Electronic Supplementary Information

Selective Adsorption of Polycyclic Aromatic Hydrocarbons by Isostructural Hydrogen-Bonded Organic Frameworks

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1. Materials and Methods

1.1 Materials

All chemicals and solvents were obtained from Sigma-Aldrich, Fisher, and Alfa Aesar. All chemicals and solvents were used as received. All gases for sorption analysis were supplied by BOC at a purity of ≥99.999%. Biphenyl-3,3',5,5'-tetra-carboxylic acid (**BPTCA**) was purchased from Manchester Organics, and [1,1′:4′,1″] terphenyl-3,3″,5,5″-tetracarboxylic acid (**TPTCA**) were purchased from Sigma-Aldrich.

1.2 General Methods

1.2.1. 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.

1.1.2. Single Crystal X-ray Diffraction (SC-XRD)

SC-XRD data sets were measured on a Rigaku MicroMax-007 HF rotating anode diffractometer (Mo-Kα radiation, λ = 0.71073 Å, Kappa 4-circle goniometer, Rigaku Saturn724+ detector); or at beamline I19, Diamond Light Source, Didcot, UK using silicon double crystal monochromated synchrotron radiation (λ = 0.6889 Å, Pilatus 2M detector). 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] Supplementary CIF files that include structure factors and responses to checkCIF alerts are available free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

1.1.3 Gas Sorption Analysis

Surface areas were measured by nitrogen sorption at 77.3 K. Powder samples were degassed on the analysis port under vacuum. Isotherm measurements were performed using a Micromeritics 2420 surface characterisation analyser equipped with a Cold-Edge technologies liquid helium cryostat chiller unit for temperature control.

1.1.4 Nuclear Magnetic Resonance (NMR)

NMR spectra were recorded on a Bruker 400 NMR spectrometer at 400 MHz (^{1}H) with deuterated DMSO as solvents.

1.1.5 Gas Chromatography (GC)

The residual concentrations of PAHs in the feedstock solvent were determined by an Agilent 7890A instrument with a flame ionisation detector (FID) with tetradecane as the internal standard. (HP-5 column, 30 m × 0.32 mm i.d. × 0.25 mm). 3 mg **BPTCA** or **TPTCA** solid was added to an *n*-hexadecane solution (1 mL) that contained **NA** or **AN** at a concentration of 200 ppm. The residual concentration of **NA** and **AN** in n-hexadecane after being immersed in HOFs for 3 hrs to reach adsorption equilibrium was tested. Then the adsorption capacity was then calculated.

1.1.6 Ultraviolet spectrum (UV)

UV-Visible absorption spectra were measured on an Agilent Cary 5000 UV-Vis Spectrometer.

2 Supplementary Data

2.1 Crystallisation of BPTCA-1

1 mg of **BPTCA** molecule was dissolved in 1 mL DMF in a small vial at RT. The vial was then inserted into a larger vial that contained 10 mL of anti-solvent. Here, the low boiling point organic solvents, $CHCl_3$, methanol, diethyl ether, ethyl acetate, and acetone, were used in the crystallisation procedure, and the small vials were left open to let the anti-solvents diffuse into the DMF solution. At the same time, the larger vial was sealed and left at RT. After two weeks, transparent colorless needle shape crystals (**BPTCA-1**) crystallised from DMF/$CHCl_3$ system, but no particles were found in the other vials.

Crystal data for **BPTCA-1** (100 K): Formula $C_{16}H_{10}O_8$; M = 330.24, orthorhombic *P*nna, colorless block shape crystals; a = 15.2243(19) Å, b = 7.1637(13) Å, c = 17.5962(19) Å; V = 1919.1(5) Å^3; ρ = 1.143 g/cm^3; Z = 4; μ(Mo-Kα) = 0.094 mm^{-1}; F (000) = 680; crystal size = 0.032 × 0.022 × 0.019 mm; T = 100 (2) K. 2213 reflections measured (4.66 < 2θ < 56.83 °), 1911 unique (R_{int} = 0.0922), 1529 ($I > 2\sigma(I)$); R_1 = 0.0919 for observed and R_1 = 0.1190 for all reflections; wR_2 = 0.2457 for all reflections; max/min difference electron density = 0.466 and -0.456 e·Å^{-3}; data/restraints/parameters = 2213/0/115; GOF = 1.048. CCDC No. 2277044.

