

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 $\geq 99.999\%$. 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-K α ($\lambda = 1.541 \text{ \AA}$) radiation. Unless stated, PXRD patterns were recorded at room temperature. Diffraction patterns were measured over the 2θ range $2\text{--}40^\circ$, 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-K α radiation, $\lambda = 0.71073 \text{ \AA}$, Kappa 4-circle goniometer, Rigaku Saturn724+ detector); or at beamline I19, Diamond Light Source, Didcot, UK using silicon double crystal monochromated synchrotron radiation ($\lambda = 0.6889 \text{ \AA}$, Pilatus 2M detector). For synchrotron X-ray data collected at Diamond Light Source ($\lambda = 0.6889 \text{ \AA}$), 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 (^1H) 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 $\times$ 0.32 mm i.d. $\times$ 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 $\text{C}_{16}\text{H}_{10}\text{O}_8$; $M = 330.24$, orthorhombic $Pnna$, colorless block shape crystals; $a = 15.2243(19) \text{ \AA}$, $b = 7.1637(13) \text{ \AA}$, $c = 17.5962(19) \text{ \AA}$; $V = 1919.1(5) \text{ \AA}^3$; $\rho = 1.143 \text{ g/cm}^3$; $Z = 4$; $\mu(\text{Mo-K}\alpha) = 0.094 \text{ mm}^{-1}$; $F(000) = 680$; crystal size = $0.032 \times 0.022 \times 0.019 \text{ mm}$; $T = 100(2) \text{ K}$. 2213 reflections measured ($4.66 < 2\theta < 56.83^\circ$), 1911 unique ($R_{\text{int}} = 0.0922$), 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 $-0.456 \text{ e}\cdot\text{\AA}^{-3}$; data/restraints/parameters = 2213/0/115; GOF = 1.048. CCDC No. 2277044.

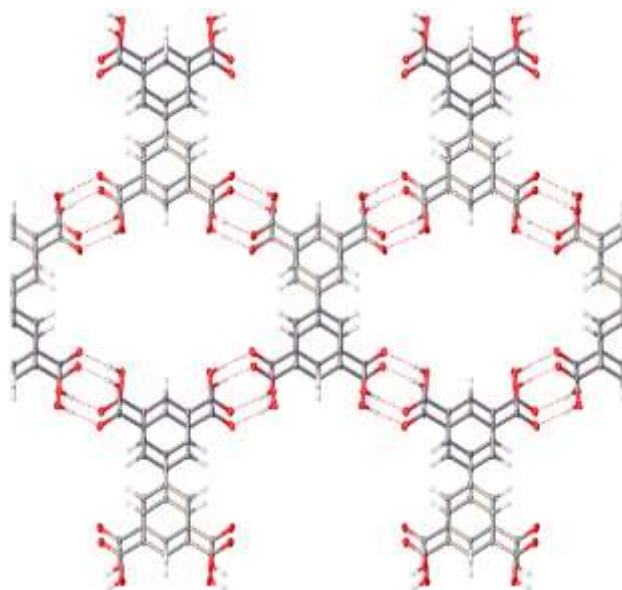


Figure S1. Crystal packing diagram of **BPTCA-1** recorded at 100 K and viewed along the b -axis. Hydrogen bonds are shown with red dashed lines. Grey: carbon, red: oxygen, white: hydrogen.

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; $a = 10.8266(7) \text{ \AA}$, $b = 31.5566(14) \text{ \AA}$, $c = 18.5503(11) \text{ \AA}$; $\beta = 105.143(7)^\circ$; $V = 6117.7(6) \text{ \AA}^3$; $\rho = 1.073 \text{ g/cm}^3$; $Z = 8$; $\mu(\text{Mo-K}\alpha) = 0.088 \text{ mm}^{-1}$; $F(000) = 2040$; crystal size = $0.052 \times 0.016 \times 0.012 \text{ mm}$; $T = 292(5) \text{ K}$. 13190 reflections measured ($3.46 < 2\theta < 60.11^\circ$), 6797 unique ($R_{\text{int}} = 0.028$), 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 $-0.252 \text{ e}\cdot\text{\AA}^{-3}$; data/restraints/parameters = 13190/0/332; GOF = 0.964. CCDC No. 2277046.

