Electronic Supplementary Information

A Non-interpenetrated Mesoporous Hydrogen-Bonded Organic Framework Constructed with 1,3,5-Tri(4-carboxyphenyl)benzene

Peng Cui[1,2*], Hanyu Zhang[1]

[1] School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, 212013, P. R. China

[2] Department of Chemistry and Materials Innovation Factory, University of Liverpool, Liverpool, L7 3NY, UK

E-mail: P.Cui@ujs.edu.cn (P. Cui)

This PDF file includes:

Materials and Methods

Figures S1-S14.

Table of Contents:

1.0 Materials and Methods

1.1 General Methods

All chemicals and solvents were obtained from Sinopharm Chemical Reagents Co., LTD. All chemicals and solvents were used as received. 1,3,5-Tri(4-carboxyphenyl)benzene (**TCPB**) was purchased from TCI. 1,3,5-Tris(4'-carboxy[1,1'-biphenyl]-4-yl)benzene (**TCBPB**) was obtained from MacLean Co., LTD.

1.1.1. Powder X-ray Diffraction (PXRD)

PXRD patterns were collected in transmission mode on samples held on thin Mylar film in aluminium well plates on a Panalytical Empyrean diffractometer, equipped with a high throughput screening XYZ stage, X-ray focusing mirror, and PIXcel detector, using Cu-Kα (λ = 1.541 Å) radiation. Unless stated, PXRD patterns were recorded at room temperature. Diffraction patterns were measured over the 2θ range 2−40°, in 0.013° steps, for 30 minutes. For *in situ* experiments, samples were loaded into borosilicate glass capillaries which were spun during data collections to improve powder averaging. PXRD data for these samples were recorded in transmission mode on a Panalytical Empyrean diffractometer, equipped with a sample spinner, X-ray focusing mirror, and PIXcel detector, using Cu-Kα (λ = 1.541 Å) radiation.

1.1.2. Single Crystal X-ray Diffraction (SCXRD)

SCXRD data sets were measured on a Bruker D8 VENTURE diffractometer (Cu-Kα radiation, λ = 1.54178 Å, Kappa goniometer, PHOTON II detector); or at beamline I19, Diamond Light Source, Didcot, UK using silicon double crystal monochromate synchrotron radiation (λ = 0.6889 Å, Pilatus 2M detector). Absorption corrections, using the multi-scan method, were performed with the program SADABS.[1,2] For synchrotron X-ray data, collected at Diamond Light Source (λ = 0.6889Å) data reduction and absorption corrections were performed with xia2.[3] Structures were solved with SHELXT,[4] or by direct methods using SHELXS,[5] and refined by full-matrix least squares on $|F|^2$ by SHELXL,[6] interfaced through the programme OLEX2.[7] Attempts were made to locate H-atom positions for all the carboxylic acid OH groups, however, due to disorder this was not possible. When this was not possible, OH group were refined using the riding model. All other H-atoms were fixed in geometrically estimated positions and refined using the riding model.

1.1.3 Scanning electron microscopy

Imaging of the crystal morphology was achieved using a Hitachi S-4800 cold Field Emission Scanning Electron Microscope (FE-SEM). Sample was prepared by depositing dry crystals on 15 mm Hitachi M4 aluminium stubs using an adhesive high purity carbon tab before coating with a 2 nm layer of cadmium using an Emitech K550X automated sputter coater. Imaging was conducted at a working distance of 8 mm and a working voltage of 3 kV using a mix of upper and lower secondary electron detectors.

1.1.4 Gas Sorption Analysis

Surface areas were measured by nitrogen sorption at 77 K. Powder samples were degassed on the analysis port under vacuum. Isotherm measurements were performed using a Micromeritics 2420 surface characterization analyser, equipped with a Cold-Edge technologies liquid helium cryostat chiller unit for temperature control.