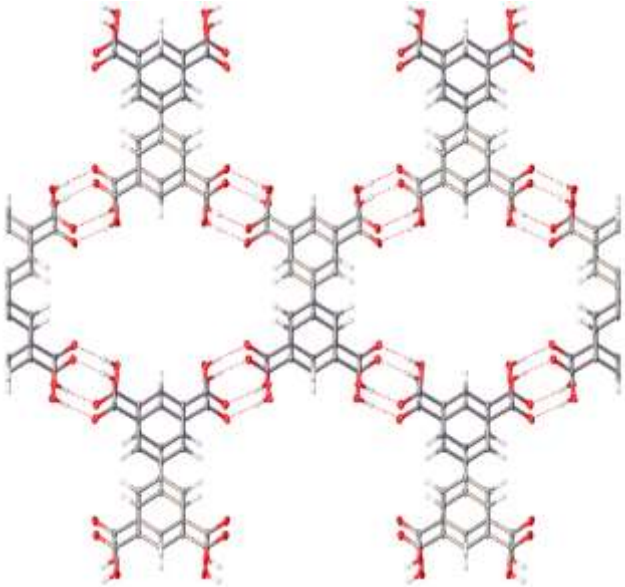

Figure S1. Crystal packing diagram of **BPTCA-1** recorded at 100 K and viewed along the *b*-axis. Hydrogen bonds are shown with red dashed lines. Grey: carbon, red: oxygen, white: hydrogen.

2.2 Formation of BPTCA-2

Firstly, the DMF and chloroform crystallisation solvents were removed with a syringe and 10 mL *n*-pentane was added to immerse the crystals fully. The *n*-pentane was refreshed every 12 hrs, and after using *n*-pentane to exchange the solvents for 5 days, the crystals were degassed at RT for 2 hrs under a dynamic vacuum to afford the activated crystals, **BPTCA-2** (yield: 78 %).

Crystal data for **BPTCA-2** (292 K): Formula $C_{24}H_{14}O_{12}$; M = 494.35, monoclinic $C2/c$, colorless block shape crystals; a = 10.8266(7) Å, b = 31.5566(14) Å, c = 18.5503(11) Å; β = 105.143(7) °; V = 6117.7(6) Å^3; ρ = 1.073 g/cm^3; Z = 8; μ(Mo-Kα) = 0.088 mm^{-1}; F (000) = 2040; crystal size = 0.052 × 0.016 × 0.012 mm; T = 292 (5) K. 13190 reflections measured ($3.46 < 2\theta < 60.11$ °), 6797 unique (R_{int} = 0.028), 6259 ($I > 2\sigma(I)$); R_1 = 0.0699 for observed and R_1 = 0.1078 for all reflections; wR_2 = 0.2436 for all reflections; max/min difference electron density = 0.487 and -0.252 e·Å^{-3}; data/restraints/parameters = 13190/0/332; GOF = 0.964. CCDC No. 2277046.

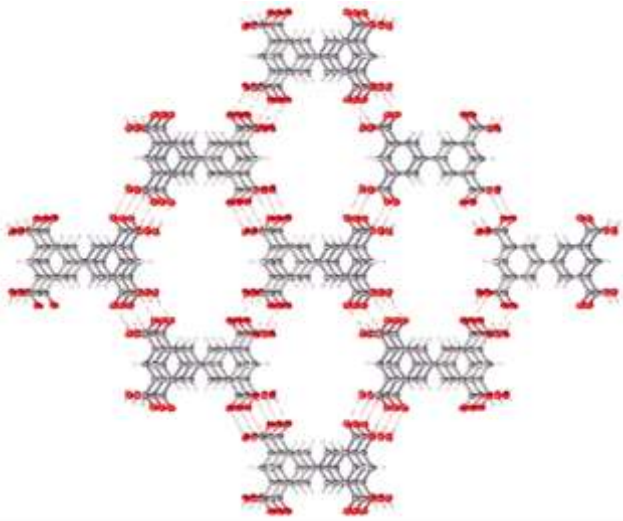

Figure S2. Crystal packing diagram of **BPTCA-2** recorded at 292 K viewed along the *a* axis. Hydrogen bonds are shown with red dashed lines. Grey: carbon, red: oxygen, white: hydrogen.

2.3 Crystallisation of TPTCA-1

1 mg of **TPTCA** was dissolved in 1 mL of DMF in a small vial at RT. This vial was then inserted into a larger vial that contained 10 mL of $CHCl_3$. The vial was left at RT for two weeks, and afterwards, transparent colorless needle shape crystals of **TPTCA-1** were found in the vial.

Crystal data for **TPTCA-1** (100 K): Formula $C_{22}H_{14}O_8$; M = 406.33, monoclinic $C2/c$, colorless block shape crystals; a = 16.4201(2) Å, b = 26.5063(3) Å, c = 7.19160(10) Å, β = 114.8240(10) °; V = 2840.83(6) Å^3; ρ = 0.950 g/cm^3; Z = 4; μ(λ = 0.6889 Å) = 0.069 mm^{-1}; F (000) = 840; crystal size = 0.042 × 0.026 × 0.02 mm; T = 100 (2) K. 2778 reflections measured (2.99 < 2θ < 70.59 °), 1998 unique (R_{int} = 0.0378), 3176 ($I > 2\sigma(I)$); R_1 = 0.0482 for observed and R_1 = 0.0568 for all reflections; wR_2 = 0.1810 for all reflections; max/min difference electron density = 0.370 and -0.291 e·Å^{-3}; data/restraints/parameters = 2778/0/144; GOF = 1.025. CCDC No. 2277047.

