Supporting Information for

2D Co-Crystallization of Molecular Homologues Promoted by Size Complementary of the Alkyl Chains at the Liquid/Solid Interface

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Contents:

1. Experimental materials and methods. BIC-Cn homologues were synthesized according to previous literature[1]. 1-octanol and 1-heptanol were purchased from Sigma-Aldrich with purity of 99%. To obtain a BIC-Cn adlayer, a droplet of BIC-Cn solution was added onto a freshly cleaved HOPG (grade ZYB) surface. As for the co-deposition of two BIC-Cn homologues, unless otherwise noted, the solutions of two BIC-Cn components were premixed. The mixed solution was then dropped on the HOPG surface. STM experiments were performed using PicoSPM (Agilent Technologies) in constant-current mode at the liquid/solid interface. STM tips were mechanically cut from Pt/Ir wire (90/10). All STM images were shown without further processing.

Molecular mechanistic simulations. MM simulations were performed with the molecular package TINKER using the MMFF force field[2-4]. A two-layer sheet of graphite was used as the HOPG surface. The model of the molecular assembled structure is proposed based on the STM results. The molecular assembly is placed 0.35 nm above the upper layer of the substrate with the alkyl chains parallel to the direction of graphite symmetry axes. During optimization, the graphite was frozen, whereas the molecular models were relaxed.

The interaction energy is estimated using adsorption energy which is defined as $\Delta E_{ad} = E_{ass+sub} - (E_{mol} + E_{sub})$, here n is the number of molecules, E_{mol} is the energy of a single molecule, E_{sub} and $E_{ass+sub}$ are the energies of the substrate and the assembled unit on the substrate respectively. The adsorption energy given in the text is divided by the area.

2. STM images of the honeycomb networks formed by pure BIC-C6, BIC-C10, BIC-C12, BIC-C14 at the 1-octanol/HOPG interface

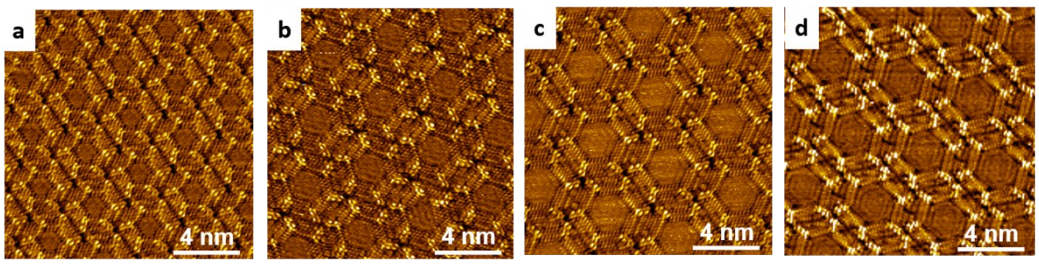

Fig. S1. High-resolution STM images of the honeycomb networks formed by (a) BIC-C6, (b) BIC-C10, (c) BIC-C12, and (d) BIC-C14. I = 1.0–1.5 nA, V = 0.9 V.

3. Molecular models for the tentative hybrid honeycomb structure in which BIC-Cn trimer doped into the hexagonal unit of the other BIC-Cn homologue.

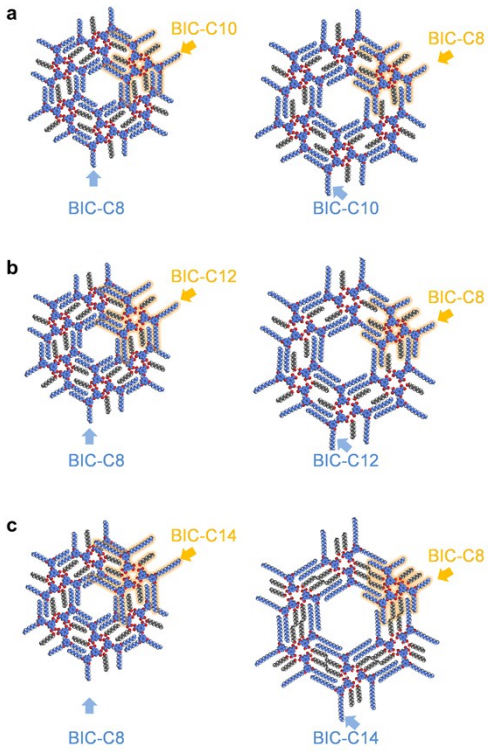

Fig. S2. Tentative doping models of a hybrid honeycomb network with (a) a BIC-C10 (BIC-C8) doped into the hexagonal unit of BIC-C8 (BIC-C10); (b) a BIC-C12 (BIC-C8) doped into the hexagonal unit of BIC-C8 (BIC-C12); (c) a BIC-C14 (BIC-C8) doped into the hexagonal unit of BIC-C8 (BIC-C14).

