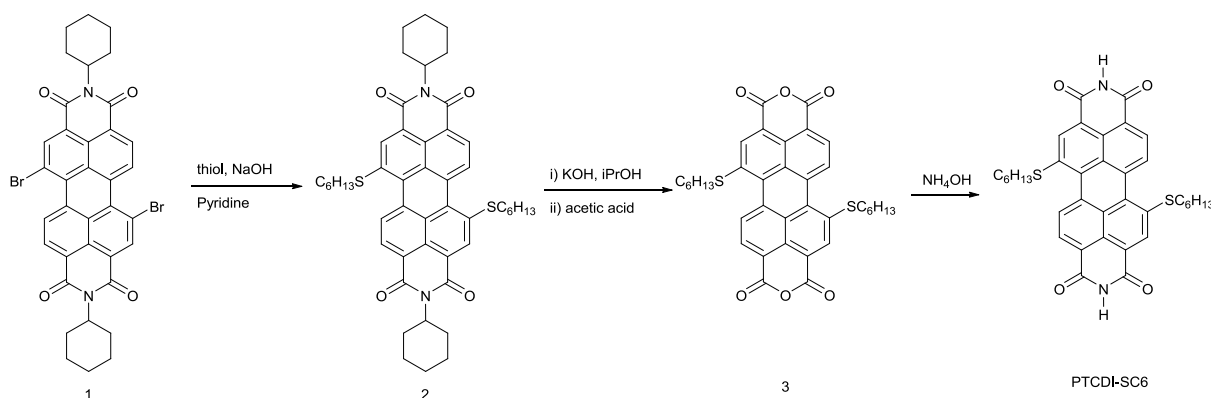
Supporting Figure 3. Self-assembly of melamine at TCB/HOPG interface at sub-monolayer coverage ($V_T = 450$ mV, $i_T = 28$ pA, 31×31 nm², 50 μ M solution).



Supporting Figure 4. Self-assembled P3 structure formed by deposition of 3:2 mixture of PTCDI-SC6 (38 μM) and melamine (25 μM) in TCB followed by 2 hours of annealing at 80 $^{\circ}\text{C}$ in a TCB saturated vial ($V_{\text{T}} = 450 \text{ mV}$, $i_{\text{T}} = 36 \text{ pA}$, $83 \times 83 \text{ nm}^2$).

Synthetic Methodology

PTCDI-SC6 was synthesized from known dibromo compound **1**¹ according to the previously developed strategy.² The compound **1** was obtained as a 80-20 mixture of 1,7- and 1,6-isomers.² The two isomers were not separated and used as a mixture for further functionalization. For the simplicity only 1,7-isomer is shown. Chemicals were purchased from Aldrich or Acros; solvents were reagent grade, distilled and dried before use according to standard procedures. Column chromatography was performed on silica gel (Aldrich 60, 230-400 mesh). ^{13}C NMR spectra were recorded on a Varian VXR-400 (101 MHz), or a Varian AMX500 (126 MHz). ^1H NMR spectra were recorded on a Varian VXR-400 (400 MHz). Chemical shifts are denoted in -unit (ppm) relative to CDCl_3 ($^1\text{H} = 7.26$, $^{13}\text{C} = 77.0$). For ^1H NMR spectroscopy, the splitting parameters are designated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), dd (double doublet). MALDI-TOF spectra were obtained with Voyager DE-Pro instrument. Thin-layer chromatography (TLC) was carried out on aluminum sheets, with visualization by UV light. Column chromatography was carried out on silica gel (230-400 Mesh) or basic alumina.