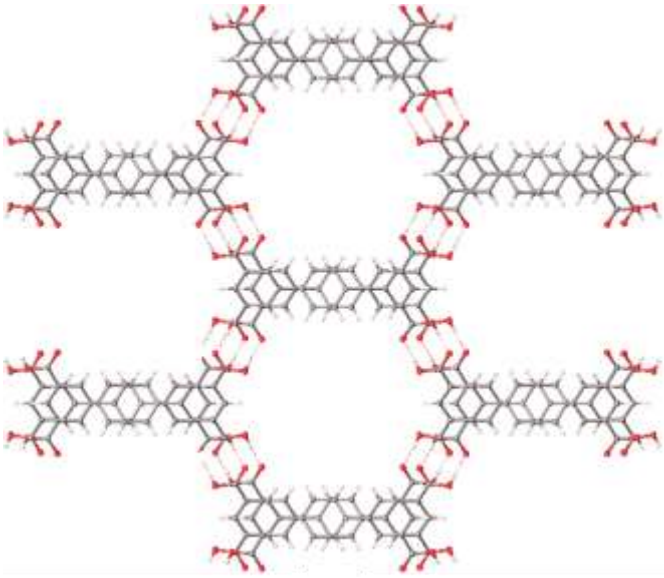

Figure S3. Crystal packing diagram of **TPTCA-1** recorded at 100 K from SCXRD viewed along the *a* axis. Hydrogen bonds are shown with red dashed lines. Grey: carbon, red: oxygen, white: hydrogen.

2.4 Formation of TPTCA-2

Firstly, the DMF and chloroform crystallisation solvents were removed with a syringe and 10 mL *n*-pentane was added to immerse the crystals fully. The *n*-pentane was refreshed every 12 hrs, and after using *n*-pentane to exchange the solvents for 5 days the crystals were degassed at RT for 2 hrs under a dynamic vacuum to afford the activated crystals, **TPTCA-2** (yield: 80 %).

Crystal data for **TPTCA-2** (291 K): Formula $C_{22}H_{14}O_8$; M = 406.33, monoclinic $I2/a$, colorless block shape crystals; a = 7.3463(3) Å, b = 26.5578(10) Å, c = 15.1916(6) Å, β = 92.149(4) °; V = 2961.8(2) Å^3; ρ = 0.902 g/cm^3; Z = 4; μ(Mo-Kα) = 0.070 mm^{-1}; F (000) = 840; crystal size = 0.05 × 0.032 × 0.019 mm; T = 291 (2) K. 10816 reflections measured (5.35 < 2θ < 58.79 °), 3213 unique (R_{int} = 0.0189), 2452 ($I > 2\sigma(I)$); R_1 = 0.0702 for observed and R_1 = 0.0912 for all reflections; wR_2 = 0.2699 for all reflections; max/min difference electron density = 0.234 and -0.212 e·Å^{-3}; data/restraints/parameters = 3213/3/141; GOF = 1.125. CCDC No. 2277048.

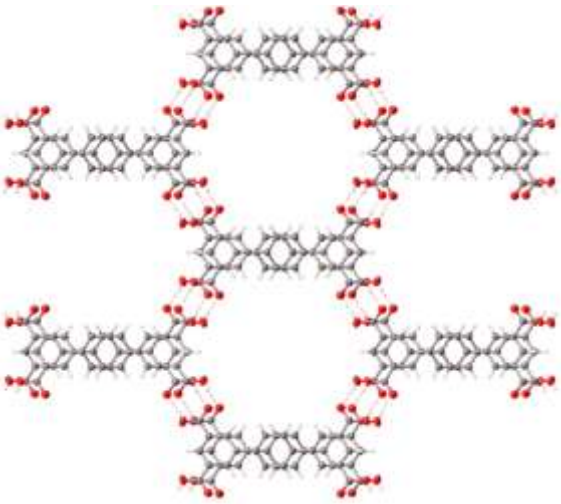

Figure S4. Crystal packing diagram of **TPTCA-2** recorded at 291 K viewed along the *a* axis. Hydrogen bonds are shown with red dashed lines. Grey: carbon, red: oxygen, white: hydrogen.

2.5 Formation of TPTCA-2_degas

The **TPTCA-2** crystals were degassed at RT for 12 hrs and **TPTCA-2_degas** was obtained.