2.0 Supplementary Data

2.1 Crystallization of TCPB-1:

TCPB (2 mg) was dissolved in THF or 1,4-dioxane (1 mL) at RT. Then the o-xylene, m-xylene, p-xylene, mesitylene, and n-butylbenzene (1 mL) was added into THF or 1,4-dioxane solutions, respectively. The solvent mixtures were left to evaporate at RT for 1-2 weeks. The tiny transparent colorless needle crystals were crystalized from dioxane/mesitylene solvent system after 2 weeks and named as **TCPB-1**. Powders or very small needle shape crystals were obtained from the other systems.

Crystal data for **TCPB-1** (200 K): Formula $C_{27}H_{18}O_6$; M = 438.41, triclinic $P\bar{1}$, colorless needle shape crystals; a = 3.7658(4) Å, b = 29.691(3) Å, c = 30.402(3) Å, α = 61.631(9) °, β = 86.803(10) °, γ = 89.946(10) °; V = 2985.1(6) Å3; ρ = 0.488 g/cm^3; Z = 2; $\mu(\lambda=0.6889)$ = 0.032 mm^{-1}; F (000) = 456; crystal size = 0.047 × 0.03 × 0.019 mm; T = 200 (2) K. 7649 reflections measured ($2.96 < 2\theta < 43.74$ °), 4436 unique (R_{int} = 0.1058), 1313 ($I > 2\sigma(I)$); R_1 = 0.1051 for observed and R_1 = 0.1824 for all reflections; wR_2 = 0.3007 for all reflections; max/min difference electron density = 0.251 and -0.291 e·Å^{-3}; data/restraints/parameters = 4436/267/304; GOF = 0.81. CCDC No. 2405943.

2.2 Formation of TCPB-2:

Following the above the crystallization of **TCPB-1**, the residual 1,4-dioxane and mesitylene crystallization solvents were removed using a syringe. *n*-Pentane (10 mL) was added to fully immerse the crystals and the vial was capped. After 12 hours, the *n*-pentane solvent was removed using a syringe and replaced with fresh *n*-pentane solvent (10 mL). This process was repeated every 12 hours for 5 days. The *n*-pentane exchanged crystal were degassed at RT under dynamic vacuum for 2 hrs to obtain the activated material, **TCPB-2**. Yield: 98 %.

2.3 C_{60} adsorption of TCPB-2:

Typically, C_{60} (5 mg) was dissolved in cyclohexane (15 mL) and **TCPB-2** (5 mg) was added into the system. The absorbance at different adsorption time was recorded with UV.

2.4 Crystallisation of TCBPB-1:

TCBPB (1 mg) was dissolved in THF (1 mL) at RT. Then the o-xylene, m-xylene, p-xylene, mesitylene, and n-butylbenzene (1 mL) was then added into THF solutions, respectively. The solvent mixture was left to evaporate at RT for 5 days. The transparent colorless rod crystals were crystalized from THF/n-butylbenzene solvent system and named as **TCBPB-1**. Powders or small needle shape crystals were obtained from the other systems.

Crystal data for **TCBPB-1** (223 K): Formula $C_{45}H_{29}O_6$; $M = 665.68$, monoclinic $P2_1$, colorless block shape crystals; $a = 28.129(3)$ Å, $b = 7.0621(6)$ Å, $c = 28.162(3)$ Å, $\beta = 100.630(7)$ °; $V = 5498.3(10)$ Å^3; $\rho = 0.804$ g/cm^3; $Z = 4$; μ(Cu-Kα) = 0.428 mm^{-1}; F (000) = 1388; crystal size = 0.15 × 0.12 × 0.11 mm; $T = 223$ K. 36785 reflections measured ($1.596 < 2\theta < 69.036$ °), 20037 unique ($R_{\mathrm{int}} = 0.0812$), 6642 ($I > 2\sigma(I)$); $R_1 = 0.0901$ for observed and $R_1 = 0.1601$ for all reflections; $wR_2 = 0.2819$ for all reflections; max/min difference electron density = 0.315 and -0.230 e·Å^{-3}; data/restraints/parameters = 20037/6915/1443; GOF = 1.005. CCDC No. 2405945.

