# Supporting information

**Computational details**

The DFT calculations were carried out using the Vienna Ab Initio Simulation Package [1] with the PBE functional [2] and the projected augmented wave (PAW) method.[3] Energy cutoff for the plane wave expansion was set to 400 eV. Primitive cells consisting of 110 and 142 atoms were used for TAPP–TPA and TAPP–QTD structures, respectively. For k–points sampling, $3 \times 3 \times 1$ mesh points were used for the structure optimization and $8 \times 8 \times 1$ for the electronic structural calculations. Optimization of structures was converged with the force on each atom less than 0.05 eV/Å, and energies were converged to $1.0 \times 10^{-5}$ eV. A 15 Å vacuum region was added along the z axis to avoid the possible interaction between the unit cell and its images. Although GGA functionals usually underestimate the band gap in the range of 0.8 eV, the semi–conductor character and their relative energy difference in band gap are consistent with the results of high–level hybrid functional.[4]

The molecular models of different polygons of $2DP_{TAPP-QTD}$ were built with Hyperchem Pro. 6.0 software, the conformation of the polygons were optimized on a single sheet of graphene representing a prototype of graphite substrate by molecular mechanics with MM+ force field.

**Experimental details**

5, 10, 15, 20-meso-tetra(4-aminophenyl)porphine (TAPP), N,N-dimethylacetamide (DMA), 2,5-bis(octyloxy)terephthalaldehyde (OTPA) and terephthalaldehyde (TPA) were purchased from J&K, and used without further treatment. 3, 3'''-Dioctyl-2, 2': 5', 5'': 2'',2'''-quaterthiophene-5, 5'''-dialdehyde (QTD) were synthesized with the method reported previously.[5] For the on-surface synthesis of 2D polymers, the monomers, TAPP, QTD and OTPA were dissolved in DMA with a mass concentration of 0.01mg/g, respectively. Then selected monomers were mixed with a desired mole ratio, a droplet (~6μL) of the mixed solution was directly deposited onto the freshly cleaved HOPG surface. And then, the samples were put into a low vacuum oven, annealed at 200℃ for 30 mins with pressure of 133 Pa. The amino-to-aldehyde mole ratio was varied in a range to optimize the coverage and connectivity of the 2D

polymers, and the detailed mole ratio is indicated in the figure captions. STM measurements were performed under room temperature at the solid-air interface with a constant current mode (Agilent 5100, USA). Detailed imaging conditions are given in the figure captions. Mechanically cut Pt/Ir (80/20) tips were used. The XY drift of STM images were corrected against the graphite lattice.

For the statistics of distribution of polygons and coordination numbers of TAPPs, about ten 80nm×80nm STM images were analyzed for $2DP_{TAPP-OTPA}$ and $2DP_{TAPP-QTD}$, respectively.
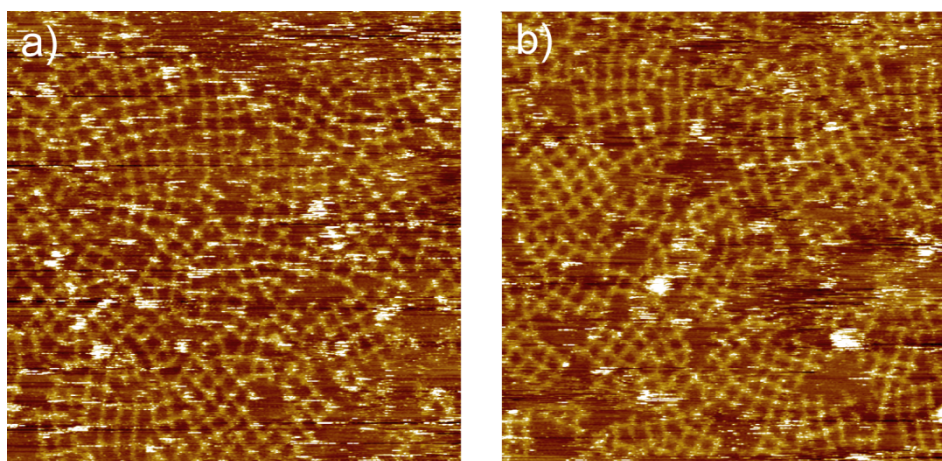


