Supporting Information

Anatomy of On-Surface Synthesized Boroxine 2D Polymers

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1. Additional characterization data (STM, infrared spectroscopy and computational).

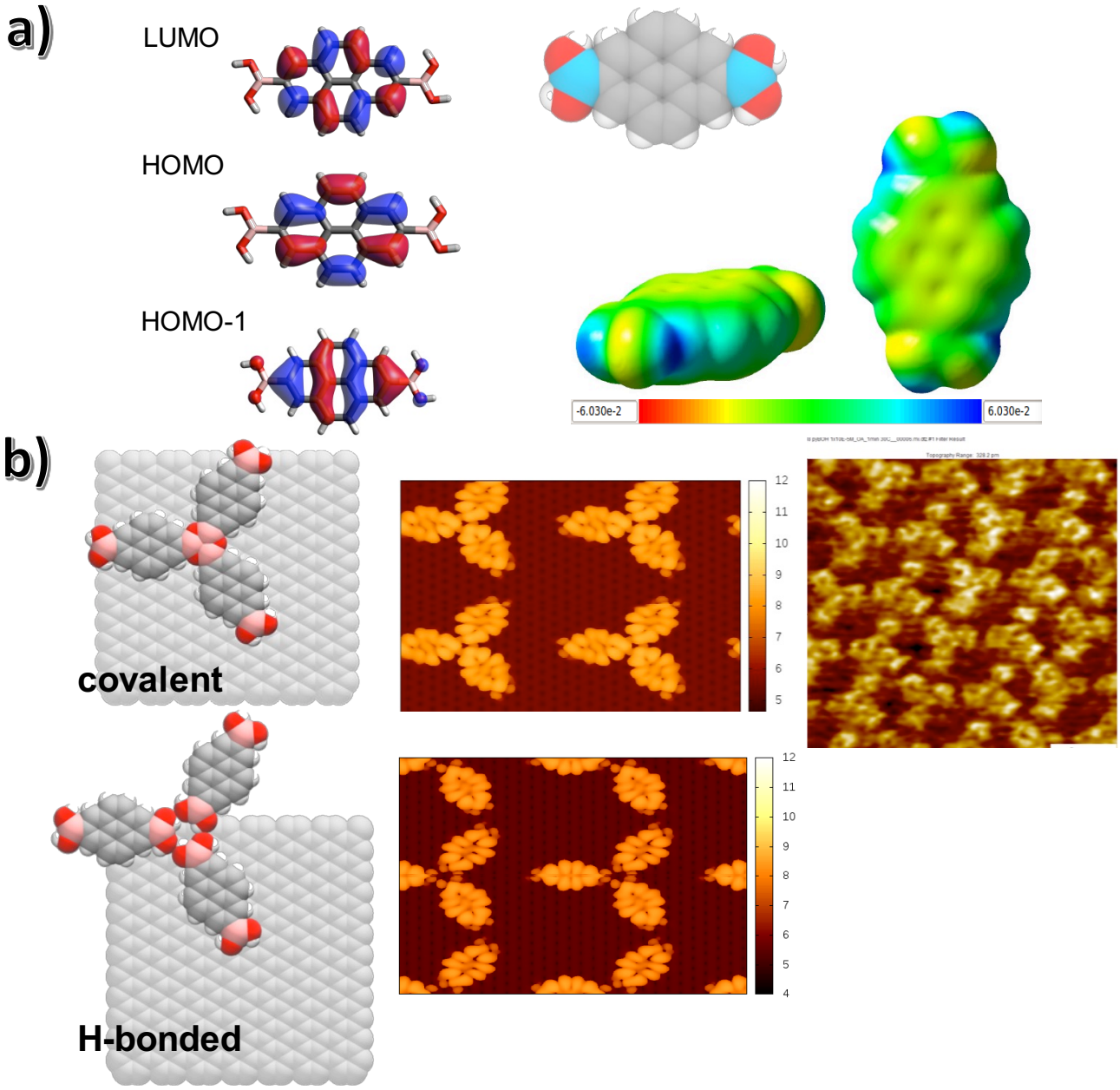


Figure S1. (a) Pyrene-2,7-diboronic acid (PDBA) molecular orbitals and electrostatic potential. (b) Atomic models, simulated images and experimental STM image for three PDBA molecules linked by covalent or hydrogen bonds adsorbed on top of graphite. For all the simulated images, color height-scale is in Å and V=+0.9 eV. The experimental STM image correspond to a digital zoom. The original STM image was obtained at the OA/HOPG interface. [PDBA] = 1.0×10^{-5} M. Imaging parameters: I_{set} = 50 pA, V_{bias} = -0.400 V.