2.5 Formation of TCBPB-2:

Following the above the crystallization of **TCBPB-1**, the residual THF and n-butylbenzene crystallization solvents were removed using a syringe. *n*-Pentane (10 mL) was added to fully immerse the crystals and the vial was capped. After 12 hours, the *n*-pentane solvent was removed using a syringe and replaced with fresh *n*-pentane solvent (10 mL). This process was repeated every 12 hours for 5 days. The *n*-pentane exchanged crystal were degassed at RT under dynamic vacuum for 2 hrs to obtain the activated material, **TCBPB-2**. Yield: 97 %.

Crystal data for **TCBPB-2** (223 K): Formula $C_{45}H_{30}O_6$; M = 666.69, monoclinic $C2/c$, colorless block shape crystals; a = 41.573(3) Å, b = 6.9976(4) Å, c = 27.654(2) Å, β = 105.992(5) °; V = 7733.4(9) Å^3; ρ = 1.145 g/cm^3; Z = 8; μ(Cu-Kα) = 0.609 mm^{-1}; F (000) = 2784; crystal size = 0.14 × 0.12 × 0.11 mm; T = 223 K. 6979 reflections measured ($3.325 < 2\theta < 68.901$ °), 6979 unique, 3717 ($I > 2\sigma(I)$); R_1 = 0.1171 for observed and R_1 = 0.1647 for all reflections; wR_2 = 0.2546 for all reflections; max/min difference electron density = 0.281 and -0.296 e·Å^{-3}; data/restraints/parameters = 6979/0/465; GOF = 1.005. CCDC No. 2405944.

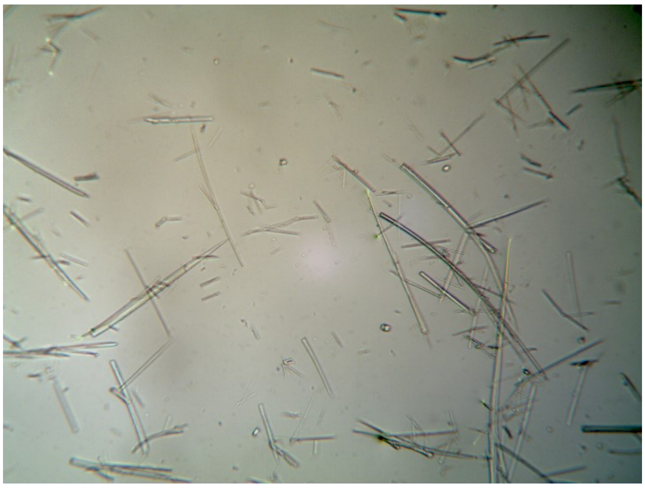

Figure S1. Optical photograph of **TCPB-1** recorded using a microscope.