4. STM images of the adlayer formed by co-deposition of BIC-C6 with BIC-C8 or BIC-C12 at the 1-octanol/HOPG interface

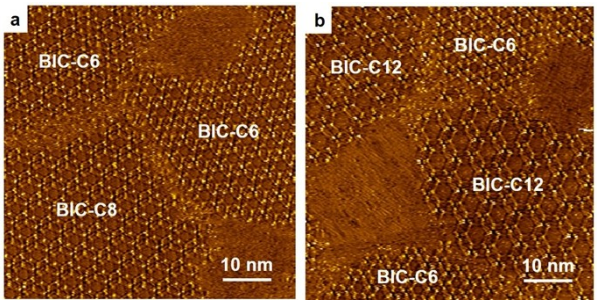

Fig. S3. STM images of the adlayer formed by (a) BIC-C6 and BIC-C8 (I = 1.2 nA, V_{bias} = 0.9 V); (b) BIC-C6 and BIC-C12 (I = 1.0 nA, V_{bias} = 0.900 V).

5. STM image and molecular model of the hybrid pinwheel tetramer structure of BIC-C6/BIC-C10 at the 1-octanol/HOPG interface

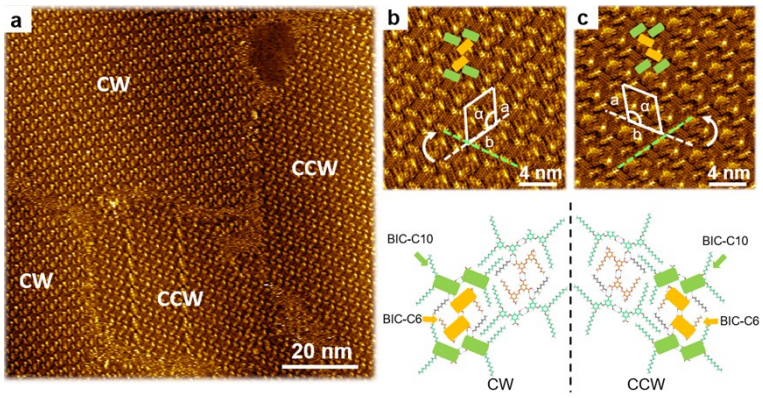

Fig. S4. (a) Large scale STM image of the hybrid pinwheel tetramer structure of BIC-C6 and BIC-C10. (b) High-resolution STM image of CW pinwheel tetramer and corresponding molecular models; (c) High-resolution STM image of CCW pinwheel tetramer and corresponding molecular models. I_{set} = 0.8–1.0 nA, V_{bias} = 0.9 V. The orange and green sticks represent the aromatic moieties of BIC-6 and BIC-C10, respectively. The green and white dashed lines imply the direction of the axis of BIC molecule and the unit cell direction **b**, respectively. White arrows identify the handedness of the structure unit. For clarity, the unadsorbed alkoxy chain in BIC-C6 are replaced by methoxy group. BIC-C6, BIC-C10 and 1-octanol in molecular models are colored orange, green, and grey, respectively.

6. Enlarged molecular model of the BIC-C6/BIC-C10 hybrid double-walled honeycomb structure.

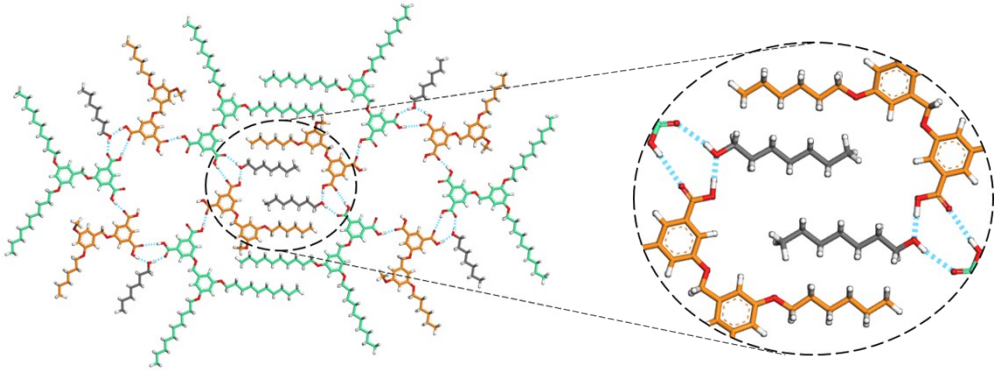

Fig. S5. Molecular model of the hybrid double-walled honeycomb network formed by BIC-C6 and BIC-C10. For clarity, the unadsorbed alkyl chain of BIC-C6 is simplified as a methoxy group. BIC-C10, BIC-C6 and 1-heptanol are colored green, orange and grey, respectively.

REFERENCE

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