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Electronic Supplementary Information (ESI) for

Influence of Core Size on Self-Assembled Molecular Networks Composed of C_{3h}-Symmetric Building Blocks

through Hydrogen Bonding Interactions: Structural Features and Chirality

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1. Details of STM Observation

All experiments were performed at 20-26 °C using a Nanoscope IIIA or V (Bruker AXS) with an external pulse/function generator (Agilent 33220A or TEXIO FGX-295) with negative sample bias. STM tips were mechanically cut from Pt/Ir wire (80%/20%, diameter 0.25 mm). For the preparation of sample solutions, 1-heptanoic acid (Wako) was used as a solvent after distillation. Solute concentrations were set from 1.0×10^{-6} to 1.5×10^{-4} M. This solution (15 or 40 μ L) was poured into a homemade liquid cell placed on a freshly cleaved basal plane of a 1 cm² piece of highly oriented pyrolytic graphite (HOPG, grade ZYB, Momentive Performance Material Quartz Inc., Strongsville, OH). When the system was annealed to promote self-assembling process, the system was heated at 80 °C for 3 h in an oven. To prevent solvent evaporation during annealing treatment, this liquid cell was covered with a stainless lid. After the heating treatment, the substrate was naturally cooled down to room temperature. Both the self-assembled molecular networks (SAMNs) and underneath graphite surface could be observed by changing the tunneling parameters during STM observations. The image distortion owing to thermal drift effects was corrected with respect to the surface lattice of the underneath graphite using the SPIP software (Scanning Probe Image Processor, SPIP, version 4.0.6 or 6.0.13, ImageMetrogy A/S, Hørsholm, Denmark). More than 9 large area STM images (image sizes: $80 \times 80 \text{ nm}^2$) were acquired per an independent experimental session. Three independent experimental sessions were performed at each condition to confirm reproducibility. The unit cell parameters were determined using more than 30 experimental data points from at least three calibrated STM images (image sizes: 30 \times 30 nm² or smaller).

2. Details of Molecular Mechanics Simulation

The molecules used for the construction of the network models of SAMNs were optimized by a semiempirical PM6 method using the Gaussian 16W version 1.1 (Gaussian, Inc.) software.¹ The initial geometries of the SAMNs were built using the GaussView 6.0.16 (Gaussian, Inc.) and ViewerLite (Accelrys, Inc.) software to fit the experimentally obtained unit cell parameters. All MM simulations were performed by the Material Studio 2017 R2 software using the Forcite module with the COMPASS force field. These molecules were placed 0.350 nm above the first layer of a bilayer graphene sheet (interlayer distance is 0.335 nm). This two-layer graphene sheet was frozen during the simulations. A cutoff value of 2.0 nm was applied for the van der Waals interactions (Lennard-Jones type).

3. Van der Waals Distances of Host Networks and Guest Molecules

To estimate the pore sizes, the hydrogen-bonded cyclic hexamers of **H3TTCA** and **DBACOOH** were extracted from the optimized honeycomb structures by MM simulations. Van der Waals distances of 1-heptanoic acid used as a solvent, as well as coronene and phthalocyanine used as guest molecules are shown in Figure S1.



Figure S1. (a) Molecular models of **H3TTCA** and its cyclic hexamer. (b) Molecular models of **DBACOOH** and its cyclic hexamer. The edge to edge distance of the pores shown in (a) and (b) are the distances between the centers of hydrogen bonded carboxy groups. (c) Molecular models of the solvent and guest molecules. In (c), van der Waals distances of the molecules are the interatomic distances between the hydrogen atoms at the terminal edges.

4. Self-Assembly of H3TTCA at the 1-HA/Graphite Interface

4.1 Additional STM Images

At the 1-HA/HOPG interfaces, no SAMN formation of **H3TTCA** was observed at the lowest concentration of 1.0×10^{-6} M. Instead, at this condition, the SAMN of 1-heptanoic acid was observed (Fig. S2a). **H3TTCA** mainly forms a honeycomb structure from middle to high solute concentrations with/without annealing treatment (Figs. S2b, c). At the middle concentration range (from 6.0×10^{-6} M to 1.0×10^{-5} M the domain size of the honeycomb structure is typically large. On the other hand, at the highest concentration (1.5×10^{-4} M), there are small disordered area in addition to the honeycomb structure (Figs. S2c, d). These experimental results are consistent with those in previous reports.²



Figure S2. (a) STM image of the SAMNs of the 1-HA molecules (concentration; 1.0×10^{-6} M, tunneling parameters; $I_{set} = 300$ pA, $V_{bias} = -0.44$ V). (b) STM image of a honeycomb structure of **H3TTCA** at the 1-HA/graphite interface (concentration; 6.0×10^{-6} M, tunneling parameters; $I_{set} = 250$ pA, $V_{bias} = -0.43$ V). (c, d) STM images of the honeycomb structure together with small disordered area formed by **H3TTCA** at the 1-HA/graphite interface (concentration; 1.5×10^{-4} M, tunneling parameters; $I_{set} = 250$ pA, $V_{bias} = -0.41$ V). White lines in (d) are domain boundaries.