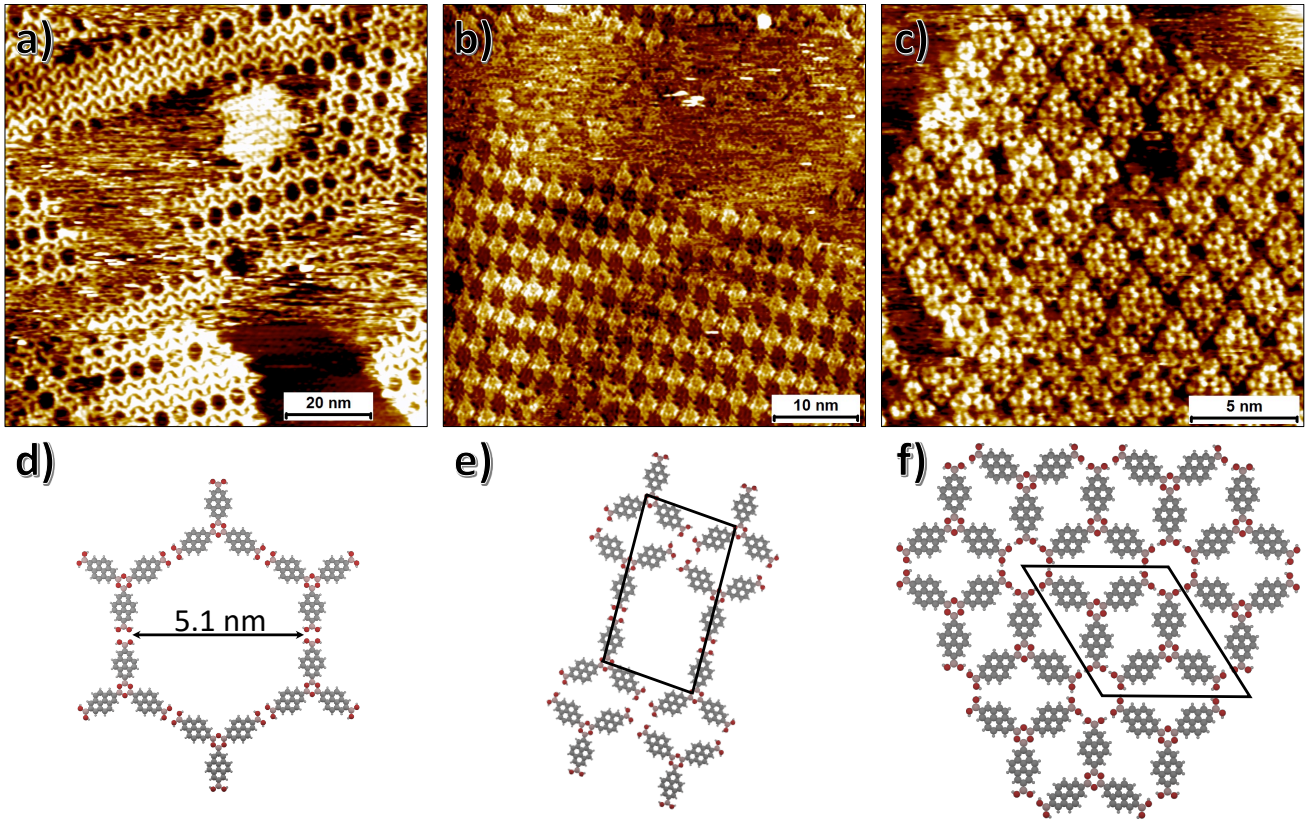


Figure S2. Apart from the three structures presented in the Figure 1 of the main text, the PDBA system forms a few other networks as displayed in the STM images presented in panels (a-c). [PDBA] = 1.5×10^{-5} M. These structures are all based on different arrangements of the covalent trimer as displayed in the tentative models displayed below the STM images in panels (d-f). Panel (a) shows the compact self-assembled network formed by covalent trimers together with hexagonal voids formed when two rows of covalent trimers meet each other. Note that these hexagonal cavities are larger than those for the 2DP with d =5.1 ± 0.4 nm. Panels (b) and (c) show alternative self-assemblies which are periodic in nature. Unit cell parameters: (b) a = 2.7 ± 0.1 nm, b = 4.8 ± 0.1 nm, γ = 86 ± 1°; (c) a = 3.0 ± 0.1 nm, b = 3.0 ± 0.1 nm, γ = 60 ± 1°. Imaging parameters: (a) I_{set} = 40 pA, V_{bias} = -0.50 V; (b) I_{set} = 60 pA, V_{bias} = -0.80 V and (c) I_{set} = 40 pA, V_{bias} = -0.80 V.

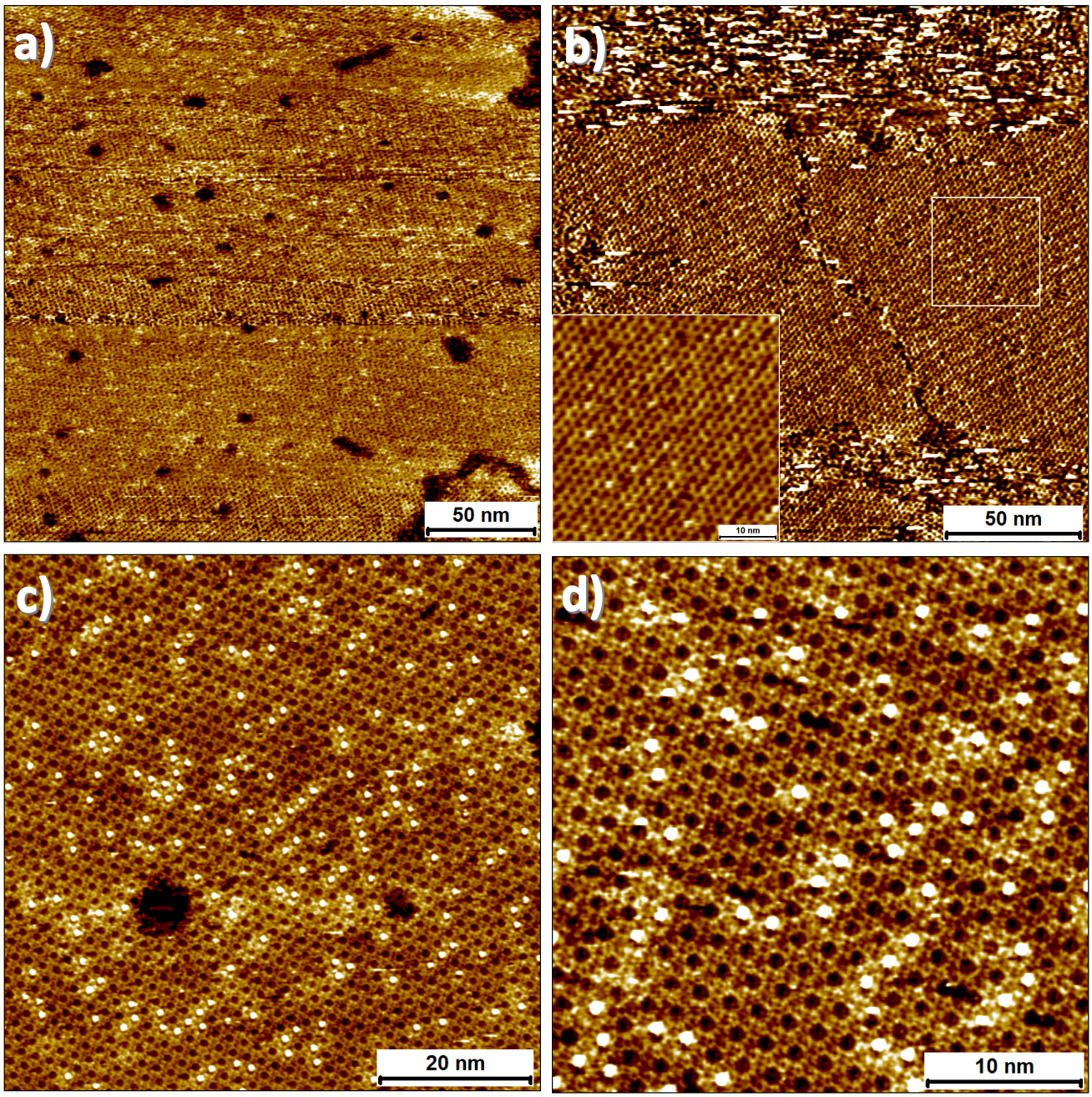


Figure S3. Additional STM images for PDBA 2DP formed at the octanoic acid/HOPG interface. [PDBA] = 1.0×10^{-4} M. The inset in (b) shows a digital zoom of the area marked by the white square in panel (a) showing the hexagonal structure of the polymer. The origin of bright features adsorbed in the hexagonal cavities of the 2DP in (c) and (d) is not clearly understood, however they could arise from immobilized PDBA monomers. The experimentally observed domain sizes range between 155 nm^2 – 22500 nm^2 at 1.0×10^{-4} M at the octanoic acid/HOPG interface. Tunneling parameters: I_{set} = 60 pA, V_{bias} = -0.30 V.

