Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Mixing behavior of p-terphenyl-3,5,3′,5′-tetracarboxylic acid with trimesic acid at the solid–liquid interface

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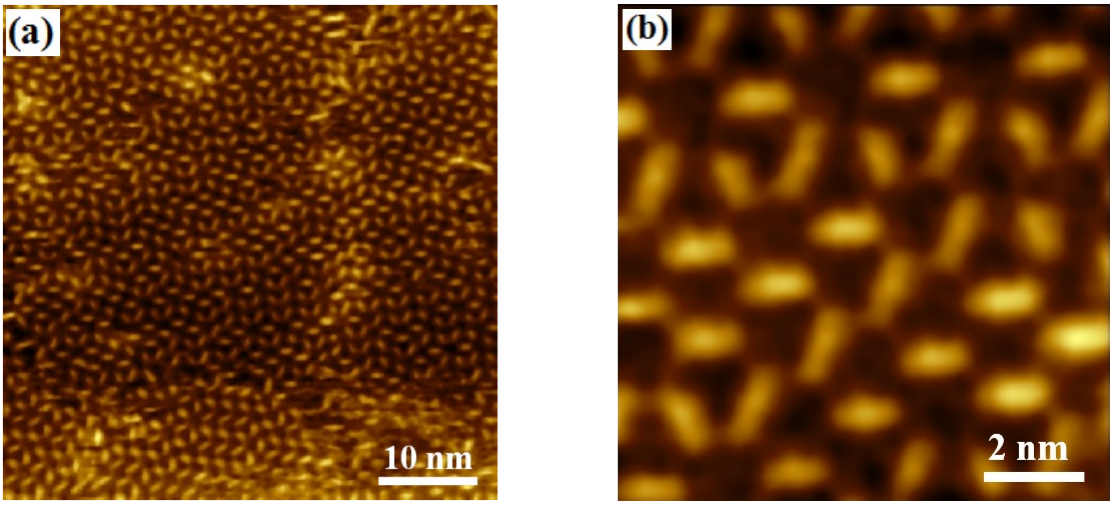

Fig. S1. (a) The STM image of TPTC monolayers at nonanoic acid/HOPG interface (I = 0.65 nA, V = -0.32 V). An interesting feather of the TPTC monolayer structure is that pores are not all equivalent. (b) Details of the assembly structure are revealed in the high-resolution image (I = 0.68 nA, V = -0.35V).

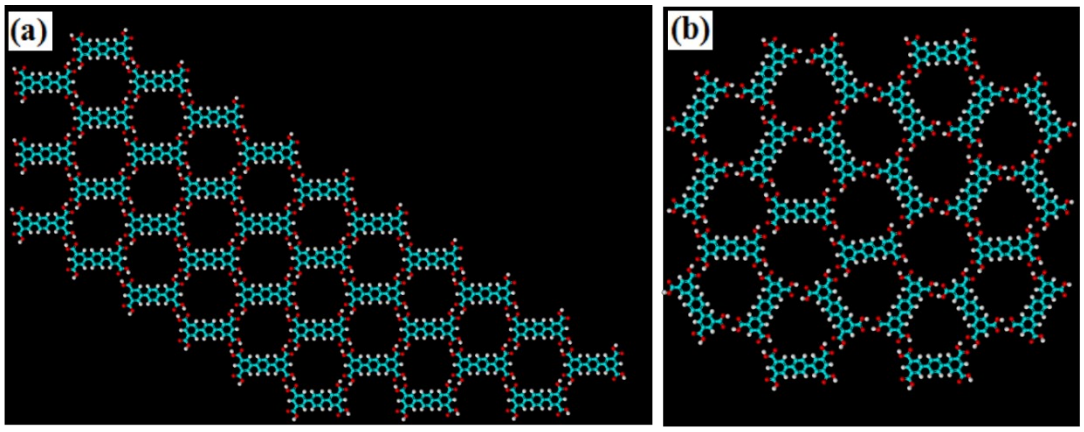

Fig. S2. Molecular models showing the ability of **TPTC** to assemble either into (a) a parallel or (b) a randomtiling network. Within the random tilingnetwork, the molecules can form H-bonds with no structural deformation. The total potential energies of the two arrangements shown above were found be identical (parallel: –123.4 kcal mol^{-1}; random tiling network: –124.1 kcal mol^{-1}).

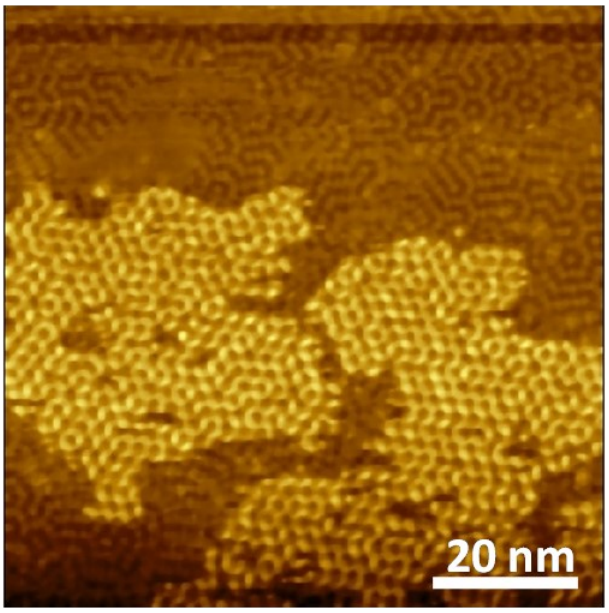

Fig. S3. STM image of the TPTC bilayer network at nonanoic acid/HOPG surface (*I* = 0.67 nA, *V* = -0.82 V). STM observations clearly show that the structure underwent no change and growth of a second layer was observed on top of the random phase by heated to 50 °C for five minutes. The domains nucleated in the TPTC monolayer in second-layer islands do not continuously join an island nucleated at different sites.