4.2 Additional STM Images of Honeycomb Structure

To determine the structural details of the honeycomb structure, the distance L_1 between the centers of benzene rings in adjacent **H3TTCA** was measured using high-resolution STM images (red arrow in Fig. S3a). A mean distance value becomes 0.78 ± 0.05 nm. Moreover, for the determination of the molecular orientation, we defined regular triangles by connecting the three benzene rings of **H3TTCA** (blue and black dotted triangles in Fig. S3b). The orientational difference between the blue and black dotted triangles is 60° .



Figure S3. (a) High-resolution STM image of the honeycomb structure of H3TTCA at the 1-HA/graphite interface (concentration; 6.0×10^{-6} M, tunneling parameters; $I_{set} = 230$ pA, $V_{bias} = -0.56$ V). Red arrow indicates the distance L_1 between the centers of the benzene rings of adjacent H3TTCA molecules. (b) High-resolution STM image of the honeycomb structure at the 1-HA/graphite interface (concentration; 1.0×10^{-5} M, tunneling parameters; $I_{set} = 300$ pA, $V_{bias} = -0.39$ V). Black and blue dotted triangles are defined by connecting three benzene rings of H3TTCA. The orientational difference between the black and blue dotted triangles is 60° .

4.3 Chirality of Honeycomb Structure

At a single molecular level, H3TTCA shows *R*- or *L*-type point chirality on a surface. The honeycomb structure consists of a *R*- or *L*-type H3TTCA molecule generating *R*- or *L*-type supramolecular chirality. This supramolecular chirality of the honeycomb structure could be differentiated by the angle α values between the short unit cell vector *a* and one of the normal axes of the graphite. The average angles α values are $12 \pm 1^{\circ}$ and $-12 \pm 1^{\circ}$ for the honeycomb structures formed by the *R*-type and *L*-type H3TTCA molecules, respectively.



Figure S4. A honeycomb structure formed by H3TTCA at the 1-HA/graphite interface. (a) STM image of a *R*-type

honeycomb structure (concentration; 6.0×10^{-6} M, tunneling parameters; $I_{set} = 100$ pA, $V_{bias} = -0.66$ V). (b) STM image of a *L*-type honeycomb structure (concentration; 6.0×10^{-6} M, tunneling parameters; $I_{set} = 120$ pA, $V_{bias} = -0.67$ V). (c, d) Molecular models of the chiral *R*- and *L*-honeycomb structures constructed by MM calculations.

5. Self-Assembly of DBACOOH at the 1-HA/Graphite Interface

5.1 Additional STM Images

At the 1-HA/graphite interface, **DBACOOH** forms different structures depending on the solute concentration and with/without annealing treatment. At a concentration of 6.0×10^{-6} M, there are type I and II structures without annealing treatment (Fig. S5a), and the type III structure is formed after annealing treatment (Fig. S5b). At a concentration of 1.5×10^{-4} M, a disordered structure is formed with/without annealing treatment (Figs. S5c,d)



Figure S5. SAMNs formed by DBACOOH at the 1-HA/graphite interface. (a) STM image of type I and II structures (concentration; 6.0×10^{-6} M, tunneling parameters; $I_{set} = 220$ pA, $V_{bias} = -0.68$ V). (b) STM image of a type III structure (concentration; 6.0×10^{-6} M, after annealing treatment, tunneling parameters; $I_{set} = 200$ pA, $V_{bias} = -0.39$ V). (c) STM image of disordered area (concentration; 1.5×10^{-4} M, tunneling parameters; $I_{set} = 210$ pA, $V_{bias} = -0.43$ V). (d) STM image of disordered area (concentration; 1.5×10^{-4} M, after annealing treatment, tunneling parameters; $I_{set} = 210$ pA, $V_{bias} = -0.43$ V). (d) STM image of disordered area (concentration; 1.5×10^{-4} M, after annealing treatment, tunneling parameters; $I_{set} = 200$ pA, $V_{bias} = -0.42$ V). The insets of (c, d) are 2D-FFT images where no periodic signals appear.

5.2 Additional STM Images of Disordered Area

A representative STM image at a high concentration of 1.5×10^{-4} M is shown in Fig. S6. **DBACOOH** molecules are densely packed with several small arrangements on a surface.