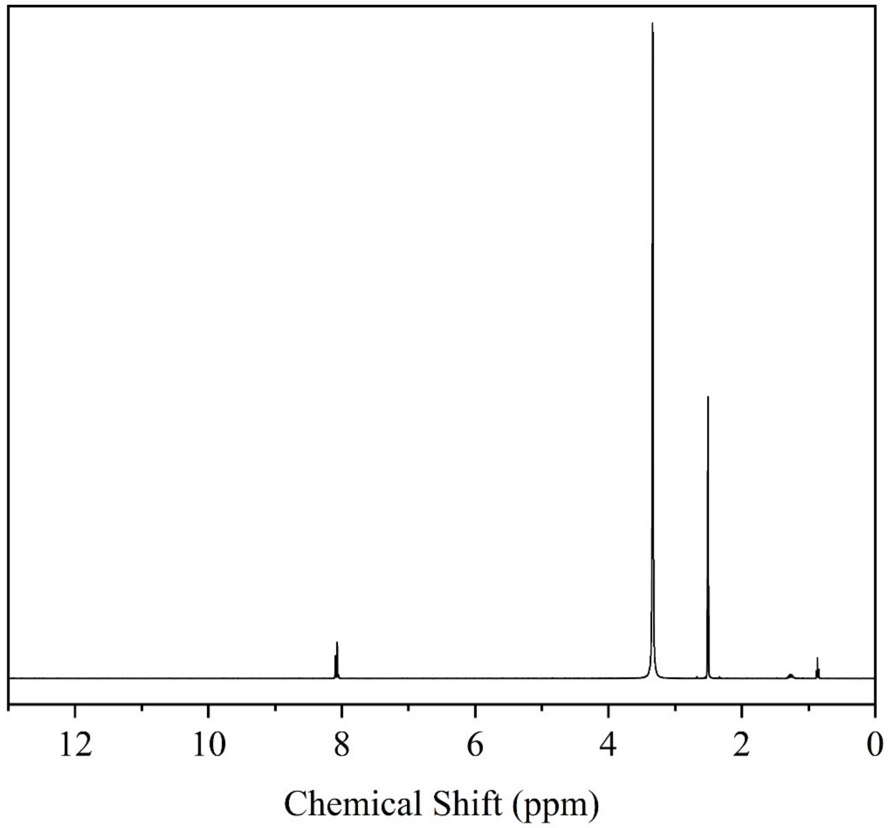

Figure S2. The ^{1}H-NMR of **TCPB-1** after pentane exchange.

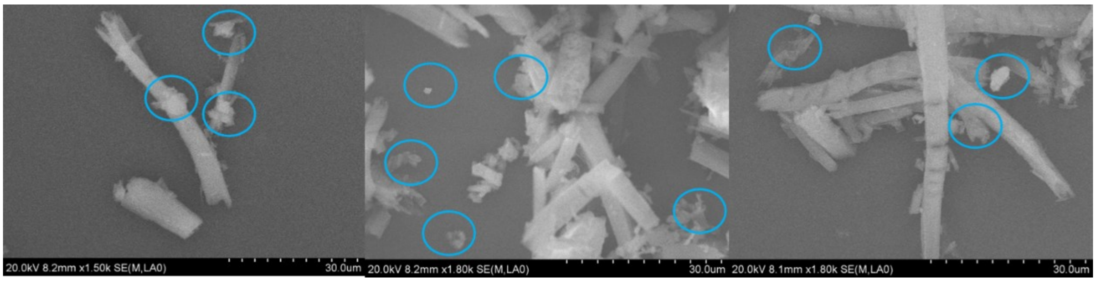

Figure S3. SEM image of **TCPB-2**. The amorphous particles were highlighted with blue cycle.

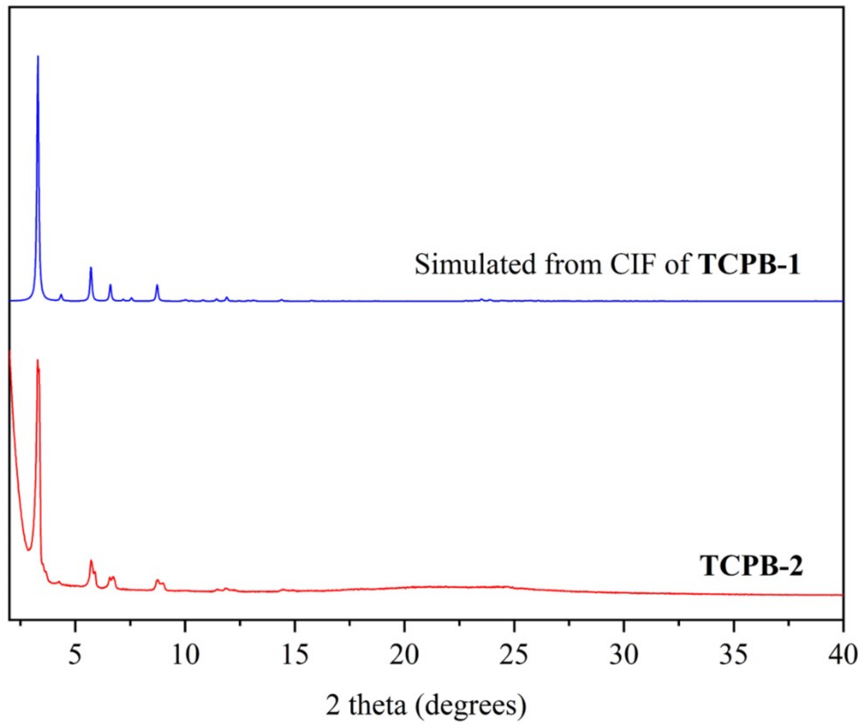

Figure S4. PXRD patterns of **TCPB-2** and simulated from CIF of **TCPB-1**.