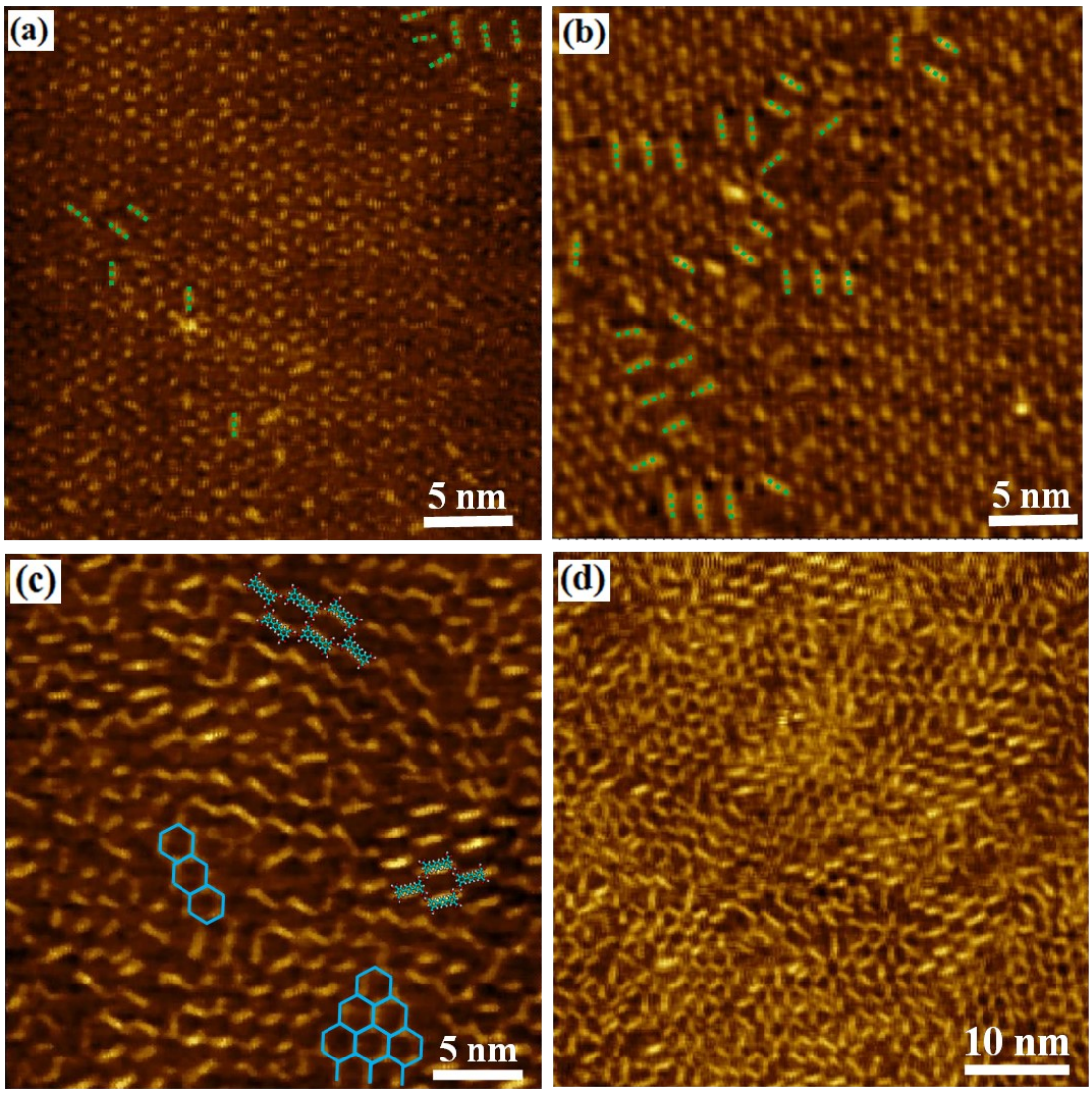

Fig. S4. STM image of the self-assembled porous flowerlike TMA/TPA structure on HOPG (I = 0.62 nA, V = −0.57 V). A droplet of a heptanoic acid solution containing TMA and BDA (a molar ratio of 3:1) was dropped onto the HOPG surface, a new kind of rectangular flowerlike porous network was formed. The length L of the hexagon is 2.8 ± 0.1 nm, Each TMA molecule links with three TMA molecules through one-third of all hydrogen bonds, forming a trimer. Meanwhile the TPA molecule acts as a bridge to connect two TMA molecules on both sides also through two pairs of O···H-O bonds, resulting in the formation of binary rectangular networks. The measured unit cell parameters are a = 2.8 ± 0.1 nm, b = 4.1 ± 0.1 nm, and α = 65 ± 1°.