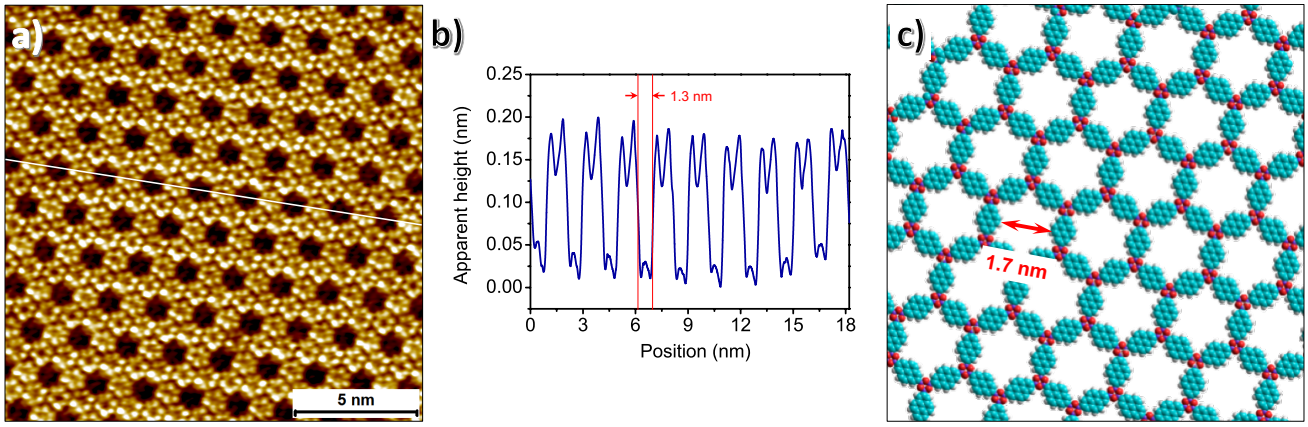
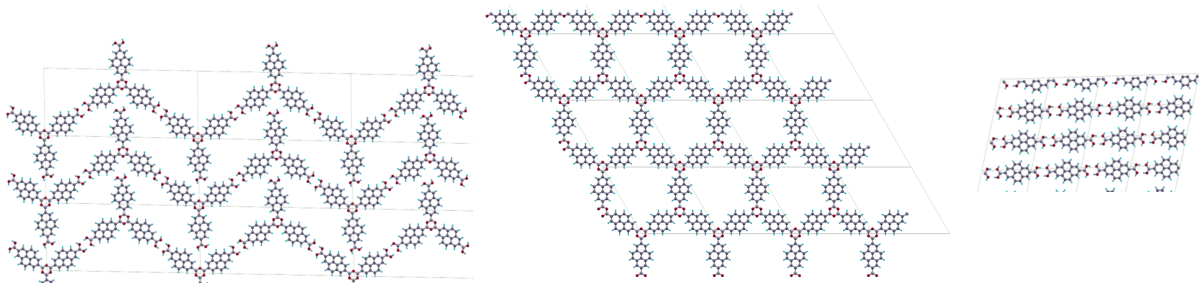


Figure S4. (a, b) STM image and a line profile showing the approximate diameter of the hexagonal cavities formed by the 2DP. (c) Molecular model showing the anticipated cavity diameter (~1.7 nm).

a)

System	A (AA)	B (AA)	Gamma (°)
PDBA trimer assembly	20.03	45.78	88.9
PDBA-2DP	22.60	22.60	60
PDBA monomer assembly	14.65	9.17	76.7

b)



PDBA trimer assembly optimized structure

2DP optimized structure

PDBA monomer self-assembly periodic structure

Figure S5. (a) Table with calculated lattice parameters of (b) optimized structures of the networks described for PDBA.

