Star-shaped two-dimensional covalent organic frameworks

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1. Materials and methods

Anhydrous DMF, anhydrous CH_2Cl_2, anhydrous acetone, bromine and bis(1,5-cyclooctadiene)nickel (0) were purchased from Wako Chemicals. Phenanthrenequinone, 2,2'-bipyridine, 1,5-cyclooctadiene and BBr_3/CH_2Cl_2 (1 mol L^{-1}) were purchased from TCI. Dimethyl sulfate and sodium hyposulfite were purchased from Kanto. Tetrabutylammonium bromide was purchased from Aldrich. 9,10-hydroxyphenathrene cyclotrimer (HPCT) was synthesized according to the reported method.[S1,S2]

^{1}H NMR spectra were recorded on JEOL models JNM-LA400 or JNM-LA500 NMR spectrometers, where chemical shifts (δ in ppm) were determined with a residual proton of the solvent as standard. Fourier transform Infrared (FT-IR) spectra were recorded on a JASCO model FT-IR-6100 infrared spectrometer. Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF MS) spectra were recorded on an Applied Biosystems BioSpectrometry model Voyager-DE-STR spectrometer in reflector or linear mode. Field-emission scanning electron microscopy (FE-SEM) was performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from $2\theta = 1.5°$ up to 60° with 0.02° increment. Nitrogen sorption isotherms were measured at 77 K with a Bel Japan Inc. model BELSORP-mini II analyzer. Before measurement, the samples were degassed in vacuum at 200 °C for more than 10 h. The Brunauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. The pore size and size distribution were derived from the sorption curve using the non-local density functional theory (NLDFT) model.

Molecular modeling were conducted using Reflex, a software package for crystal determination from XRD patterns, implemented in MS modeling ver 4.4 (Accelrys Inc.).[S2]

Adsorption isotherm simulations were performed under the 'Sorption' module of Materials Studio. The Metropolis Monte Carlo method was utilized for calculation of the nitrogen adsorption in the framework under forty fugacity steps in a logarithmic scale. Universal force field was selected for the energy calculation. All simulations included random insertion/deletion,

translation, and rotation moves of molecules with equal probabilities. Atoms in Star-COFs were fixed at their crystallographic positions. An LJ cutoff distance of 15.0 Å was used. The Ewald & Groups technique was used to compute the electrostatic interactions. All GCMC simulations included a 1,000,000 cycles equilibration period followed by a 10,000,000 cycles production run. The AA stacking unit cells (*P*1) reduced from eclipsed *P*6/mmm (**bnn**) structures were used for simulations of the N_2 adsorption isotherms at 77 K. For the final isotherms, the fugacity was transformed into P/P_0 units and loading per cell was transformed into cm^3 (STP) g^{-1} units. The Brunauer-Emmett-Teller (BET) model was used over the obtained isotherms in the $0.05 < P/P_0 < 0.30$ ranges to obtain the BET surface area.

2. Synthetic Procedure

Star-COF-1. A mixture of HPCT (12.5 mg, 0.02 mmol) and BDBA (5.0 mg, 0.03 mmol) in mesitylene/dioxane (2 mL, 1/1 by vol.) was degassed in a 10-mL pyrex tube by three freeze-pump-thaw cycles. The tube was sealed and heated at 120 ºC for 7 days. The precipitate was collected by centrifugation, washed with anhydrous acetone, and dried at 120 ºC under vacuum overnight, to give a yellow solid in 84% isolation yield. Elemental Analysis: C (78.74), H (2.64); Cacl.: C (80.69), H (2.39).

Star-COF-2. A mixture of HPCT (12.5 mg, 0.02 mmol) and PDBA (8.7 mg, 0.03 mmol) in mesitylene/dioxane (2 mL, 1/1 by vol.) was degassed in a 10-mL pyrex tube by three freeze-pump-thaw cycles. The tube was sealed and heated at 120 ºC for 7 days. The precipitate was collected by centrifugation, washed with anhydrous acetone, and dried at 120 ºC under vacuum overnight, to give a yellow solid in 92% isolation yield. Elemental Analysis: C (84.52), H (2.73); Cacl.: C (83.86), H (2.56).

Star-COF-3. A mixture of HPCT (12.5 mg, 0.02 mmol) and BPDA (7.3 mg, 0.03 mmol) in mesitylene/dioxane (2 mL, 1/1 by vol.) was degassed in a 10-mL pyrex tube by three freeze-pump-thaw cycles. The tube was sealed and heated at 120 ºC for 7 days. The precipitate was collected by centrifugation, washed with anhydrous acetone, and dried at 120 ºC under vacuum overnight, to give a yellow solid in 88% isolation yield. Elemental Analysis: C (83.24), H (3.65); Cacl.: C (81.96), H (3.44).