Crystal data for **TPTCA-2_degas** (211 K): Formula $C_{22}H_{14}O_8$; M = 406.33, monoclinic $I2/a$, colorless block shape crystals; a = 9.364(4) Å, b = 27.147(5) Å, c = 10.077(5) Å, β = 116.60(5) °; V = 2290.3(18) Å^3; ρ = 1.178 g/cm^3; Z = 4; μ(λ = 0.6889 Å) = 0.091 mm^{-1}; F (000) = 840; crystal size = 0.04 × 0.02 × 0.015 mm; T = 211 (2) K. 1195 reflections measured (7.78 < 2θ < 54.19 °), 689 unique (R_{int} = 0.0924), 582 ($I > 2\sigma(I)$); R_1 = 0.0618 for observed and R_1 = 0.1059 for all reflections; wR_2 = 0.1626 for all reflections; max/min difference electron density = 0.233 and -0.194 e·Å^{-3}; data/restraints/parameters = 1195/6/140; GOF = 0.919. CCDC No. 2277049.

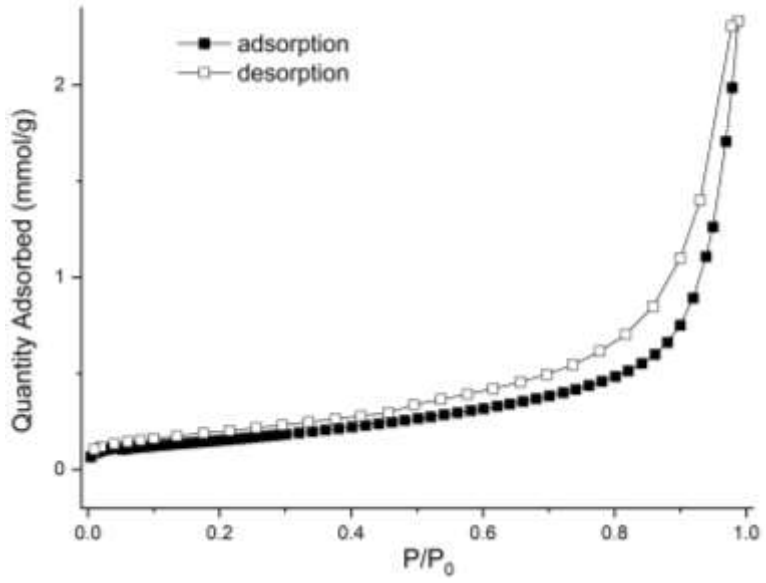

Figure S5. The N_2 sorption isotherms of **BPTCA-2** recorded at 77 K.

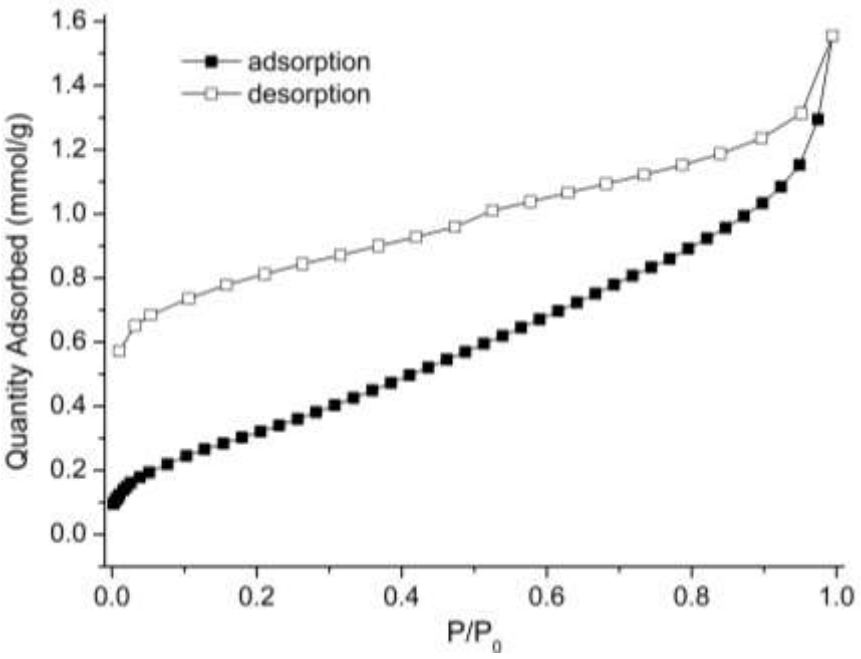

Figure S6. The N_2 sorption isotherms of **TPTCA-2_degas** recorded at 77 K.