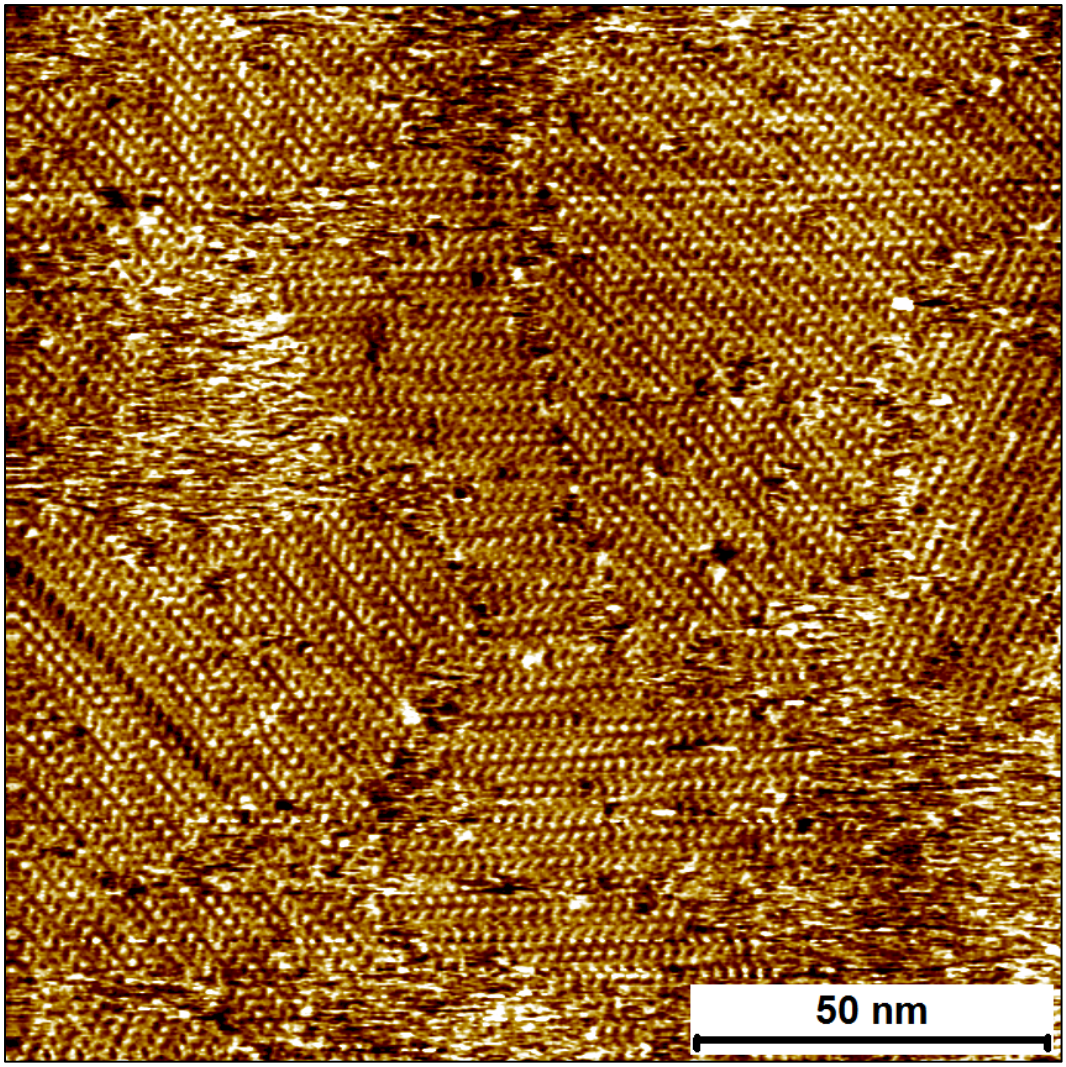


Figure S6. Large scale STM image (150 × 150 nm^2) showing domains obtained *via* self-assembly of the PDBA covalent trimers. [PDBA] = 1.5 × 10^{-5} M. Imaging parameters: I_{set} = 60 pA, V_{bias} = -0.40 V.

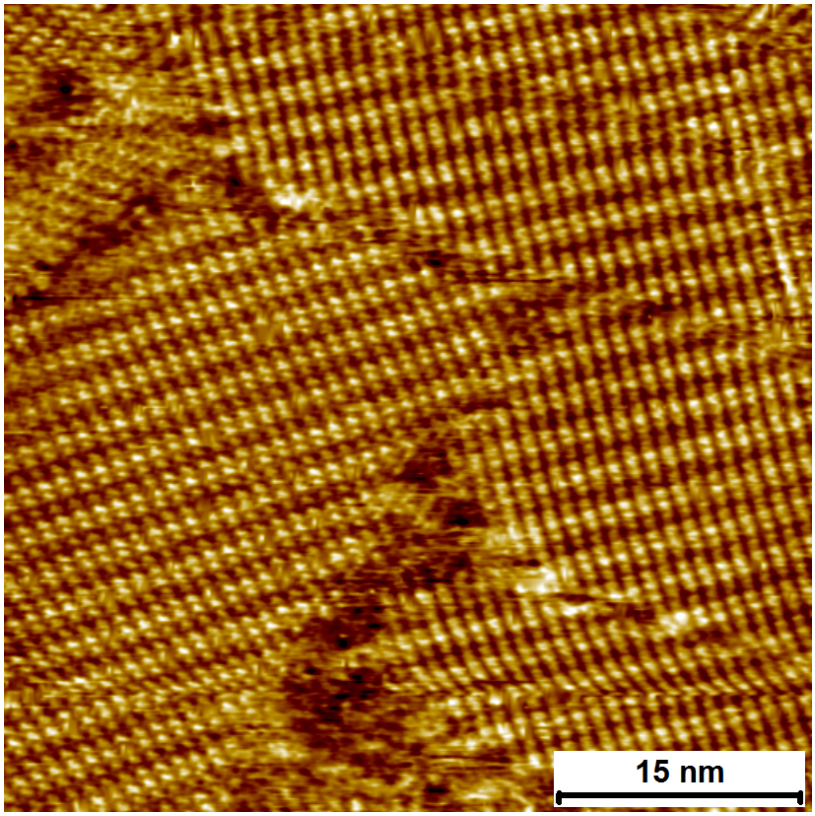


Figure S7. Additional STM image showing the hydrogen bonded self-assembled monolayers formed by PDBA monomers at the octanoic acid/HOPG interface. [PDBA] = 3.8×10^{-4} M. Imaging parameters: I_{set} = 1.0 nA, V_{bias} = -0.20 V.

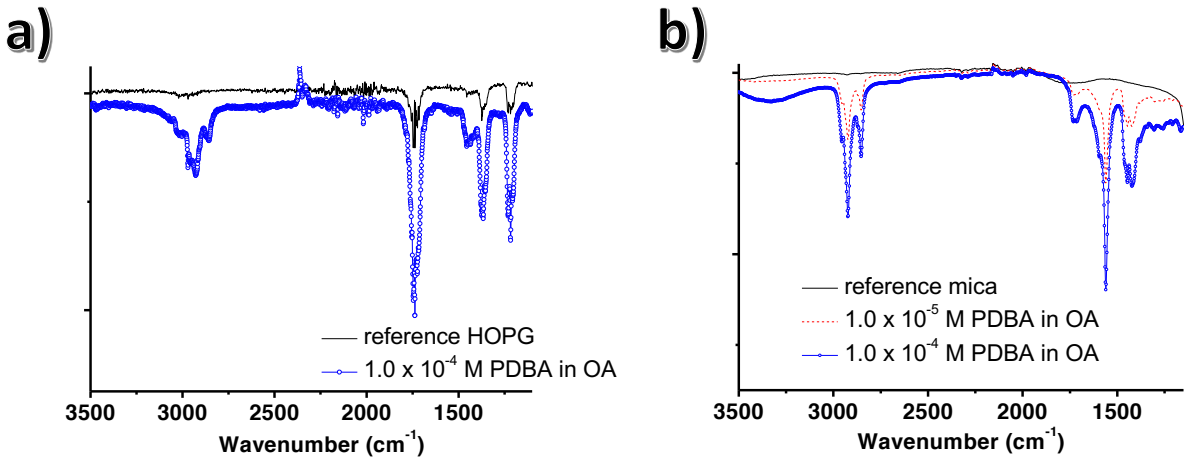


Figure S8. ATR FT-IR spectra of dry thin films prepared from PDBA solutions at different concentrations and supported on HOPG (a) and mica (b). The spectra of the bare substrates are represented as reference.