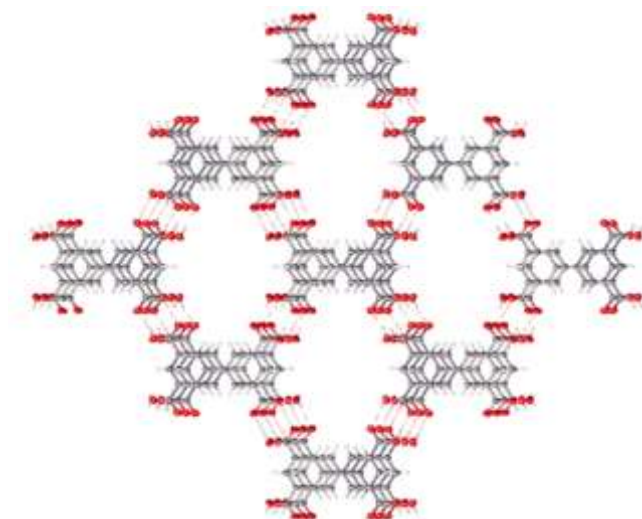


Figure S2. Crystal packing diagram of **BPTCA-2** recorded at 292 K viewed along the a axis. Hydrogen bonds are shown with red dashed lines. Grey: carbon, red: oxygen, white: hydrogen.

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 $\text{C}_{22}\text{H}_{14}\text{O}_8$; $M = 406.33$, monoclinic $C2/c$, colorless block shape crystals; $a = 16.4201(2) \text{ \AA}$, $b = 26.5063(3) \text{ \AA}$, $c = 7.19160(10) \text{ \AA}$, $\beta = 114.8240(10)^\circ$; $V = 2840.83(6) \text{ \AA}^3$; $\rho = 0.950 \text{ g/cm}^3$; $Z = 4$; $\mu(\lambda = 0.6889 \text{ \AA}) = 0.069 \text{ mm}^{-1}$; $F(000) = 840$; crystal size = $0.042 \times 0.026 \times 0.02 \text{ mm}$; $T = 100(2) \text{ K}$. 2778 reflections measured ($2.99 < 2\theta < 70.59^\circ$), 1998 unique ($R_{\text{int}} = 0.0378$), 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 $-0.291 \text{ e}\cdot\text{\AA}^{-3}$; data/restraints/parameters = $2778/0/144$; GOF = 1.025 . CCDC No. 2277047.

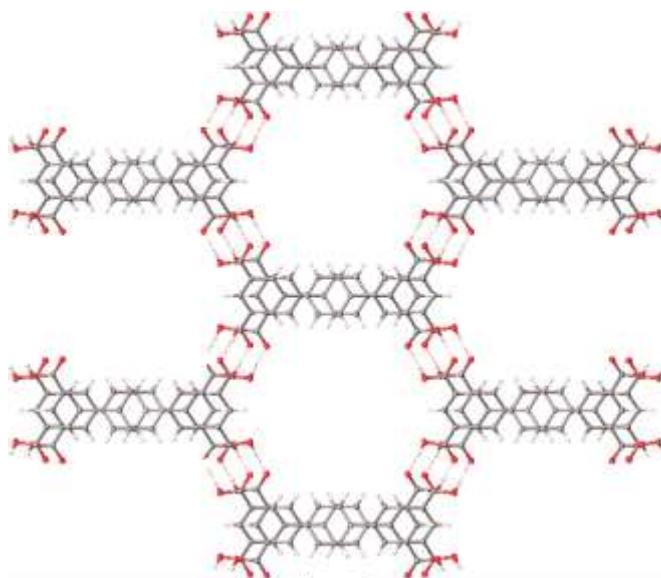


Figure S3. Crystal packing diagram of **TPTCA-1** recorded at 100 K from SCXRD viewed along the a axis. Hydrogen bonds are shown with red dashed lines. Grey: carbon, red: oxygen, white: hydrogen.