Figure S1. STM images of the $2DP_{TAPP-OTPA}$. Bended molecule backbones can be frequently seen, highlight its flexibility, this also generate defects in the $2DP_{TAPP-OTPA}$. Imaging areas are both 80nm×80nm. $V_{bias}$ = 300 mV, $I_{set}$ = 30 pA.
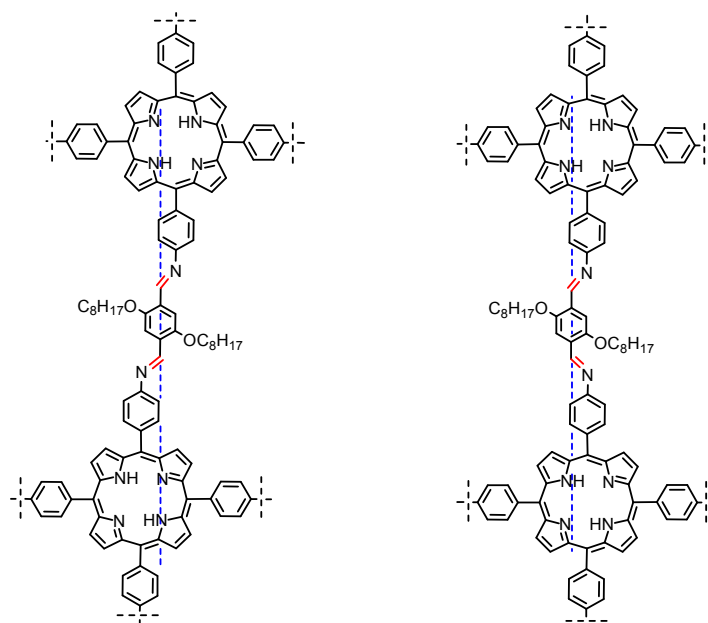


Figure S2. An enlarged schematic illustration for the *trans* and *cis*-conformation of

the imine linkage. Here *trans*-conformation refers to the conformation where the two imine bonds (highlighted with red color) point to opposite directions with respect to the molecular axis of OTPA (blue dotted line), while in the *cis*-conformation they point to the same side. In the *trans*-conformation the phenyl groups of two TAPP connected by the imine linkage resides on opposite side of the OTPA axis, while in *cis*-conformation they directly point to each other, this can serve as an indication for the identification of conformation of the imine linkage.
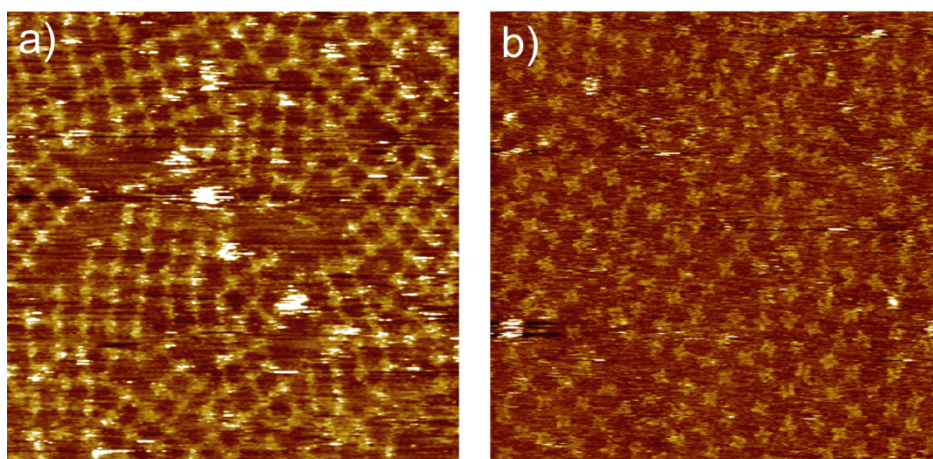