3. PXRD simulations

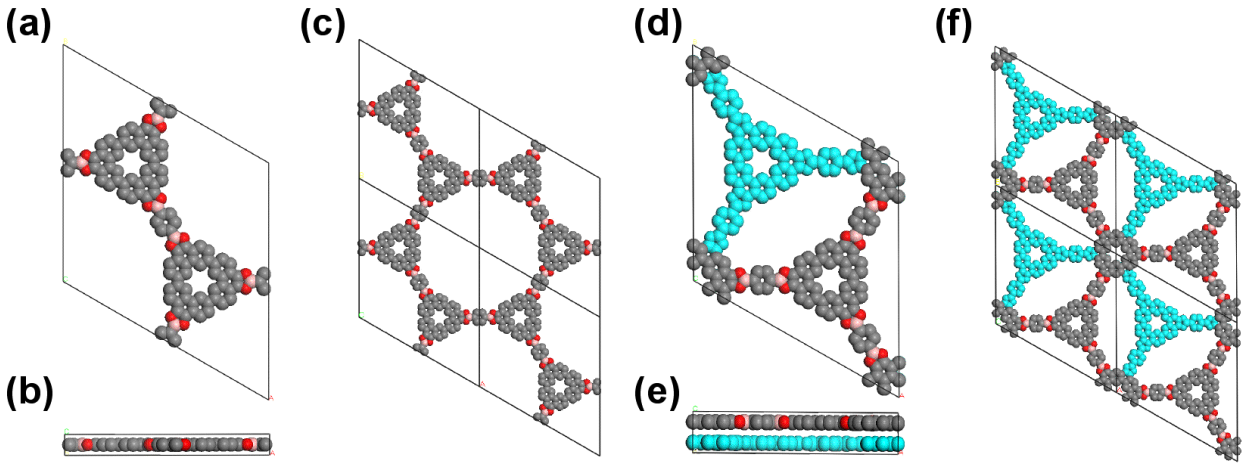

Fig. S1 (a and **b)** View of the 1 × 1 *P*6/mmm unit cell along the *z* **(a)** and *y* **(b)** axes of Star-COF-1. (**c**) View of the 2 × 2 *P*6/mmm unit cell along the *z* axes of Star-COF-1. **(d** and **e)** View of the 1 × 1 *P*63/mmc unit cell along the *z* **(d)** and *y* **(e)** axes of Star-COF-1. (**f**) View of the 2 × 2 *P*63/mmc unit cell along the *z* axes of Star-COF-1.

Table S1 Fractional atomic coordinates for Star-COF-1.

Star-COF-1	
Hexagonal, *P*6/mmm, R_p = 5.54%, R_{wp} = 8.86% a = b = 38.52, c = 3.38	
atom	*x*, *y*, *z*
C1	0.0229, 0.5427, 0.5000
C2	0.0441, 0.5215, 0.5000
C3	0.1521, 0.5941, 0.5000
C4	0.1885, 0.6307, 0.5000
C5	0.1885, 0.6673, 0.5000
C6	0.2253, 0.7041, 0.5000
C7	0.2621, 0.7041, 0.5000
C8	0.2621, 0.6674, 0.5000
C9	0.2253, 0.6307, 0.5000
O1	0.1118, 0.5854, 0.5000
B1	0.0868, 0.5431, 0.5000