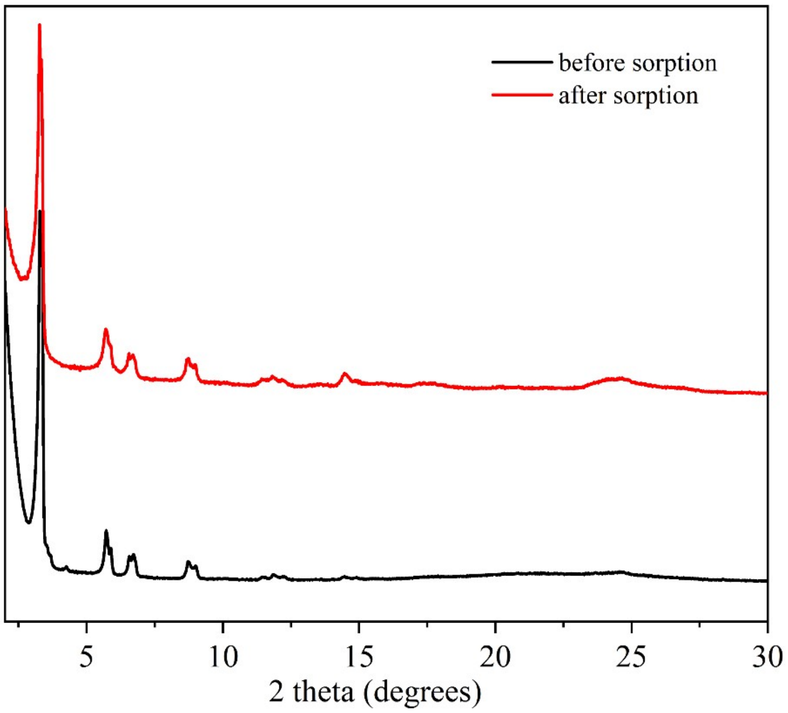

Figure S5. PXRD patterns of **TCPB-2** before (black) and after N_2 sorption (red).

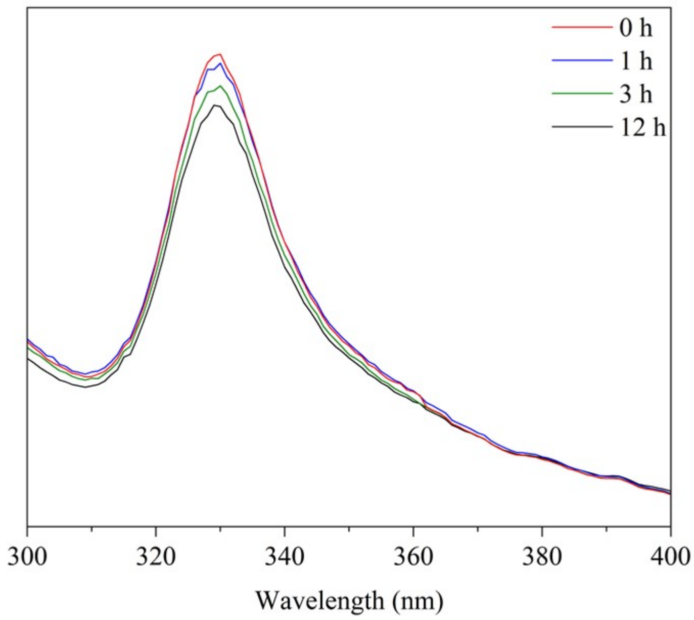

Figure S6. The UV spectrum of C_{60}/cyclohexane solution with **TCPB-2** was added for different time.