Figure S3. STM images of 2DP$_{TAPP-OTPA}$ obtained with positive (a) and negative (b) bias. With positive bias both the TAPP and OTPA moieties can be clearly seen while with negative bias only the TAPP parts appear with high contrast. Imaging conditions, $V_{bias}$ = 300 mV, $I_{set}$ = 33 pA for (a), $V_{bias}$ = -199 mV, $I_{set}$ = 17 pA for (b). Imaging areas are both 50nm×50nm.
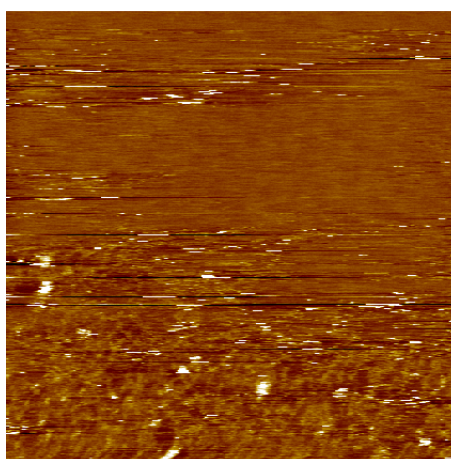


Figure S4. STM images of the 2DP$_{TAPP-TPA}$. Due to the absence of alkoxy group, 2DP$_{TAPP-TPA}$ is relatively unstable, can be easily destroyed by the tip scanning. Imaging area: 100nm×100nm, slow scanning direction: upward. Imaging conditions,

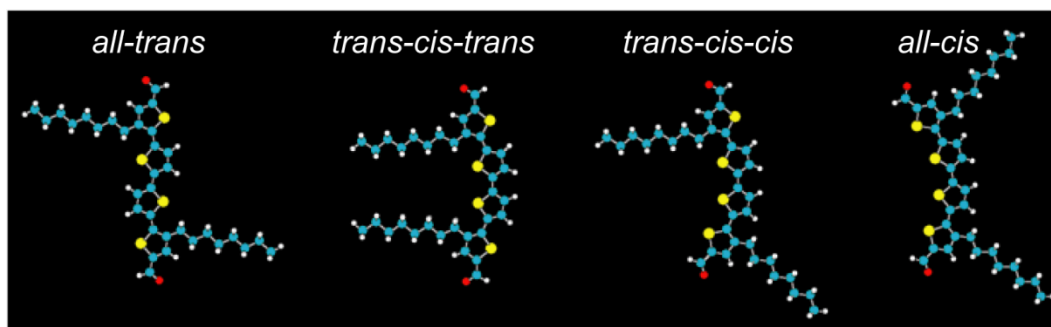$V_{bias} = -600$ mV, $I_{set} = 28$ pA



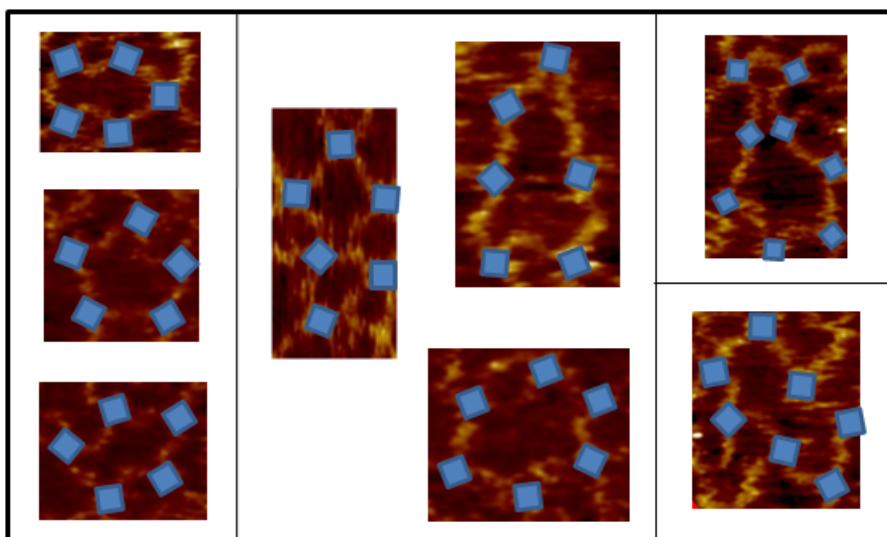Figure S5. Representative conformations of QTD, from all-*trans* to all-*cis* conformation.