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; $a = 7.3463(3) \text{ \AA}$, $b = 26.5578(10) \text{ \AA}$, $c = 15.1916(6) \text{ \AA}$, $\beta = 92.149(4)^\circ$; $V = 2961.8(2) \text{ \AA}^3$; $\rho = 0.902 \text{ g/cm}^3$; $Z = 4$; $\mu(\text{Mo-K}\alpha) = 0.070 \text{ mm}^{-1}$; $F(000) = 840$; crystal size = $0.05 \times 0.032 \times 0.019 \text{ mm}$; $T = 291(2) \text{ K}$. 10816 reflections measured ($5.35 < 2\theta < 58.79^\circ$), 3213 unique ($R_{\text{int}} = 0.0189$), 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 $-0.212 \text{ e}\cdot\text{\AA}^{-3}$; data/restraints/parameters = 3213/3/141; GOF = 1.125. CCDC No. 2277048.

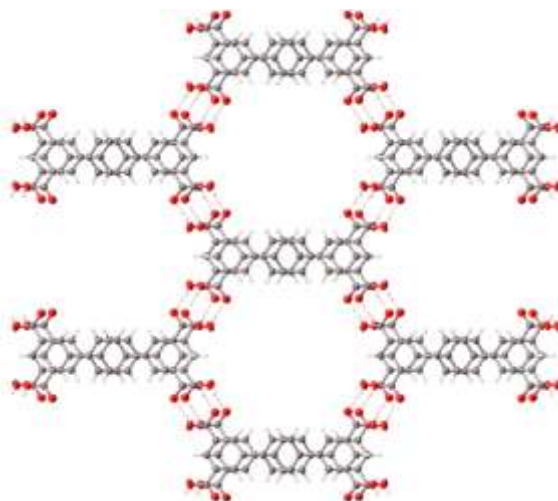


Figure S4. Crystal packing diagram of **TPTCA-2** recorded at 291 K viewed along the a axis. Hydrogen bonds are shown with red dashed lines. Grey: carbon, red: oxygen, white: hydrogen.

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; $a = 9.364(4) \text{ \AA}$, $b = 27.147(5) \text{ \AA}$, $c = 10.077(5) \text{ \AA}$, $\beta = 116.60(5)^\circ$; $V = 2290.3(18) \text{ \AA}^3$; $\rho = 1.178 \text{ g/cm}^3$; $Z = 4$; $\mu(\lambda = 0.6889 \text{ \AA}) = 0.091 \text{ mm}^{-1}$; $F(000) = 840$; crystal size = $0.04 \times 0.02 \times 0.015 \text{ mm}$; $T = 211(2) \text{ K}$. 1195 reflections measured ($7.78 < 2\theta < 54.19^\circ$), 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 $-0.194 \text{ e}\cdot\text{\AA}^{-3}$; data/restraints/parameters = $1195/6/140$; GOF = 0.919 . CCDC No. 2277049.

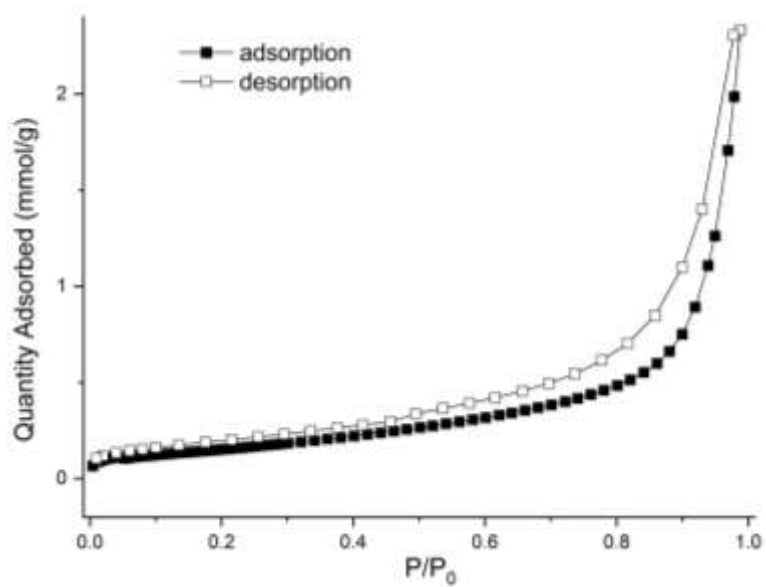


Figure S5. The N₂ sorption isotherms of **BPTCA-2** recorded at 77 K.

