Supporting Information

The self-assembled flower structures formed by C_3-Symmetric aromatic carboxylic acids with meta-carboxyl groups

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S1. Experimental section

S1.1 Sample preparation

H_6BHB and H_6BTE were purchased from Extension Scientific. COR and 1-heptanoic acid were purchased from J&K Scientific. All these materials were used without further purification. 1-Heptanoic acid functioned as solvent to dissolve H_6BHB, H_6BTE and COR, and the concentrations of H_6BHB, H_6BTE and COR were controlled below 10^{-4} mol·L^{-1}. The assemblies were prepared by subsequent deposition of the components onto a freshly cleaned HOPG (grade ZYB, NTMDT, Russia) surface. All experiments were performed at room temperature. H_6BHB or H_6BTE solution was deposited on HOPG, and then detected by STM. Afterwards, COR dissolved in 1-heptanoic acid was added to the mono-component system of H_6BHB and H_6BTE followed by STM detection. The low concentration of COR solution was controlled below 10^{-5} mol·L^{-1}.

S1.2 STM detection

The STM measurements were performed on a Nanoscope IIIa (Bruker, USA). In this work, all the images were recorded using the constant current mode under ambient conditions. As STM probes, mechanically cut Pt/Ir tips (80/20) were used.

S1.3 DFT calculations

In these work, theoretical analysis was carried out with DFT-D schemes based on DMol3 code[1]. Two-dimensional supramolecular periodic structures at 1-heptanoic acid/HOPG interface were illuminated by periodic boundary conditions (PBC). In the local spin density approximation (LSDA), the Perdew-Burke-Ernzerh parameterization of the local exchange correlation energy was used to explain exchange and correlation.[2] All-electron spin-unrestricted Kohn–Sham wave functions were further expanded on account of local atomic orbital. The numerical basis sets were preferred to the large system and calculated all-electron ones, which were on the medium grid. In the self-consistent field procedure, the convergence standard of the energy and electron density was chosen as 10^{-5} a.u.. The lattice parameters and adsorbates geometries were optimized against the experimental data. The optimized cell parameters and interaction energies between molecules would be adopted when the energy and density convergence meet the standard requirements. To evaluate the interactions between the HOPG substrate and the adsorbate, a model system was established. There was almost no difference when the adsorbate was adsorbed on graphite or graphene, so we considered the matrix to be an infinite graphene monolayer and applied PBC in the calculation. The graphene layer was referred to as a periodic arrangement of orthorhombic unit cells including two carbon atoms, wherein the distance in the normal direction in the superlattice was 40 Å. The Brillouin region was sampled using a graphene supercell and a 1 x 1 x 1 *k*-point grid to achieve the establishment of the model system. The interaction energy, E_{inter}, of adsorbates with graphite is given by $E_{inter}=E_{tot(adsorbates/graphene)}-E_{tot(isolated\ adsorbates\ in\ vacuum)}-E_{tot(graphene)}$.