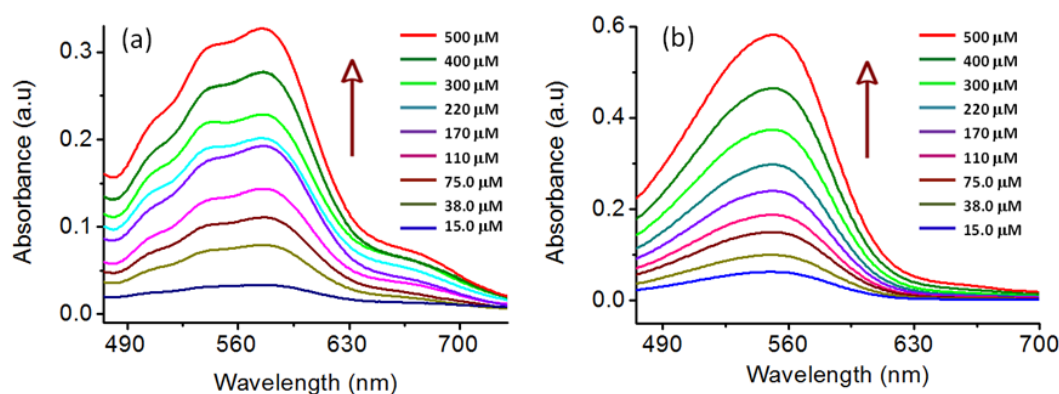


N,N'-Dicyclohexyl-1,7-dibromoperylene-3,4:9,10-tetracarboxylic acid bisimide (2): Compound **1** (500 mg, 0.76 mmol), NaOH (76 mg, 1.89 mmol) and 1-hexanethiol (268 mg, 2.27 mmol) were suspended in pyridine (25 mL) and heated under reflux overnight. After cooling to room temperature, the mixture was poured into 10% HCl and extracted with CH₂Cl₂. The CH₂Cl₂ phase was dried over Na₂SO₄, filtered and CH₂Cl₂ was evaporated. The crude mixture was purified by column chromatography with hexane/ CH₂Cl₂ (1:6) as eluent yielding 458 mg (83 %) of compound **2**. ¹H NMR (CDCl₃): δ=8.75 (d, J=8 Hz, 2H), 8.71 (s, 2H), 8.63 (d, J=8 Hz, 2H), 5.05 (m, 2H), 3.14 (t, J=7 Hz, 4H), 2.59 (m, 4H), 1.2-2.0 (m, 32H), 0.86 (t, J=7 Hz, 6H) ppm; ¹³C NMR (CDCl₃): δ=164.5, 164.4, 138.5, 133.1, 132.9, 131.9, 130.3, 129.3, 129.2, 126.1, 122.7, 122.3, 121.2, , 54.5, 49.8, 36.7, 31.5, 29.6, 28.8, 26.9, 26.1, 22.8, 14.3 ppm; MALDI-TOF MS: m/z calcd for C₄₈H₅₄N₂O₄S₂: 787.08, found 787.24.

N,N'-Dicyclohexyl-1,7- Dipropylthioperylene-3,4:9,10-tetracarboxylic Acid Bisimide (3): A mixture of 25 mg (0.04 mmol) of **2**, 225 mg (4.0 mmol) of KOH, and 2 mL of i-PrOH was brought to reflux. The mixture was stirred for 1.5 h and poured under stirring into 8 mL of AcOH. The precipitate was filtered, re-dissolved in CH₂Cl₂ and washed with water. The organic phase was dried over Na₂SO₄, filtered and CH₂Cl₂ was evaporated to yield compound **3** (15 mg, 76%). ¹H NMR (CDCl₃): δ=8.93 (d, J=8 Hz, 2H), 8.74 (s, 2H), 8.69 (d, J=8 Hz, 2H), 3.22 (t, J=7 Hz, 4H), 1.70 (m, 4H), 1.2-1.5 (m, 12H), 0.86 (t, J=7 Hz, 6H) ppm; ¹³C NMR (CDCl₃): δ=160.1, 159.7, 140.2, 133.9, 133.4, 132.7, 131.3, 130.3, 129.7, 127.3, 118.9, 118.3, 31.2, 29.8, 28.7, 28.2, 22.9, 14.1 ppm; MALDI-TOF MS: m/z calcd for C₃₆H₃₂O₆S₂: 624.77, found 624.58.

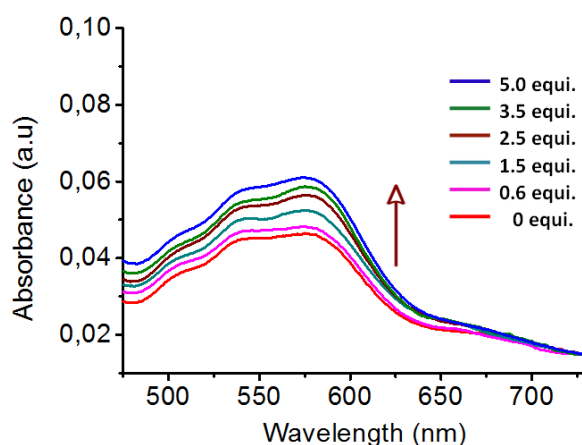
1,7- Dipropylthioperylene-3,4:9,10-tetracarboxylic acid bisimide (PTCDI-SC6): Compound **3** (30 mg, 0.048 mmol) was suspended in NH₄OH (5 mL) and heated under reflux for 24 hours. The reaction mixture was cooled to room temperature and poured into acetic acid (10 ml) cooled in an ice bath. The formed precipitate was filtered and dried in an oven overnight to yield **PTCDI-SC6** as a dark blue powder (16 mg, 53 %). The compound exhibited low solubility in common organic solvents including standard NMR solvents. MALDI-TOF MS: m/z calcd for C₃₆H₃₂O₆S₂: 622.80, found 623.68.

Uv-Vis spectra of PTCDI-SC6 With varying concentration:



Supporting Figure 5. Uv-Vis absorption spectra of PTCDI-SC6 with varying concentration from $(1.5 \times 10^{-5} \text{ M} - 5.0 \times 10^{-4} \text{ M})$ recorded in (a) 1,2,3- trichlorobenzene (TCB) and (b) tetrahydrofuran (THF), at room temperature.

Uv-Vis spectra of PTCDI-SC6 in presence of melamine:



Supporting Figure 6. Uv-vis absorption spectra of PTCDI-SC6 ($2.0 \times 10^{-5} \text{ M}$) recorded in 1,2,3- trichlorobenzene (TCB) with varying concentration of melamine at room temperature.

¹ Würthner, F.; et al., *J. Org. Chem.* **2004**, 69, 7933-7939.

² Perdigão, L. M. A.; et al., *Chem. Eur. J.* **2008**, 14, 7600-7607.