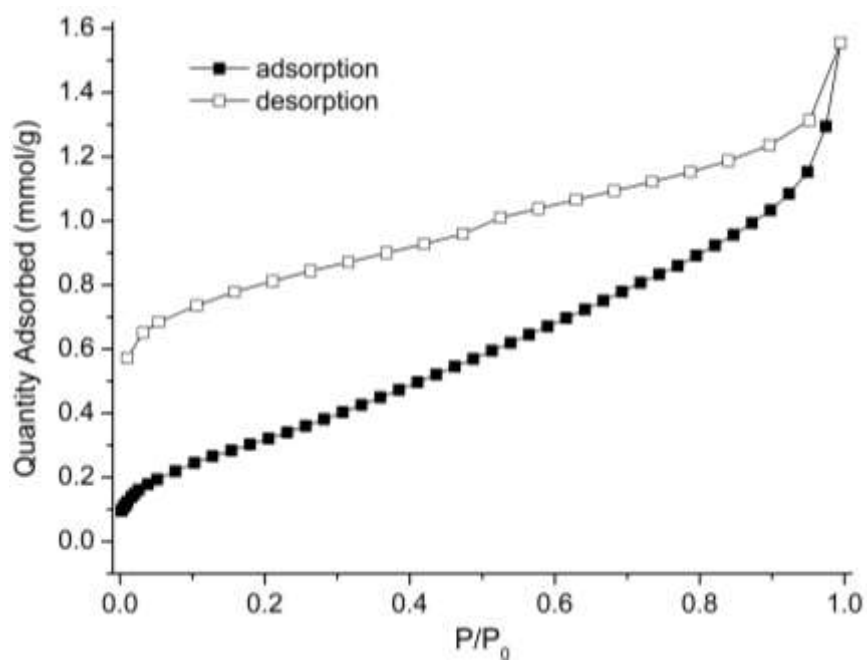


Figure S6. The N₂ sorption isotherms of **TPTCA-2_degas** recorded at 77 K.