References

1 B. Delley, J. Chem. Phys. 2000, 113, 7756-7764;
2 J. P. Perdew, Y. Wang, Phys. Rev. B. 1992, 45, 13244-13249.

S2. Large-scale STM image of H_6BHB and H6BTE self-assembly structures

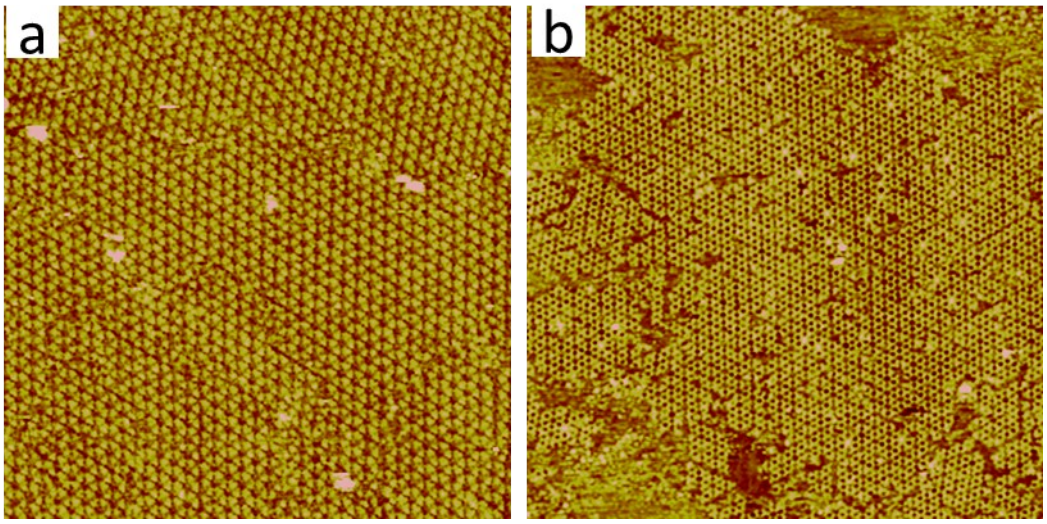

Fig. S1 (a) Large-scale STM images of H_6BHB structures at the 1-heptanoic acid/HOPG interface (I_{set} = 299.1 pA, V_{bias} = 699.8 mV, 84.3 nm × 84.3 nm); (b) Large-scale STM images of H_6BTE structures at the 1-heptanoic acid/HOPG interface (I_{set} = 299.9 pA, V_{bias} = 699.9 mV, 103.2 nm × 103.2 nm).

S3. Large-scale STM image of H_6BHB/COR co-assembly structures

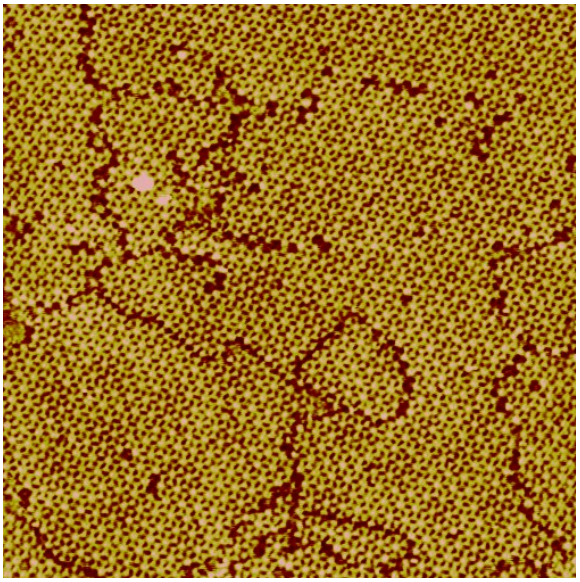

Fig. S2 Large-scale STM images of H_6BHB/COR structures at the 1-heptanoic acid/HOPG interface (I_{set} = 299.1 pA, V_{bias} = 699.6 mV, 92.5 nm × 92.5 nm).

S4. Concentration regulation of H_6BHB/ H_6BTE co-assembly structures

The concentration regulation of H_6BHB/ H_6BTE co-assembly structures has been investigated as shown in Fig. S3. The solutions with different concentrations of H_6BHB and H_6BTE are 20%, 40% and 80% saturated H_6BHB and H_6BTE solutions respectively. Mixing two solutions in equal volumes to obtain a mixture with a H_6BHB:H_6BTE molar ratio of 1:4, 1:2, 1:1, 2:1 and 4:1. The results show that the two molecules are still phase separated by changing the stoichiometry in the mixture, but the ratio of area occupancy of H_6BHB and H_6BTE changes as the change of the molar ratio, the higher the molecular molar ratio, the higher the area occupancy rate. When the ratio of H_6BHB:H_6BTE was 4:1, the H_6BTE molecules were almost unobserved and the H_6BHB occupied the whole surface. The H_6BHB areas are marked in red lines.