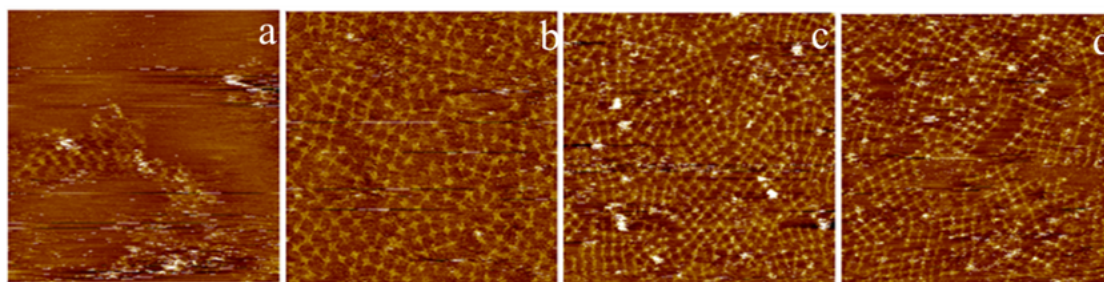Figure S6. Enlarged STM images of other polygons observed in 2DP$_{TAPP-QTD}$.



Figure S7. STM images of 2DP$_{TAPP-OTPA}$ obtained with different amino to aldehyde ratios. a) 5:1, b) 3:1, c) 1:1 and d) 1:2. Imaging area: a, c, d, 80nm×80nm, b, 55.2nm × 55.2nm. Imaging conditions, $V_{bias} = 300$ mV, $I_{set} = 30$ pA for a) and b), $V_{bias} = -700$ mV, $I_{set} = 28$ pA for c) and d).
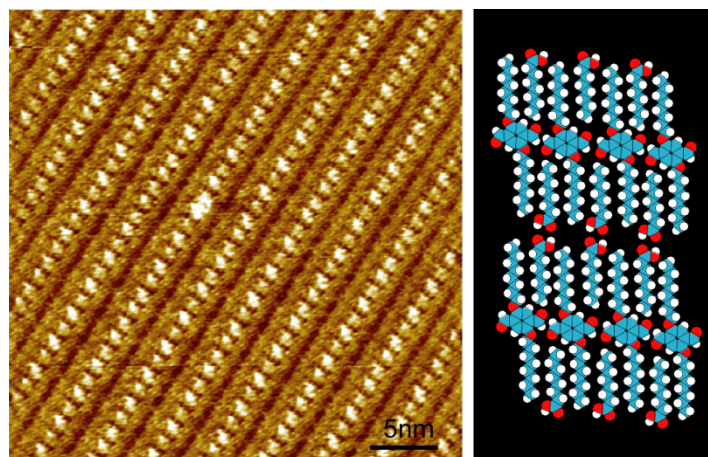
Figure S8. STM image and tentative modle of the assembly of OTDA at the octanoic acid-graphite interface with concentration of 1.0 mg/g. With lower concentration no stable adsorption can be observed, different from that of QTD, for which stable assembly can be observed with concentration as low as 0.02 mg/g. Imaging conditions, $V_{bias}$ = 600 mV, $I_{set}$ = 30 pA

**References:**

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