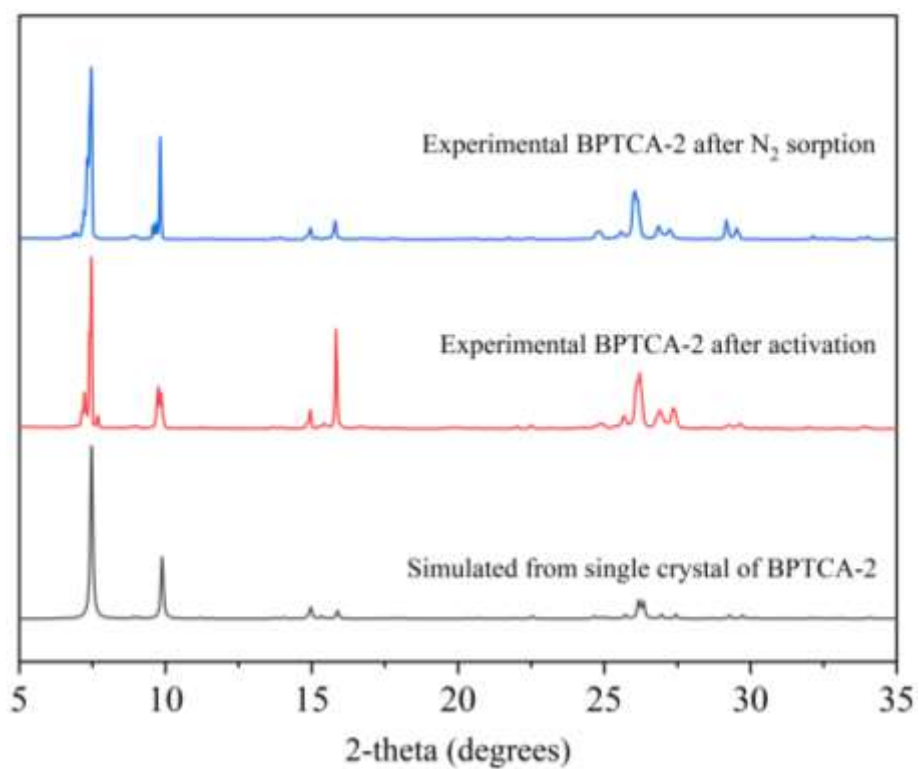


Figure S7. PXRD patterns of **BPTCA-2**. Black: simulation from the SC-XRD structure recorded at 292 K; red: experimental PXRD of **BPTCA-2** after activation; blue: experimental PXRD of **BPTCA-2** after the N₂ sorption test.

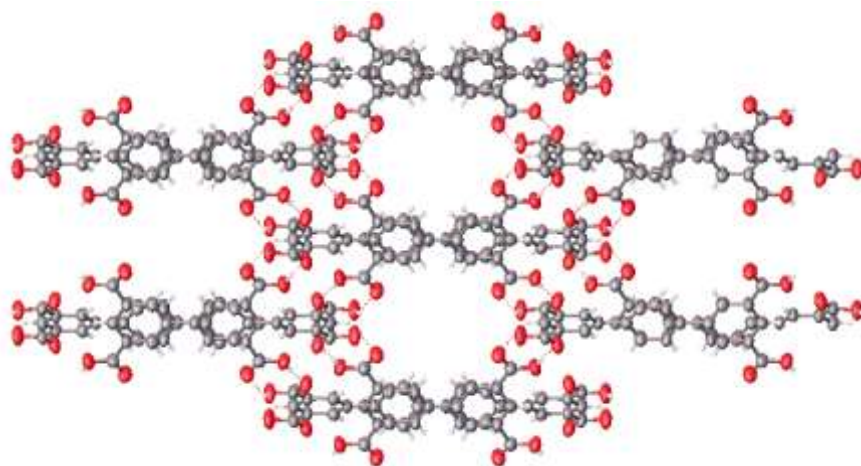


Figure S8. Crystal packing diagram of **TPTCA-2_degas** recorded at 211 K viewed along the *a*-axis. Hydrogen bonds are shown with red dashed lines. Grey: carbon, red: oxygen, white: hydrogen.