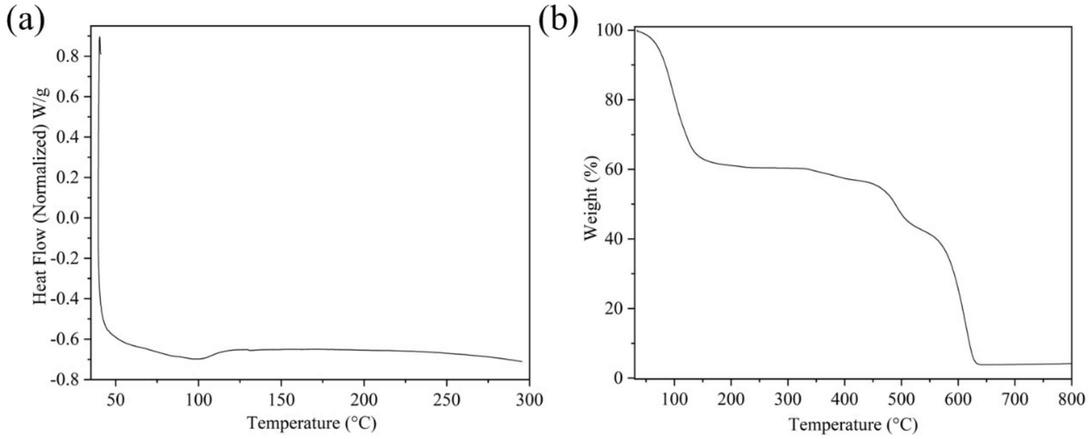

Figure S7. (a) The DSC plot of **TCPB-2**; (b) TGA plot for **TCPB-1** isolated directly from *n*-pentane under nitrogen.

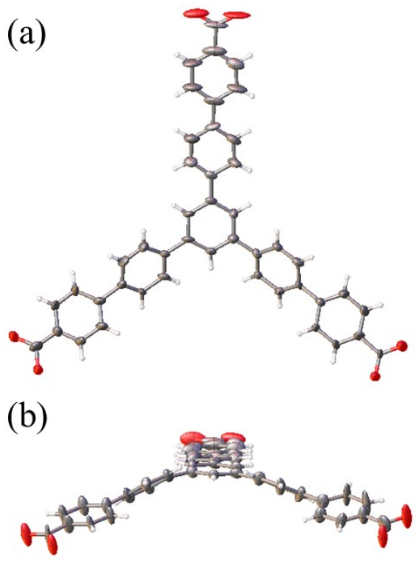

Figure S8. Displacement ellipsoid plot of **TCBPB** from the single crystal structure of **TCBPB-1**. a) front view; b) side view. Ellipsoids displayed at 50% probability level. Grey: carbon, red: oxygen, white: hydrogen.