Peak (cm^{-1})	**Assignment**
3267	O–H stretch from the unreacted monomers and from the end $B(OH)_2$ groups at the surface of crystallites
2955	Aromatic C—H stretch
2923	Aromatic C—H stretch
2853	Aromatic C—H stretch
1596	C=C stretch for fused aromatics
1464	C═C vibrational mode for p-substituted pyrene unit
1446	C═C vibrational mode for p-substituted pyrene unit
1422	C═C vibrational mode
1378	B–O stretching
1343	B–O stretching
1305	C–C stretching
1230	C–O stretching
1163	C–H in-plane bending modes

Table S1. Peak assignments for ATR FT-IR spectrum of the PDBA dry film obtained after evaporation of octanoic acid-DMSO (1×10^{-4} M) solution on mica (as compared to FT-IR spectra of the corresponding bulk 2D COF).[1, 2]

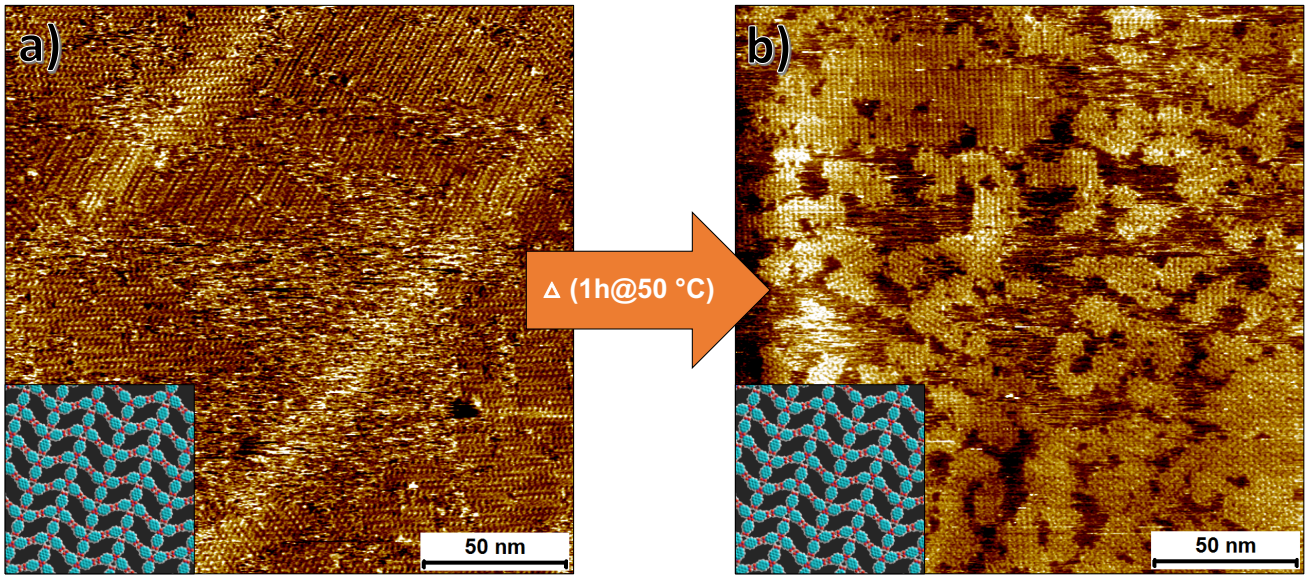


Figure S9. STM images showing the lack of structural transition upon annealing (50 °C for 1 hour) the self-assembled network formed by covalent trimers of PDBA at the octanoic acid/HOPG interface. [PDBA] = 1.5×10^{-5} M. The domains become more compact while still retaining the composition before annealing and no transition to the hexagonal 2DP is observed. Imaging parameters: I_{set} = 60 pA, V_{bias} = -0.40 V.

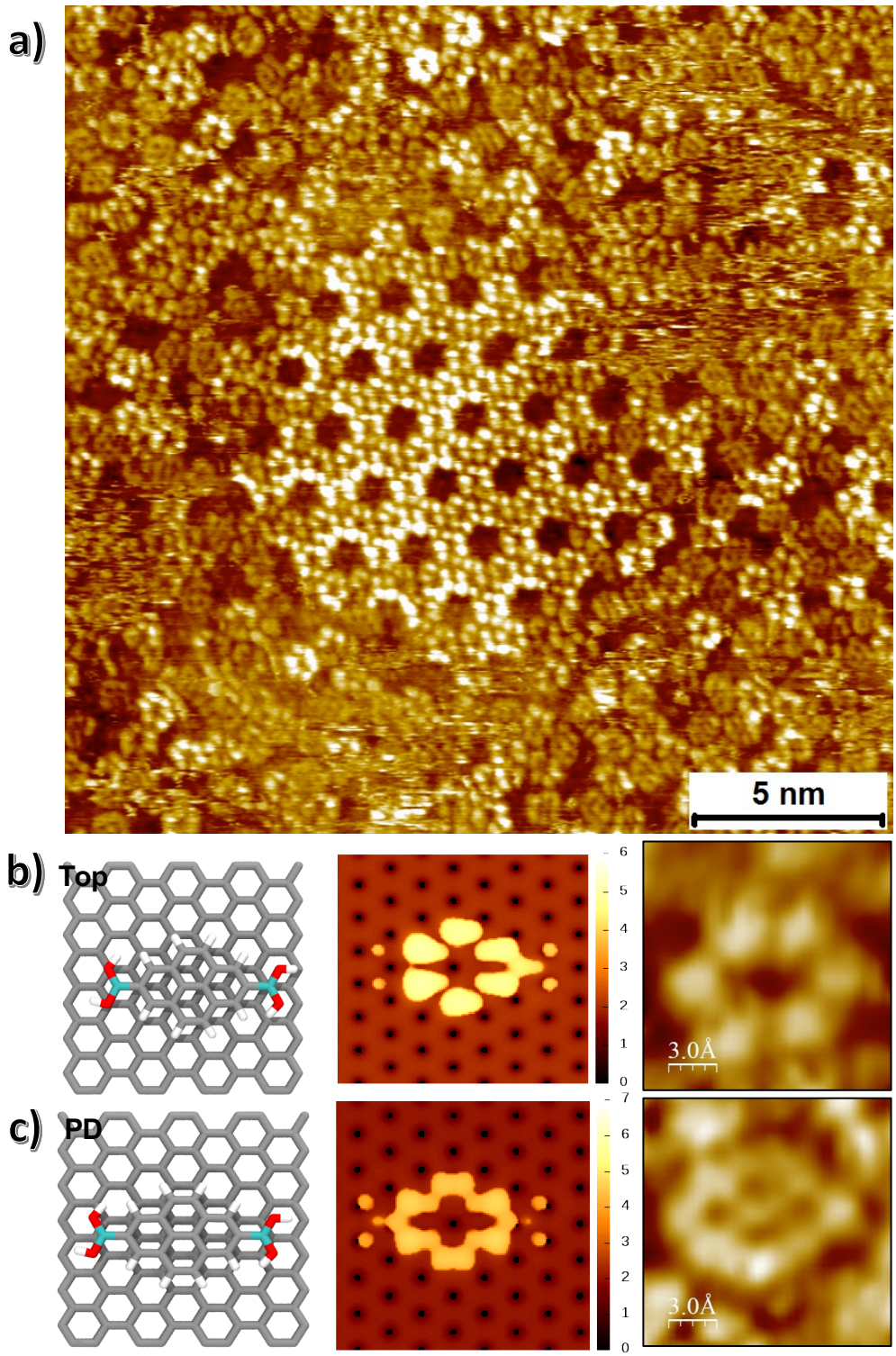


Figure S10. (a) Reproduction of the STM image presented in Figure 3c of the main text. (b,c) Atomic models, simulated images and experimental STM images for (b) Bernal stacking of PDBA on top of the graphite lattice, and (c) parallel-displaced (PD) adsorption. For the simulated images, color height-scale is in Å and V=-0.4 eV. Experimental images correspond to digital zooms. Original STM images were obtained at the OA/HOPG interface. [PDBA] = 2.5×10^{-5} M. Imaging parameters: I_{set} = 40 pA, V_{bias} = -0.200 V.