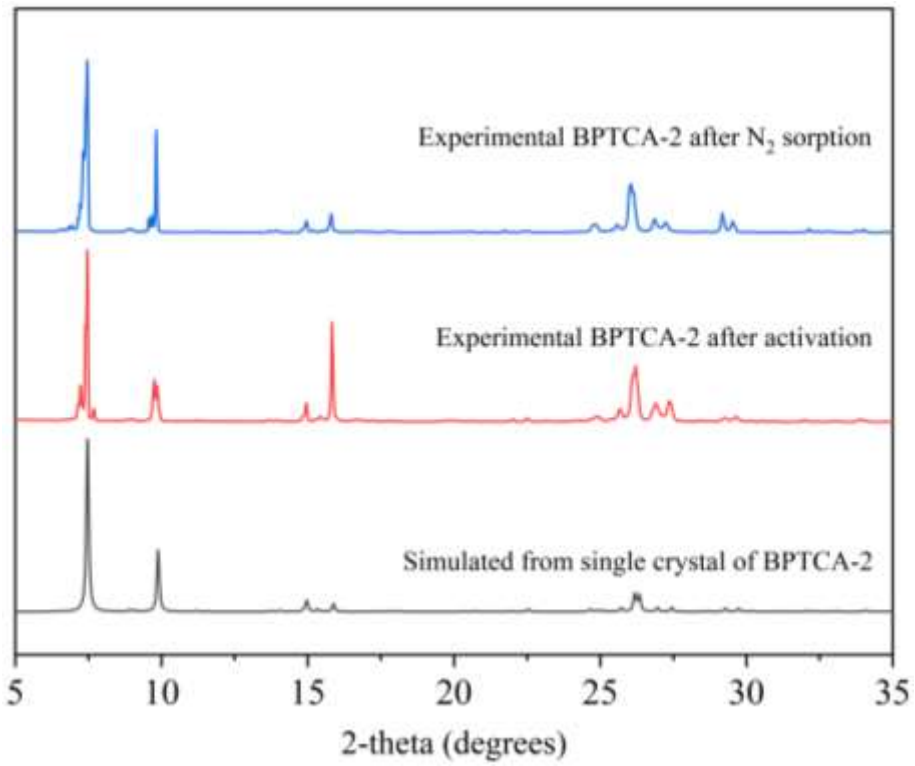

Figure S7. PXRD patterns of **BPTCA-2**. Black: simulation from the SC-XRD structure recorded at 292 K; red: experimental PXRD of **BPTCA-2** after activation; blue: experimental PXRD of **BPTCA-2** after the N_2 sorption test.

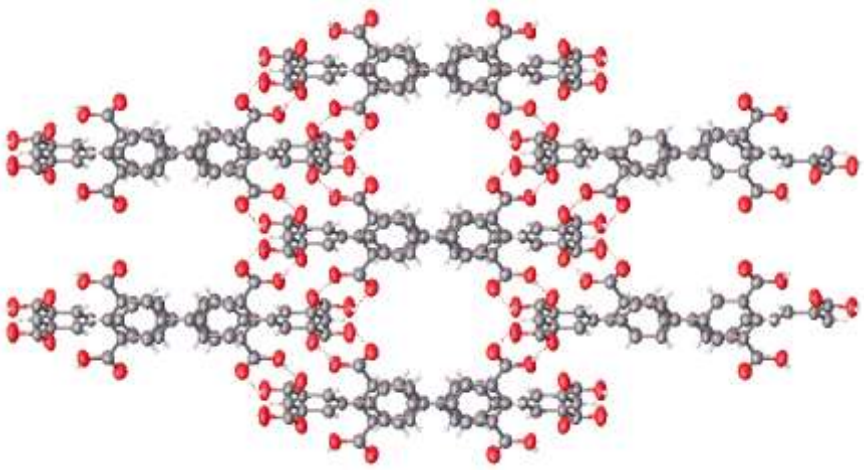

Figure S8. Crystal packing diagram of **TPTCA-2_degas** recorded at 211 K viewed along the *a*-axis. Hydrogen bonds are shown with red dashed lines. Grey: carbon, red: oxygen, white: hydrogen.