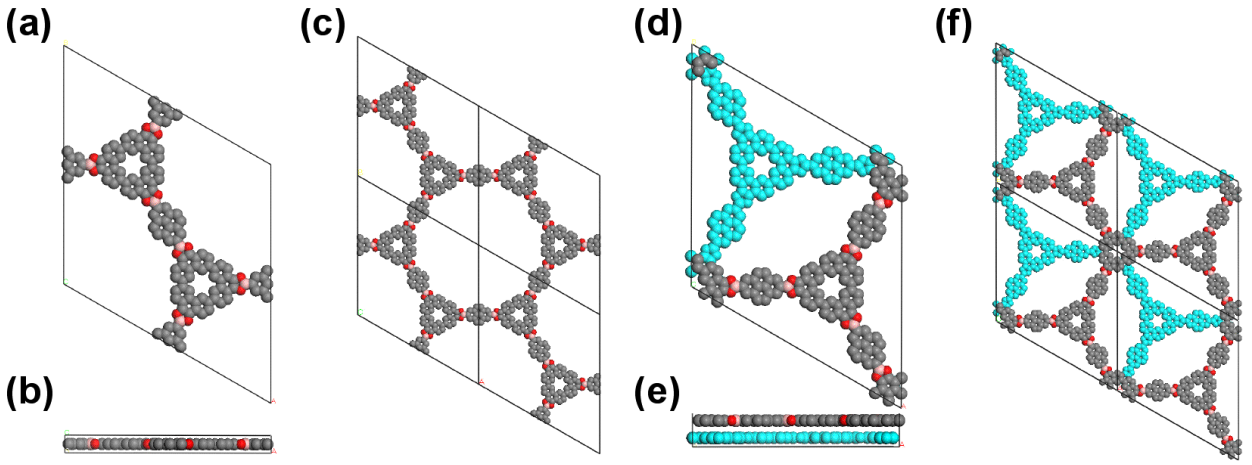

Fig. S2 (a and **b)** View of the 1 × 1 *P*6/mmm unit cell along the *z* **(a)** and *y* **(b)** axes of Star-COF-2. (**c**) View of the 2 × 2 *P*6/mmm unit cell along the *z* axes of Star-COF-2. **(d** and **e)** View of the 1 × 1 *P*63/mmc unit cell along the *z* **(d)** and *y* **(e)** axes of Star-COF-2. (**f**) View of the 2 × 2 *P*63/mmc unit cell along the *z* axes of Star-COF-2.

Table S2 Fractional atomic coordinates for Star-COF-2.

Star-COF-2	
Hexagonal, *P*6/mmm, R_p = 5.01%, R_{wp} = 2.79% a = b = 46.33, c = 3.42	
atom	*x*, *y*, *z*
C1	0.0188, 0.5639, 0.5000
C2	0.0365, 0.5461, 0.5000
C3	0.0165, 0.5083, 0.5000
C4	0.0721, 0.5639, 0.5000
C5	0.0876, 0.5437, 0.5000
C6	0.1802, 0.6067, 0.5000
C7	0.2109, 0.6373, 0.5000
C8	0.2110, 0.6682, 0.5000
C9	0.2394, 0.6966, 0.5000
C11	0.2703, 0.6966, 0.5000
C12	0.2703, 0.6658, 0.5000
C13	0.2418, 0.6373, 0.5000
O1	0.1438, 0.5987, 0.5000
B1	0.1213, 0.5607, 0.5000

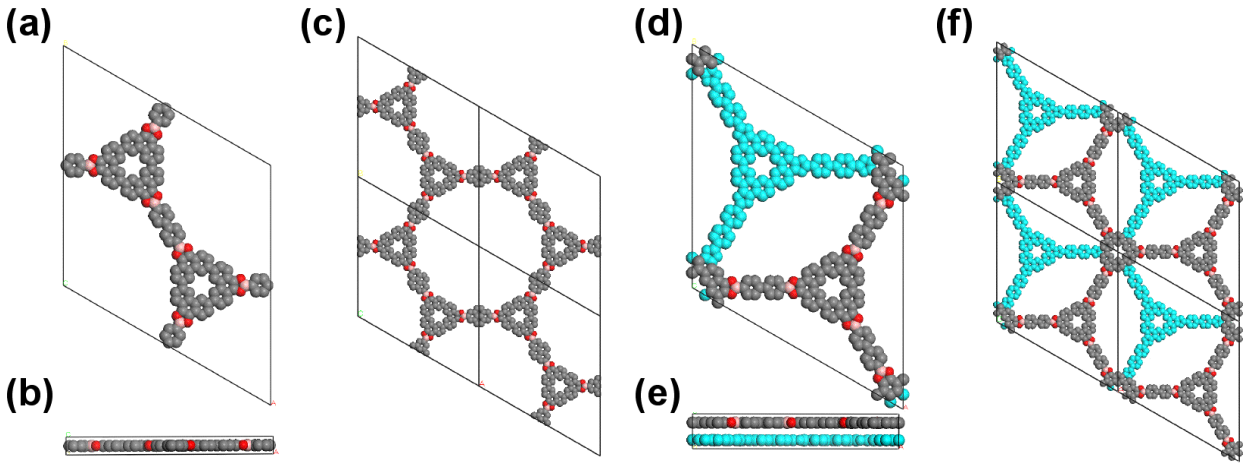

Fig. S3 (a and **b)** View of the 1 × 1 *P*6/mmm unit cell along the *z* **(a)** and *y* **(b)** axes of Star-COF-3. (**c**) View of the 2 × 2 *P*6/mmm unit cell along the *z* axes of Star-COF-3. **(d** and **e)** View of the 1 × 1 *P*63/mmc unit cell along the *z* **(d)** and *y* **(e)** axes of Star-COF-3. (**f**) View of the 2 × 2 *P*63/mmc unit cell along the *z* axes of Star-COF-3.