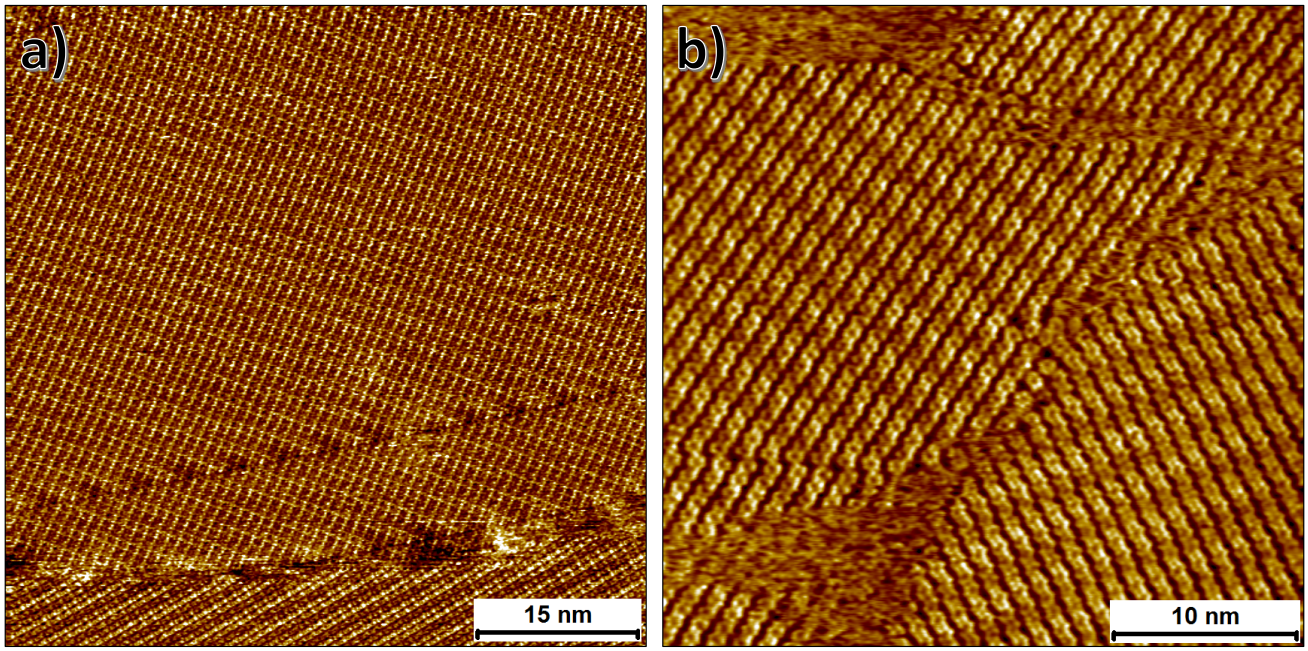


Figure S11. Additional STM images showing the self-assembled networks of PDBA monomers at the TCB/HOPG interface. [PDBA] = 1.0×10^{-4} M. Imaging parameters: I_{set} = 50 pA, V_{bias} = -0.400 V.