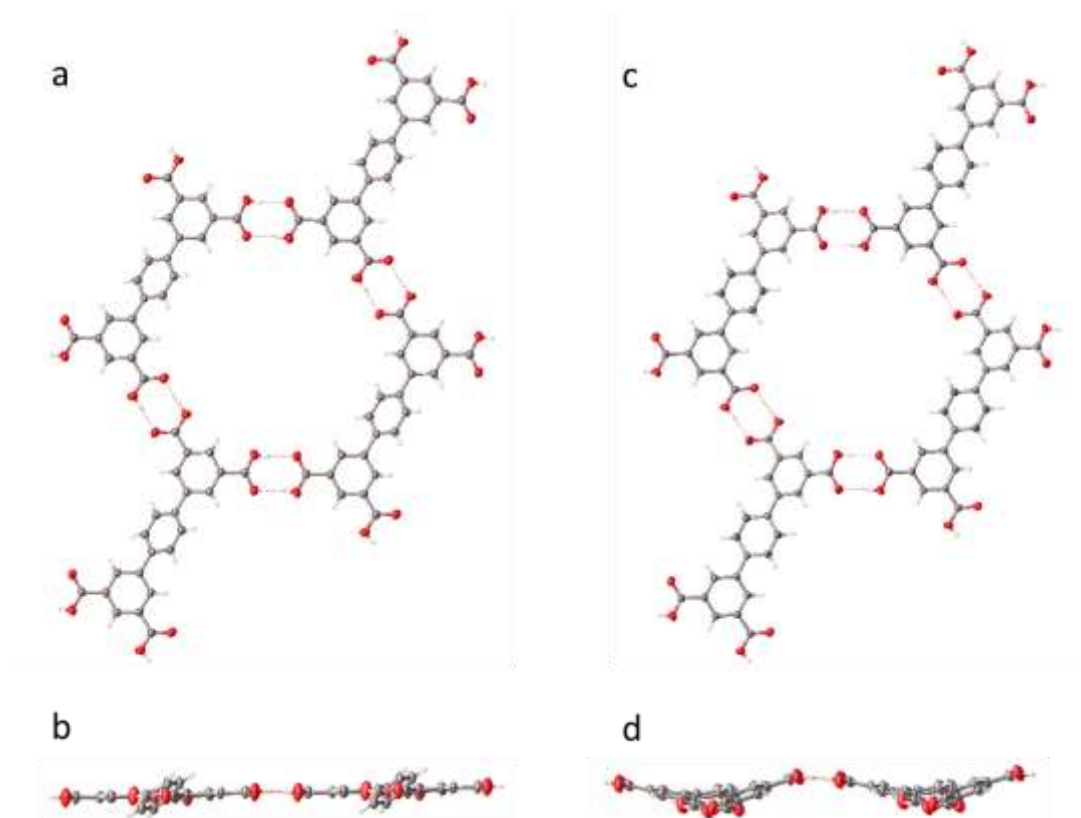


Figure S9. Comparison between the **sql** net in **TPTCA-2** (a) and side view (b); the **sql** net in **TPTCA-2_degas** (c) and side view (d). Hydrogen bonds are shown with red dashed lines. Grey: carbon, red: oxygen, white: hydrogen.

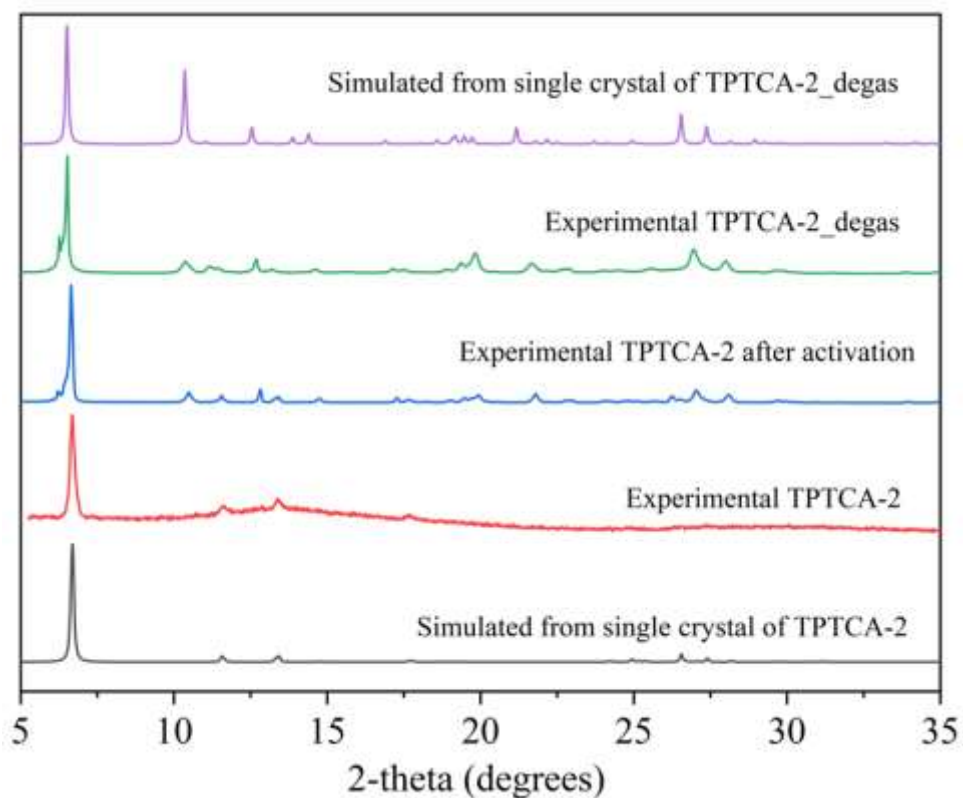


Figure S10. PXRD patterns of **TPTCA-2**. Black: simulation from the SC-XRD structure of **TPTCA-2**; red: experimental PXRD of **TPTCA-2**; blue: experimental PXRD of **TPTCA-2** after activation; green: experimental PXRD of **TPTCA-2_degas**; purple: simulation from the SC-XRD structure of **TPTCA-2_degas**.