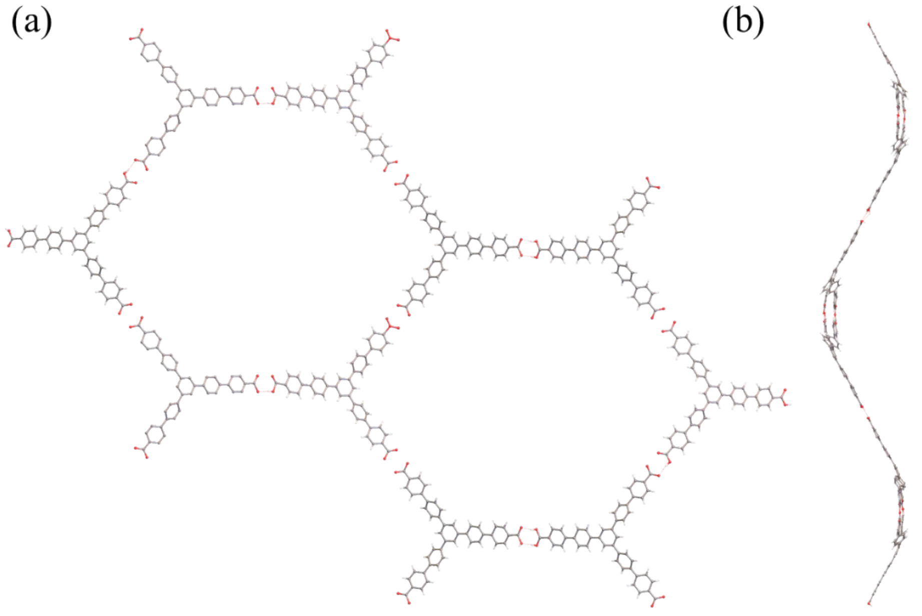

Figure S9. Displacement of hcb networks from the single crystal structure of **TCBPB-1**. a) front view; b) side view. Grey: carbon, red: oxygen, white: hydrogen.

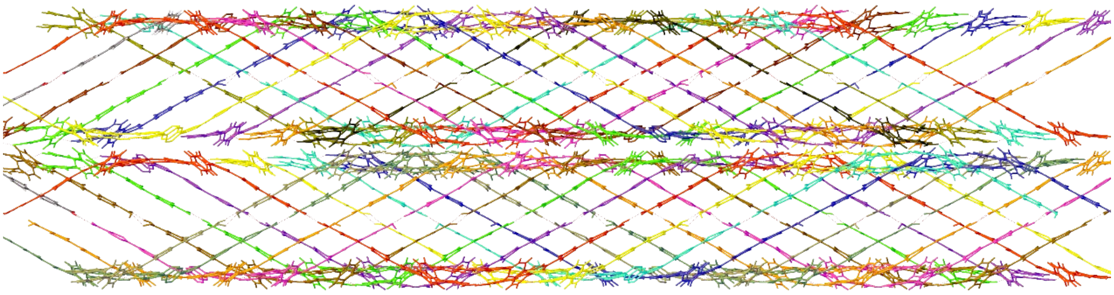

Figure S10. Displacement of 11-fold interpenetrated structure from the single crystal structure of **TCBPB-1**, different colour represented different hcb networks.

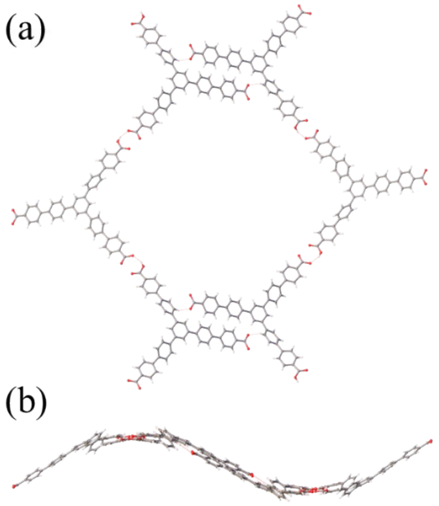

Figure S11. Displacement of basic networks from the single crystal structure of **TCBPB-2**. a) front view; b) side view. Grey: carbon, red: oxygen, white: hydrogen.

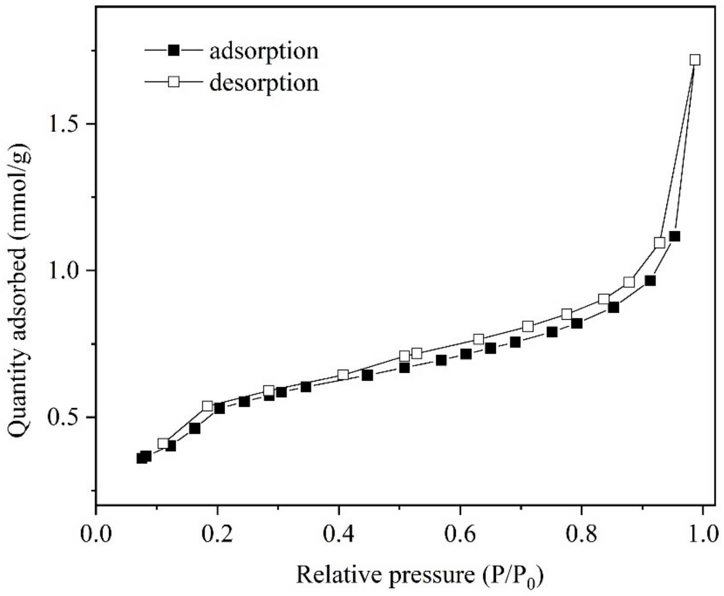

Figure S12. N_2 sorption isotherms for **TCBPB-2** recorded at 77 K.