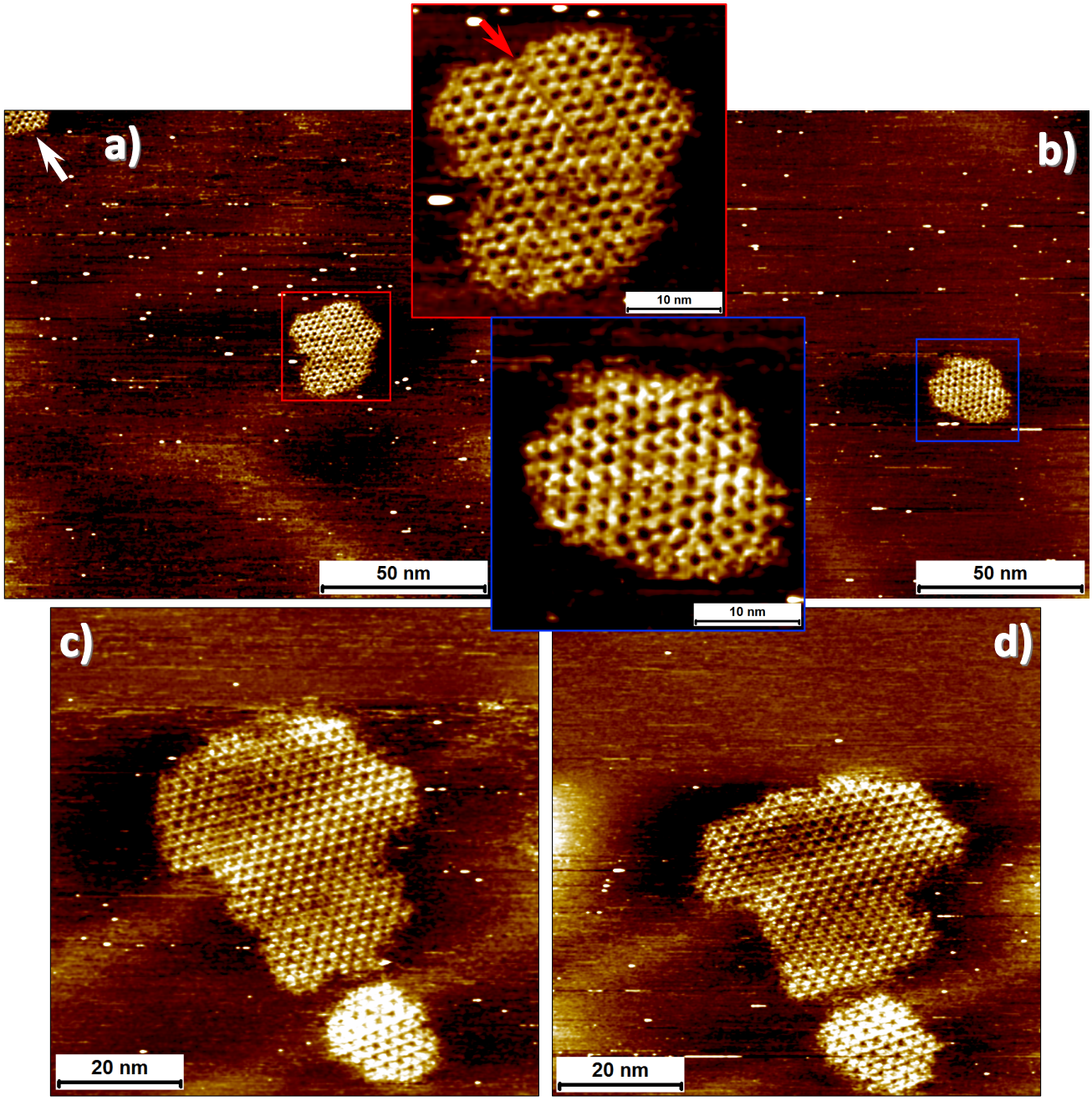


Figure S12. Additional STM images showing PDBA 2DP crystallites observed upon deposition of 1×10^{-4} M TCB solution of PDBA monomers on the surface of HOPG. These islands are typically 10 to 20 nm across and are separated from each other by few hundred nanometers on the HOPG surface. The white arrow in panel (a) shows a second 2DP crystallite. The STM images marked by red and blue borders are digital zooms of the areas marked by same colors in panel (a) and panel (b). The red arrow highlights a line defect propagating through the 2DP island. (c) and (d) show sequential STM images obtained on the same polymer island showing the changes in its shape as a function of time and STM scanning. Imaging parameters: I_{set} = 50 pA, V_{bias} = -0.4 V

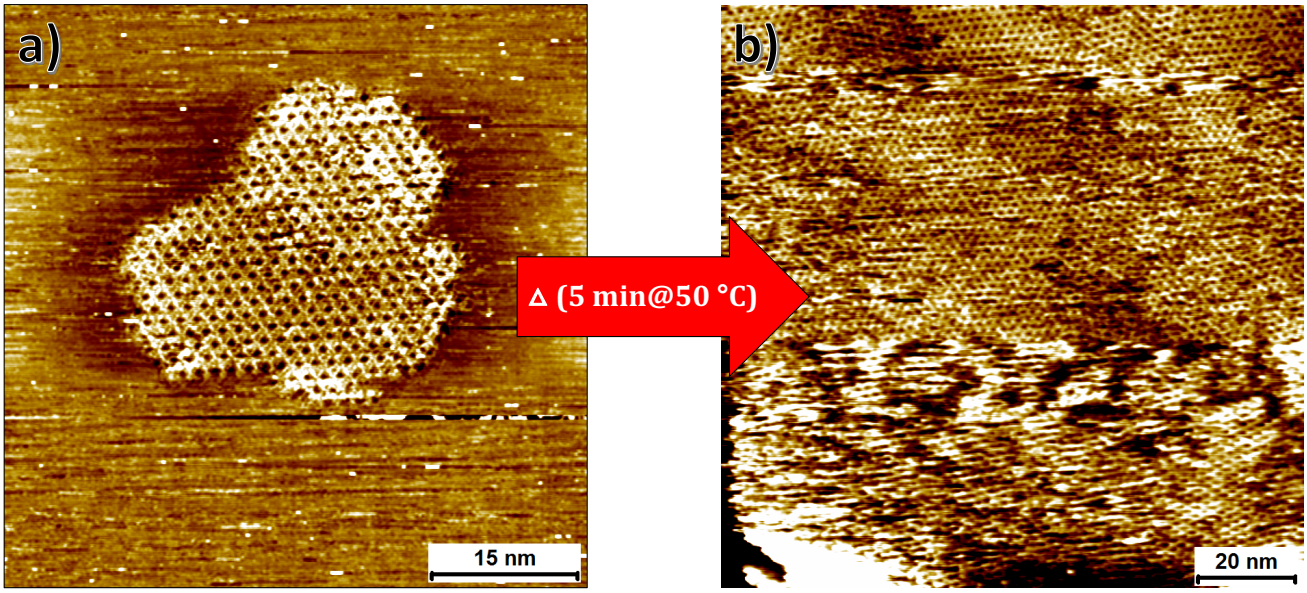


Figure S13. Representative STM data showing the transition of the small 2D crystallites obtained from TCB solutions ([PDBA] = 1×10^{-4} M) into extended domains of PDBA 2DP at the octanoic acid/HOPG interface. Imaging parameters: I_{set} = 50 pA, V_{bias} = -0.40 V