Figure S6. STM image of disordered area (concentration; 1.5×10^{-4} M, tunneling parameters; $I_{set} = 210$ pA, $V_{bias} =$

-0.41 V).

5.3 Details of MM Simulations of the Type I Structure

The unit cell of the type I structure includes eight **DBACOOH** molecules. Based on the positions of the DBA cores in the STM images, we concluded that a cyclic hexamer is consisted of *L*- or *R*-type molecules. To determine the chirality of the **DBACOOH** molecule located outside the cyclic hexamer, we constructed three possible model structures (8R, 7R+1L, and 6R+2L structures in Figs. S7a, b, and c) and compared them with the STM images. The type I structure consisting of a single enantiomer (Fig. S7a) nicely matches the experimental results.



Figure S7. Three molecular models of a type I structure consisting of (a) eight *R*-type molecules, (b) seven *R*-type and one *L*-type molecules, and (c) six *R*-type and two *L*-type molecules.

5.4 Supramolecular Chirality of the Type I Structure

The type I structure is chiral as it is composed of either only *R*-type or *L*-type molecules. The supramolecular chirality of the type I structure is determined by the angle α value between the unit cell vector a and one of the normals of the main symmetry axes of graphite. The average angle α values are $27 \pm 1^{\circ}$ and $-27 \pm 1^{\circ}$ for the type I structures of the *R*-type and *L*-type molecules, respectively.



Figure S8. Type I structure formed by DBACOOH at the 1-HA/graphite interface. (a) STM image of a type I (8L)

structure (concentration; 6.0×10^{-6} M, tunneling parameters; $I_{set} = 200$ pA, $V_{bias} = -0.40$ V). (b) STM image of a type I (8*R*) structure (concentration; 1.0×10^{-5} M, tunneling parameters; $I_{set} = 210$ pA, $V_{bias} = -0.46$ V). (c, d) Corresponding molecular models of the chiral type I structures constructed by MM calculations.

5.5 Details of MM Simulations of the Type II Structure

The unit cell of the type II structure includes four **DBACOOH** molecules. From the positions of the DBA cores in the STM images, we considered that the type II structure consists of homo- or hetero-dimers. To determine the structural details, we constructed four possible model structures (4R, 3R+1L, and 2R+2L structures in Figs. S9a, b, and c) and compared them with the STM images. The type II structure consisting of equal amounts of both homodimers (R,R and L,L) (Fig. S9c) nicely matches the experimental data.



Figure S9. Molecular models of three Type II structures composed of (a) 4R, (b) 3R+1L, and (c) 2R+2L molecules.

5.6 Chirality of the Type II Structure

The type II structure is a 2D-racemate in view of its composition (an equal amount of the *R*-type or *L*-type molecule). However, the type II structure shows a handedness differentiated by the domain orientations with respect to the graphite lattice. The average angle α values are $0.2 \pm 0.3^{\circ}$ and $-0.1 \pm 0.3^{\circ}$, respectively.



Figure S10. Type II structure formed by DBACOOH at the 1-HA/graphite interface. (a) STM image of a type II (2R+2L) structure having a positive angle α value (concentration; 6.0×10^{-6} M, tunneling parameters; $I_{set} = 200$ pA, $V_{bias} = -0.47$ V). (b) STM image of a type II (2R+2L) structure having a negative angle α value (concentration; 6.0×10^{-6} M, tunneling parameters; $I_{set} = 200$ pA, $V_{bias} = -0.47$ V). (b) STM image of a type II (2R+2L) structure having a negative angle α value (concentration; 6.0×10^{-6} M, tunneling parameters; $I_{set} = 200$ pA, $V_{bias} = -0.47$ V).

 10^{-6} M, tunneling parameters; $I_{set} = 200$ pA, $V_{bias} = -0.41$ V). (c, d) Molecular models of corresponding type II structures with different orientations constructed by MM calculations.

5.7 Detailed MM Model of Type III Structure

For the modeling of the type III structure, we performed MM simulations for three possible combinations of chirality at the single molecular level (4R, 3R+1L and 2R+2L) to check their consistency with the STM images. The type III structure consisting of a single enantiomer agrees with the STM image.

In the type III structure, the **DBACOOH** molecules were observed to be densely arranged in a linear fashion. The unit cell of the type III structure includes four **DBACOOH** molecules. We constructed four possible model structures, a homochiral structure (4R) and three heterochiral structures (3R+1L, 2R+2L–A, and 2R+2L–B, Figs. S11a, b, c, and d) and compared them with the contrast of the STM images. As a result, the type III structure consisting of a single enantiomer (4R, Fig. S11a) nicely matches the experimental data.