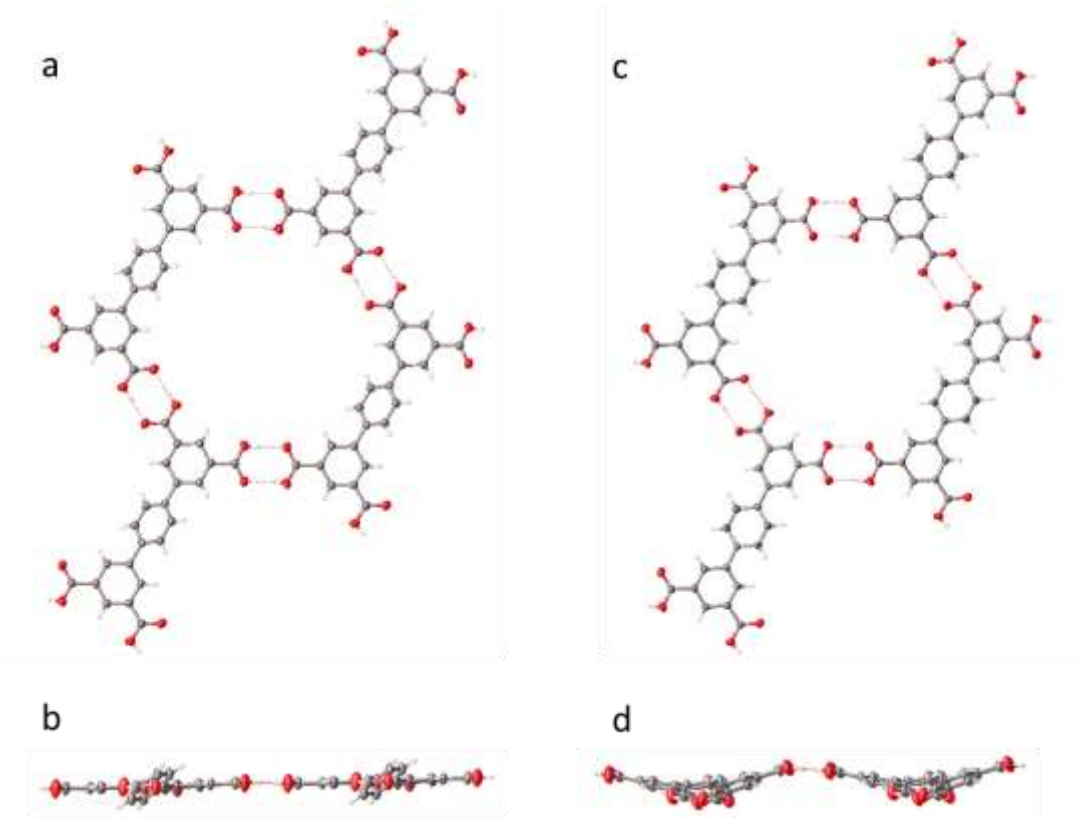

Figure S9. Comparison between the **sql** net in **TPTCA-2** (a) and side view (b); the **sql** net in **TPTCA-2_degas** (c) and side view (d). Hydrogen bonds are shown with red dashed lines. Grey: carbon, red: oxygen, white: hydrogen.

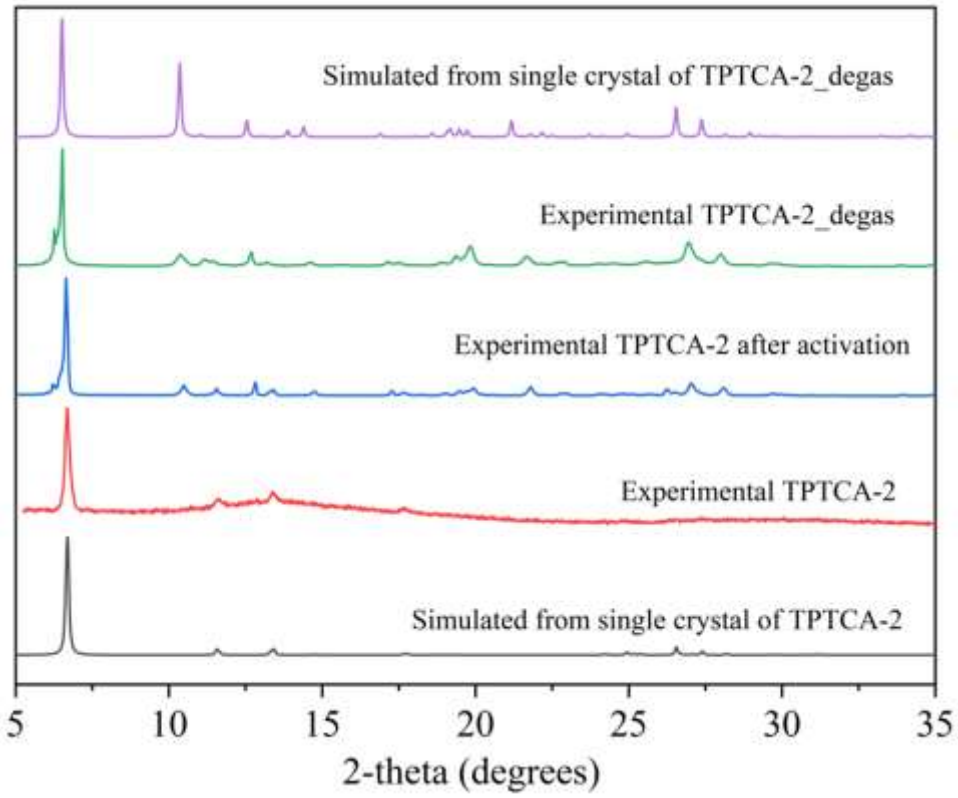

Figure S10. PXRD patterns of **TPTCA-2**. Black: simulation from the SC-XRD structure of **TPTCA-2**; red: experimental PXRD of **TPTCA-2**; blue: experimental PXRD of **BPTCA-2** after activation; green: experimental PXRD of **TPTCA-2_degas**; purple: simulation from the SC-XRD structure of **TPTCA-2_degas**.