Table S3 Fractional atomic coordinates for Star-COF-3.

Star-COF-3	
Hexagonal, *P*6/mmm, R_p = 5.82%, R_{wp} = 2.97% a = b = 46.83, c = 3.41	
atom	*x*, *y*, *z*
C1	0.0164, 0.5078, 0.5000
C2	0.0360, 0.5439, 0.5000
C3	0.0715, 0.5617, 0.5000
C4	0.0892, 0.5439, 0.5000
C5	0.1296, 0.6055, 0.5000
C6	0.2104, 0.6363, 0.5000
C7	0.2104, 0.6670, 0.5000
C8	0.2411, 0.6976, 0.5000
C9	0.2717, 0.6975, 0.5000
C10	0.2717, 0.6662, 0.5000
C11	0.2411, 0.6363, 0.5000
O1	0.1458, 0.5982, 0.5000
B1	0.1247, 0.5616, 0.5000

4. Simulated nitrogen sorption isotherms

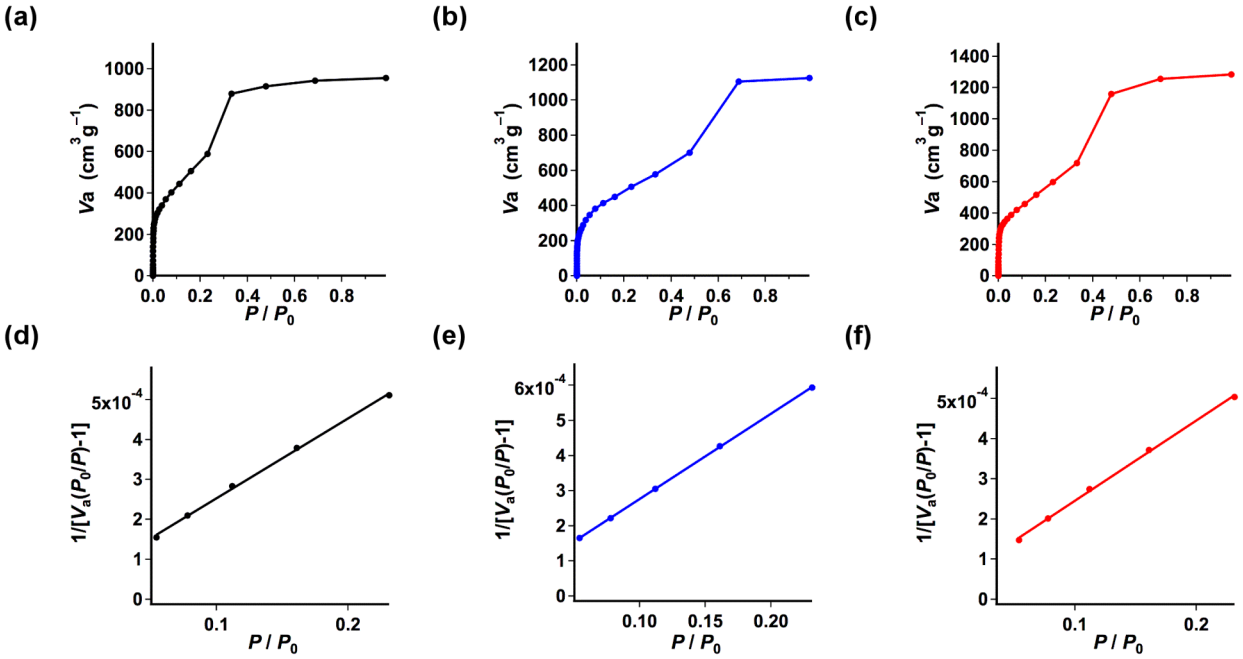

Fig. S4 (a-c) Simulated N_2 adsorption isotherm of **a**) Star-COF-1, **b**) Star-COF-2, **c**) Star-COF-3. **(d-f)** BET plot of the simulated N_2 adsorption isotherm of **d**) Star-COF-1, **e**) Star-COF-2, **f**) Star-COF-3.

5. References

S1. J. Zhang, X. Wang, Q. Su, L. Zhi, A. Thomas, X. Feng, D. S. Su, R. Schlögl and K. Müllen, *J. Am. Chem. Soc.*, 2009, **131,** 11296.

S2. L. A. Estrada and D. C. Neckers, *Org. Lett.*, 2011, **13**, 3304.

S3. Accelrys, Material Studio Release Notes, Release 4.4, Accelrys Software, San Diego, 2008.