Figure S11. Molecular models of four Type III structures, (a) 4R, (b) 3R+1L, (c) 2R+2L-A, and (d) 2R+2L-B structures.

5.8 Chirality of the Type III Structure

The supramolecular chirality of the type III structure could be differentiated by the angle α value. The average angle α values are $13 \pm 1^{\circ}$ and $-13 \pm 1^{\circ}$ for the type III structures formed by the *R*-type and *L*-type molecules, respectively.



Figure S12. Type III structures formed by **DBACOOH** at the 1-HA/graphite interface. (a) STM image of a type III (2*R*) structure (concentration; 6.0×10^{-6} M, tunneling parameters; $I_{set} = 200$ pA, $V_{bias} = -0.47$ V). (b) STM image of

a type III (2*L*) structure (concentration; 6.0×10^{-6} M, tunneling parameters; $I_{set} = 200$ pA, $V_{bias} = -0.39$ V). (c, d) Molecular models of the chiral *R*- and *L*-type III structures constructed by MM calculations.

6. Host-Guest Systems

6.1 Additional STM Image of a Honeycomb Structure with Co-adsorbed Phthalocyanine Molecule



Figure S13. (a) STM image of a honeycomb structure with co-adsorbed phthalocyanine molecule (concentration; 1.0 $\times 10^{-5}$ M, tunneling parameters; $I_{set} = 300$ pA, $V_{bias} = -0.39$ V). (b) STM image of a type III structure prepared by the same sample solution after annealing treatment (concentration; 1.0×10^{-5} M, tunneling parameters; $I_{set} = 200$ pA, $V_{bias} = -0.58$ V).

6.2 Chirality of a Honeycomb Structure with Co-Adsorbed Phthalocyanine Molecule

In a honeycomb structure, *R*-type or *L*-type **DBACOOH** molecules are connected through complementary hydrogen bonding interactions ($R_2^2(8)$). The supramolecular chirality (*R* or *L*) of the two-component honeycomb structure is determined by the angle α value between the unit cell vector *a* and one of the normal axes of the graphite. The average angle α values are $17 \pm 1^\circ$ and $-17 \pm 1^\circ$ for the honeycomb structure formed by the *R*-type and *L*-type **DBACOOH** molecules, respectively.



Figure S14. Honeycomb structures formed by a mixture of **DBACOOH** and phthalocyanine at the 1-HA/graphite interface. (a) STM image of a honeycomb (2*R*) structure (concentration; 1.0×10^{-5} M, tunneling parameters; $I_{set} = 220$ pA, $V_{bias} = -1.09$ V). (b) STM image of a honeycomb (2*L*) structure (concentration; 1.0×10^{-5} M, tunneling parameters; $I_{set} = 200$ pA, $V_{bias} = -0.68$ V). (c, d) Corresponding molecular models of the chiral honeycomb (*R* and *L*) structures constructed by MM calculations.

6.3 Additional STM Image of a Honeycomb Structure with Co-Adsorbed Coronene Molecules



Figure S15. STM images of two-component structures formed by a mixture of **DBACOOH** and coronene at the 1-HA/graphite interface. (a) STM image of a two-component structure (concentration; 1.0×10^{-5} M, tunneling parameters; $I_{set} = 200$ pA, $V_{bias} = -0.61$ V). (b) STM image of a type III structure prepared from the same sample solution after annealing treatment (concentration; 1.0×10^{-5} M, tunneling parameters; $I_{set} = 210$ pA, $V_{bias} = -0.47$ V).

6.4 Chirality of Honeycomb Structure with Co-Adsorbed Coronene Molecule

The average angles α values are $17 \pm 1^{\circ}$ and $-17 \pm 1^{\circ}$ for the honeycomb structure with co-adsorbed coronene molecules formed by the *R*-type or *L*-type **DBACOOH** molecules, respectively.



Figure S16. Two-component structure formed by a mixture of **DBACOOH** and coronene at the 1-HA/graphite interface. (a) STM image of a *L*-type honeycomb structure (concentration; 1.0×10^{-5} M, tunneling parameters; $I_{set} = 210$ pA, $V_{bias} = -0.66$ V). (b) STM image of a *R*-type honeycomb structure (concentration; 1.0×10^{-5} M, tunneling parameters; $I_{set} = 210$ pA, $V_{bias} = -0.66$ V). (b) STM image of a *R*-type honeycomb structure (concentration; 1.0×10^{-5} M, tunneling parameters; $I_{set} = 210$ pA, $V_{bias} = -0.69$ V). (c, d) Molecular models of the chiral honeycomb structures constructed by MM calculations.

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