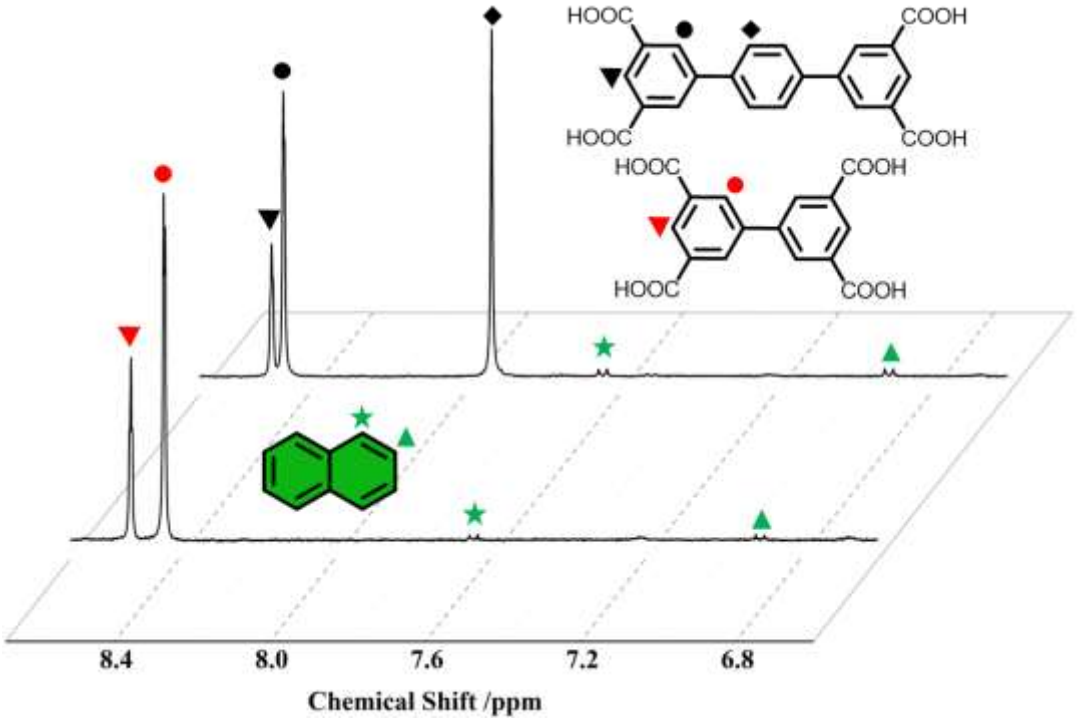

Figure S11. The ^{1}H NMR spectrum (DMSO-d_6) of **BPTCA-2⊃NA** and **TPTCA-2⊃NA**. The characteristic peaks of **BPTCA**, **TPTCA**, and **NA** molecules were marked with red, black, and green symbols, respectively.

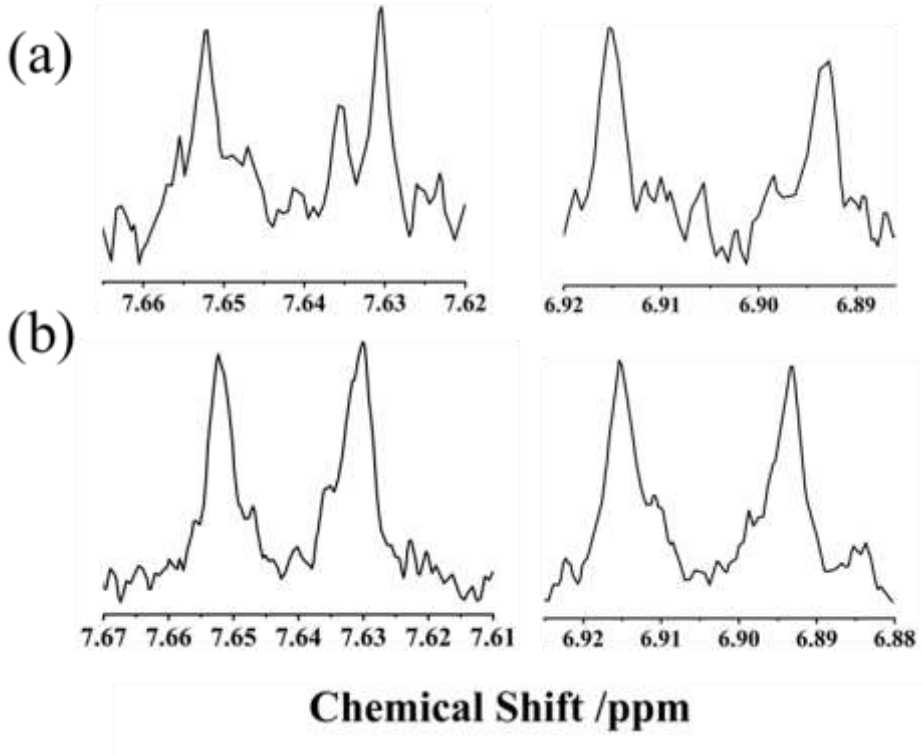

Figure S12. The amplifying ^{1}H NMR spectrum of **NA** in (a) **BPTCA-2⊃NA**; (b) **TPTCA-2⊃NA**.