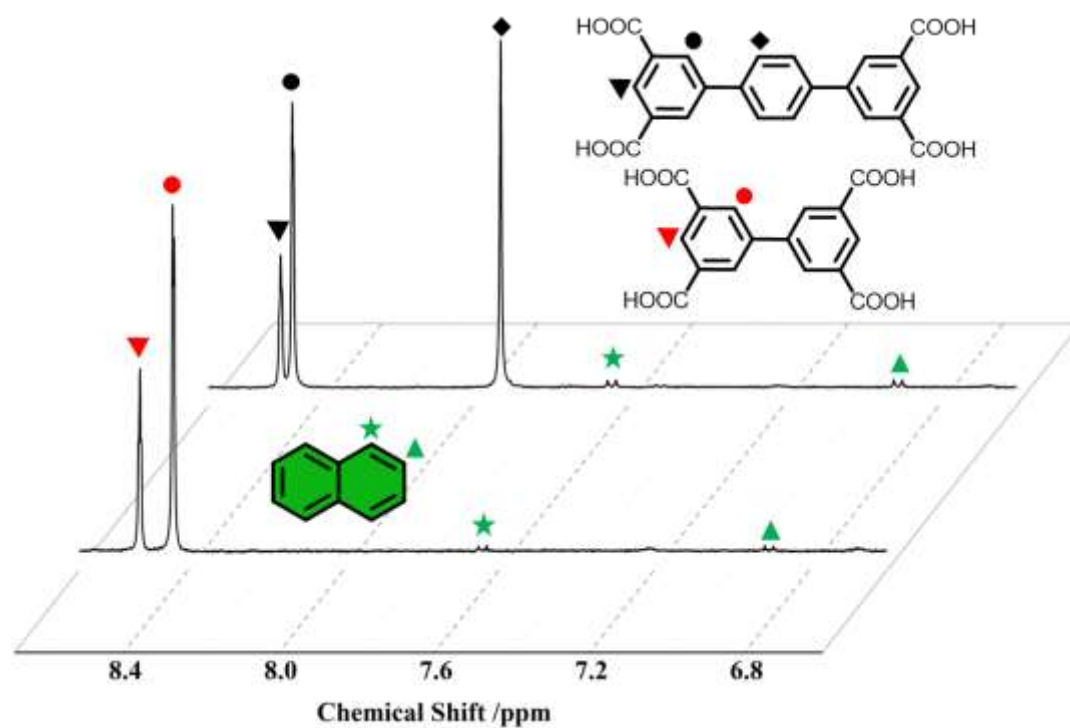


Figure S11. The ^1H NMR spectrum ($\text{DMSO-}d_6$) of **BPTCA-2>NA** and **TPTCA-2>NA**. The characteristic peaks of **BPTCA**, **TPTCA**, and **NA** molecules were marked with red, black, and green symbols, respectively.