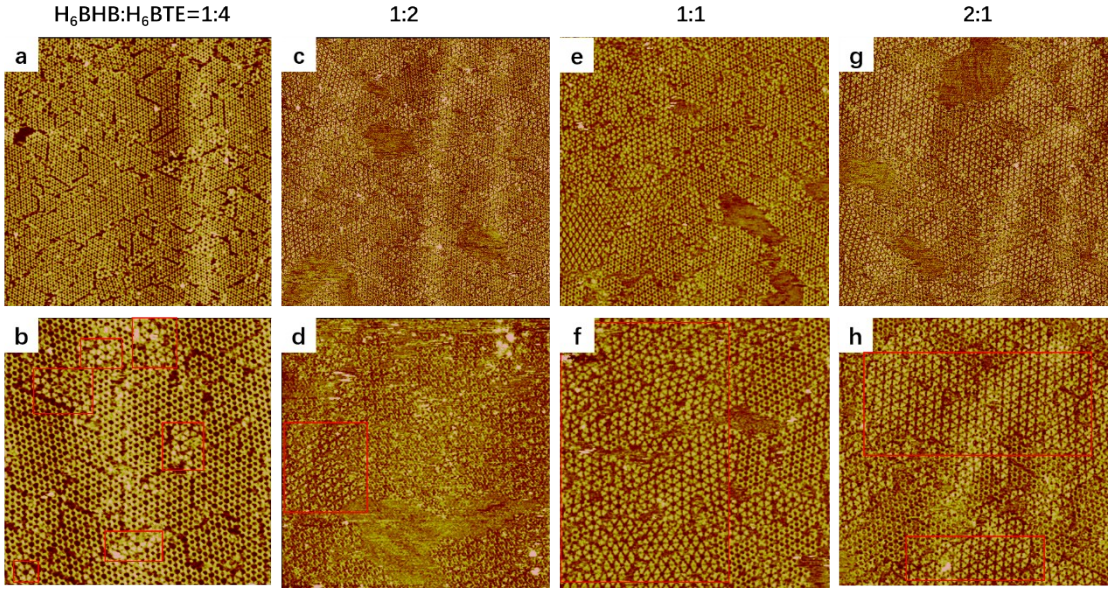

Fig. S3 (a) Large-scale STM images of H_6BHB:H_6BTE molar ratio of 1:4 structures at the HA /HOPG interface (I_{set} = 299.1 pA, V_{bias} = 699.9 mV, 120 nm × 120 nm), (b) high-resolution STM images of H_6BHB:H_6BTE molar ratio of 1:4 (I_{set} = 299.1 pA, V_{bias} = 699.9 mV, 58 nm × 58 nm), (c) large-scale STM images of H_6BHB:H_6BTE molar ratio of 1:2 structures at the HA /HOPG interface (I_{set} = 299.9 pA, V_{bias} = 699.9 mV, 120 nm × 120 nm), (d) high-resolution STM images of H_6BHB:H_6BTE molar ratio of 1:2 (I_{set} = 299.8 pA, V_{bias} = 699.9 mV, 69 nm × 69 nm), (e) large-scale STM images of H_6BHB:H_6BTE molar ratio of 1:1 structures at the HA /HOPG interface (I_{set} = 299.1 pA, V_{bias} = 699.9 mV, 102 nm × 102 nm), (f) high-resolution STM images of H_6BHB:H_6BTE molar ratio of 1:1 (I_{set} = 299.1 pA, V_{bias} = 699.9 mV, 65 nm × 65 nm), (g) large-scale STM images of H_6BHB:H_6BTE molar ratio of 2:1 structures at the HA /HOPG interface (I_{set} = 299.1 pA, V_{bias} = 699.8 mV, 99 nm × 99 nm), (h) high-resolution STM images of H_6BHB:H_6BTE molar ratio of 2:1 (I_{set} = 299.1 pA, V_{bias} = 699.8 mV, 66 nm × 66 nm). The H_6BHB areas are marked in red lines.