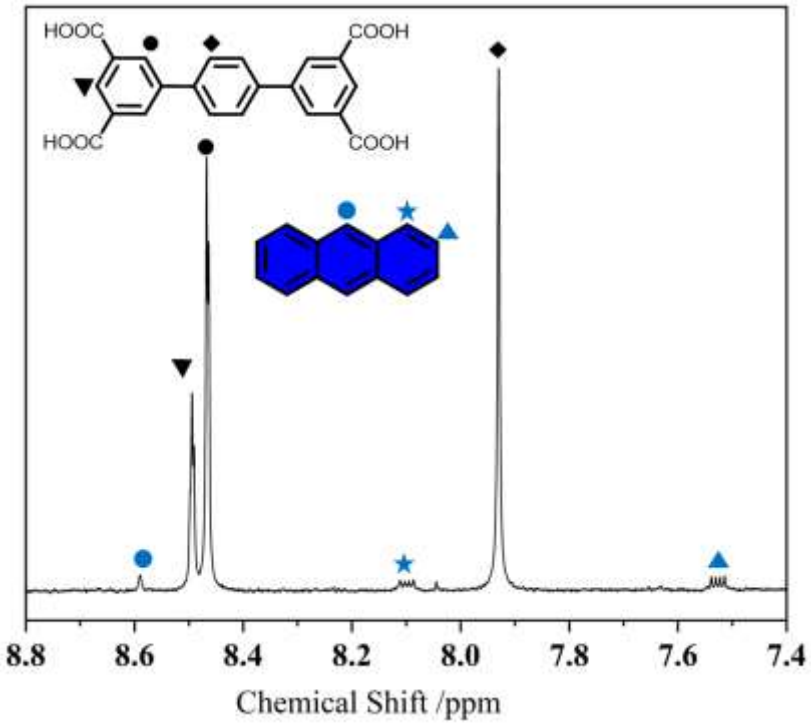

Figure S13. The ^{1}H NMR spectrum (DMSO-d_6) of **TPTCA-2** immersed in *n*-hexadecane solution containing 200 ppm of **AN** or **NA** for 3 hrs.

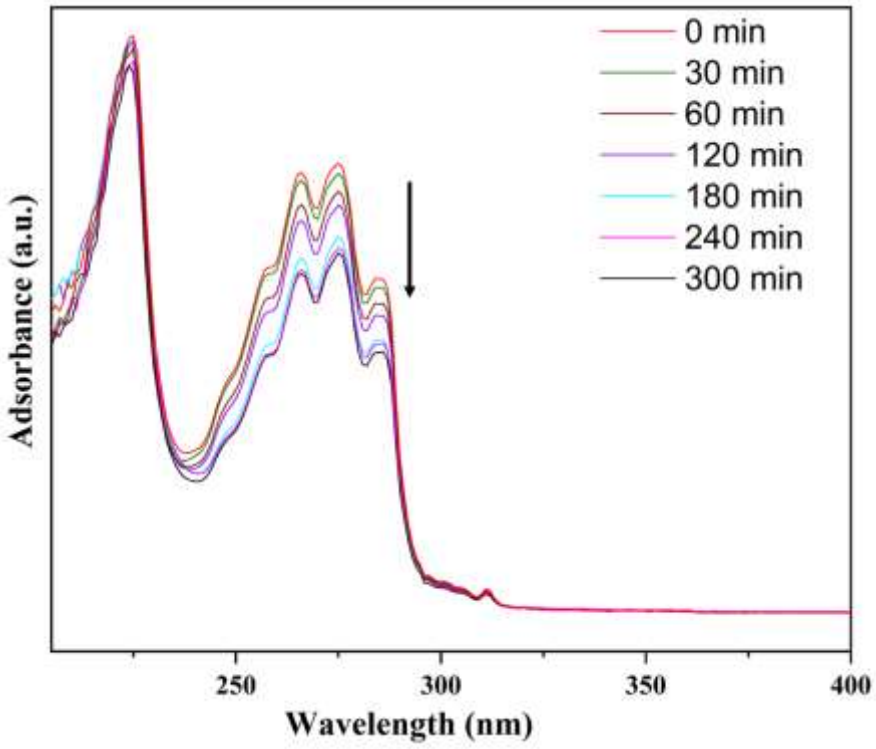

Figure S14. The UV spectrum of **NA** immersed in **BPTCA-2** from the start of the measurement to 300 mins.

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