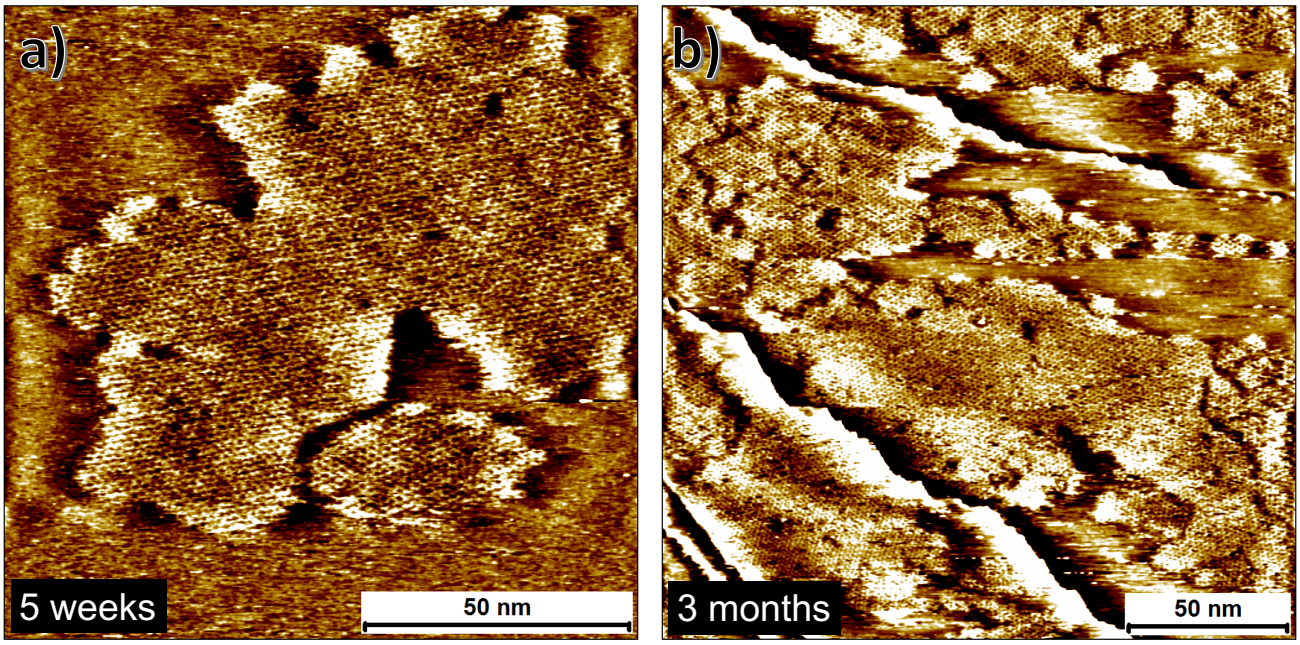


Figure S14. STM images showing the influence of ageing time on the size of 2DP crystallites deposited directly on the surface. [PDBA] = 1.0×10^{-4} M. The experimentally observed domain sizes range between 1520 nm^2 – 16000 nm^2 at this concentration. Imaging parameters: (a) I_{set} = 40 pA, V_{bias} = -0.350 V; (b) I_{set} = 50 pA, V_{bias} = -0.450 V.

2. UV-visible spectroscopy.

Molecule	$\lambda_{max\ (s0\rightarrow s1)}$ (nm)	ε_{max} ($mol^{-1}cm^{-1}$)	$\lambda_{max\ (s1\rightarrow s2)}$ (nm)	ε_{max} ($mol^{-1}cm^{-1}$)	λ_{em} (nm)	$(\bar{\nu}_{abs} - \bar{\nu}_{em})$ (cm^{-1})
PDBA	395	1570 ±100	338	32000 ±1200	399	250
Reference trimer (T)	384	3280 ±130	337	122800 ±2700	386	140

Table S2. Spectroscopic data for PDBA and the reference molecule **T** in OA and TCB solutions. ε_{max} for pyrene in cyclohexane is 54 000 $mol^{-1}cm^{-1}$ at 335.2 nm.[3]

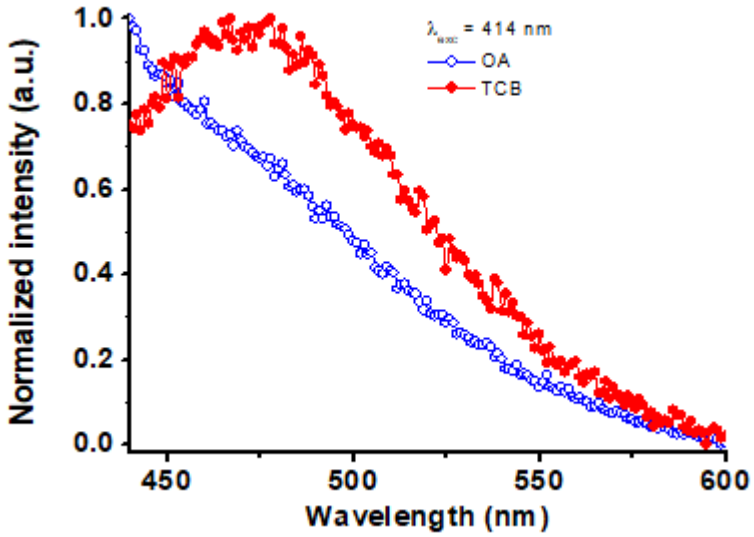


Figure S15. Normalized emission spectra of PDBA in octanoic acid solution (blue) and TCB solution (red) on mica. The excitation wavelength used was 414 nm.

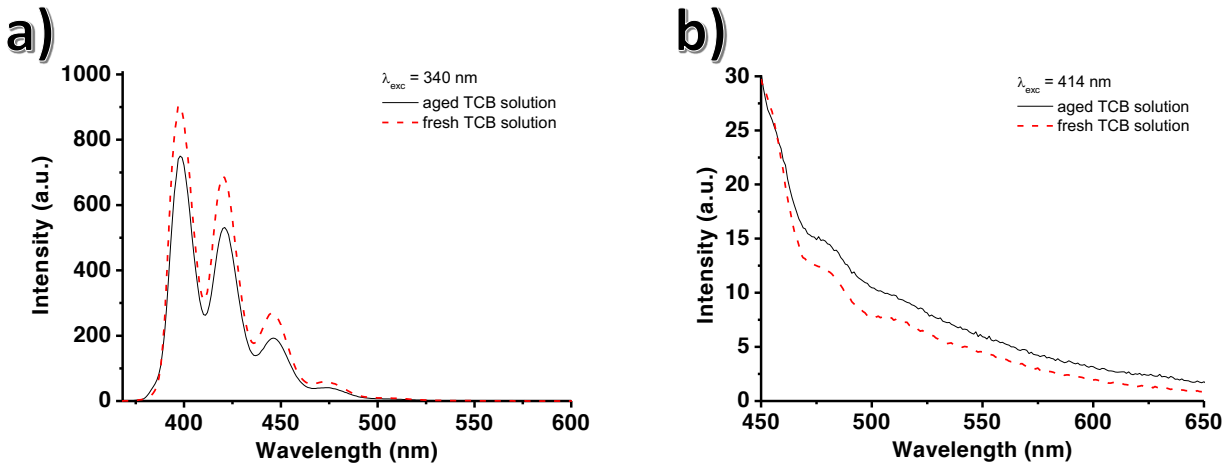


Figure S16. Emission spectra of PDBA in TCB upon excitation at 340 nm (a) and 414 nm (b). The black solid line corresponds to four-months aged solution and the dashed red line to a freshly prepared solution. The concentration of both PDBA TCB solutions is 1.0×10^{-4} M. The decrease of intensity of the band corresponding to the $S_0 \rightarrow S_2$ transition for the aged solution upon excitation at 340 nm; and the increase of the intensity of the structureless band for the aged solution upon excitation at 414 nm, indicate the larger amount of higher order π–π stacked species in the aged solution.

3. Additional references.

1. Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O'Keeffe, M.; Matzger, A. J.; Yaghi, O. M., Porous, Crystalline, Covalent Organic Frameworks. *Science* **2005,** *310*, 1166-1170.
2. Wan, S.; Guo, J.; Kim, J.; Ihee, H.; Jiang, D., A Photoconductive Covalent Organic Framework: Self-Condensed Arene Cubes Composed of Eclipsed 2D Polypyrene Sheets for Photocurrent Generation. *Angew. Chem. Int. Ed.* **2009,** *48*, 5439-5442.
3. Berlman, I. B., In *Handbook of Fluorescence Spectra of Aromatic Molecules*, Second Edition ed.; Berlman, I. B., Ed. Academic Press: New York, 1971; pp 67-95.