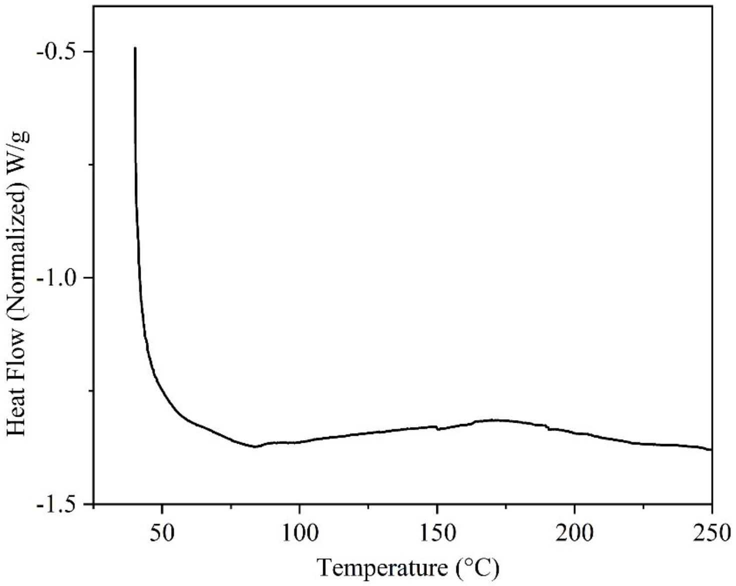

Figure S13. The DSC plot of **TCBPB-2**.

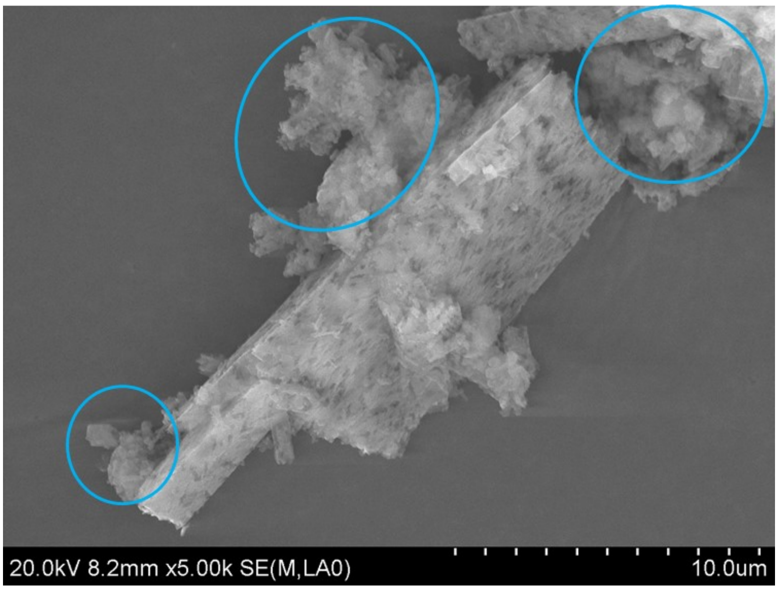

Figure S14. SEM image of **TCBPB-2**. The amorphous particles were highlighted with blue cycle.

Reference

1 G. M. Sheldrick, 2008.

2 L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3–10.

3 G. Winter, D. G. Waterman, J. M. Parkhurst, A. S. Brewster, R. J. Gildea, M. Gerstel, L. Fuentes-Montero, M. Vollmar, T. Michels-Clark, I. D. Young, N. K. Sauter and G. Evans, *Acta Crystallogr. Sect. D Struct. Biol.*, 2018, **74**, 85–97.

4 G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Adv.*, 2015, **71**, 3–8.

5 G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.*, 2008, **64**, 112–122.

6 G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 3–8.

7 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.