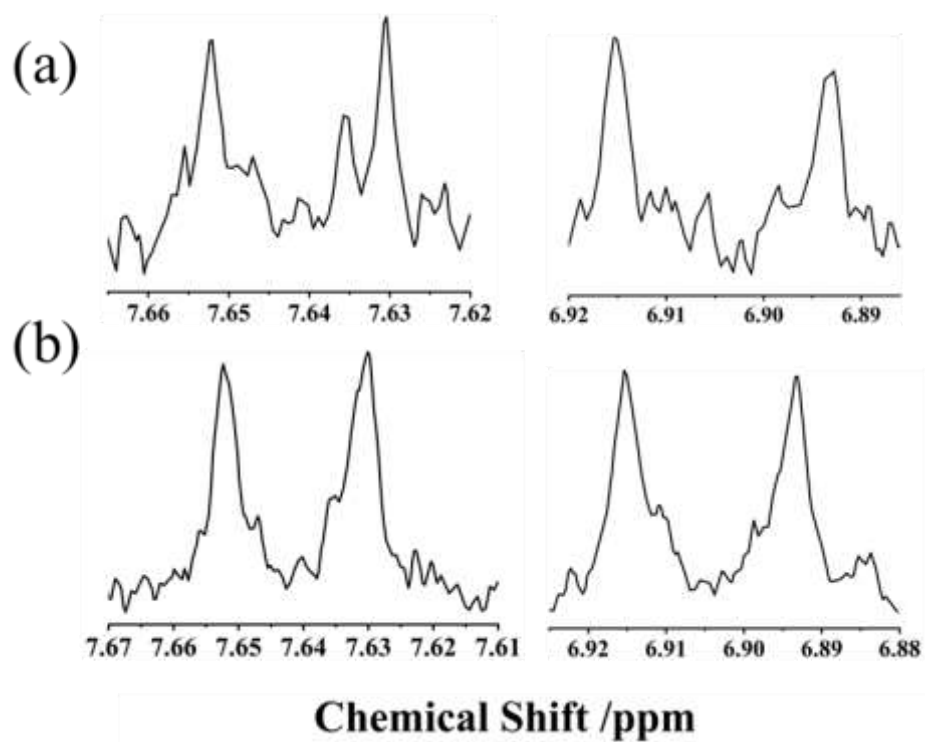


Figure S12. The amplifying ^1H NMR spectrum of NA in (a) BPTCA-2-NA; (b) TPTCA-2-NA.

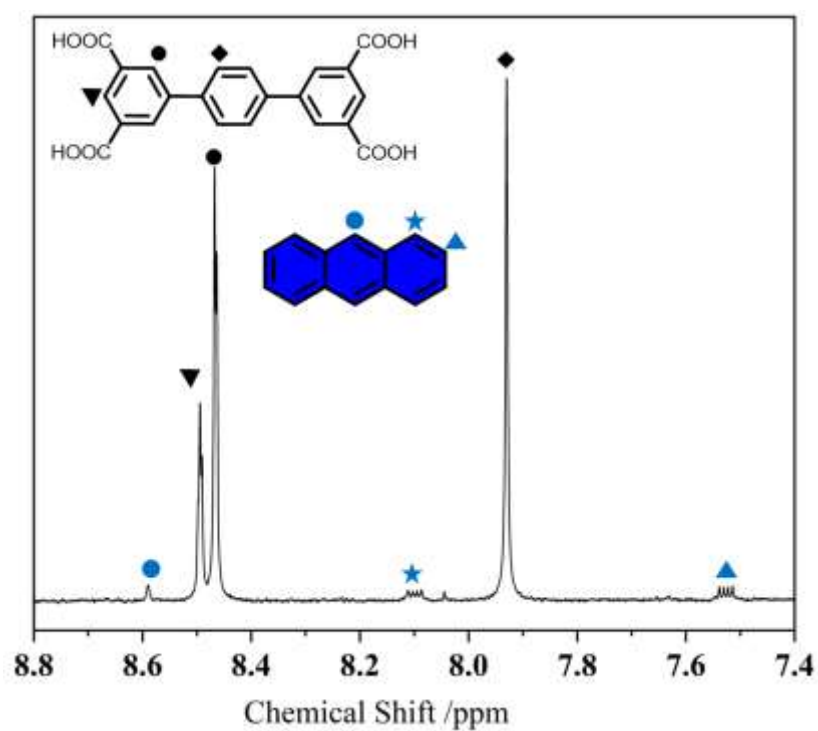


Figure S13. The ^1H NMR spectrum ($\text{DMSO-}d_6$) of **TPTCA-2** immersed in *n*-hexadecane solution containing 200 ppm of **AN** or **NA** for 3 hrs.

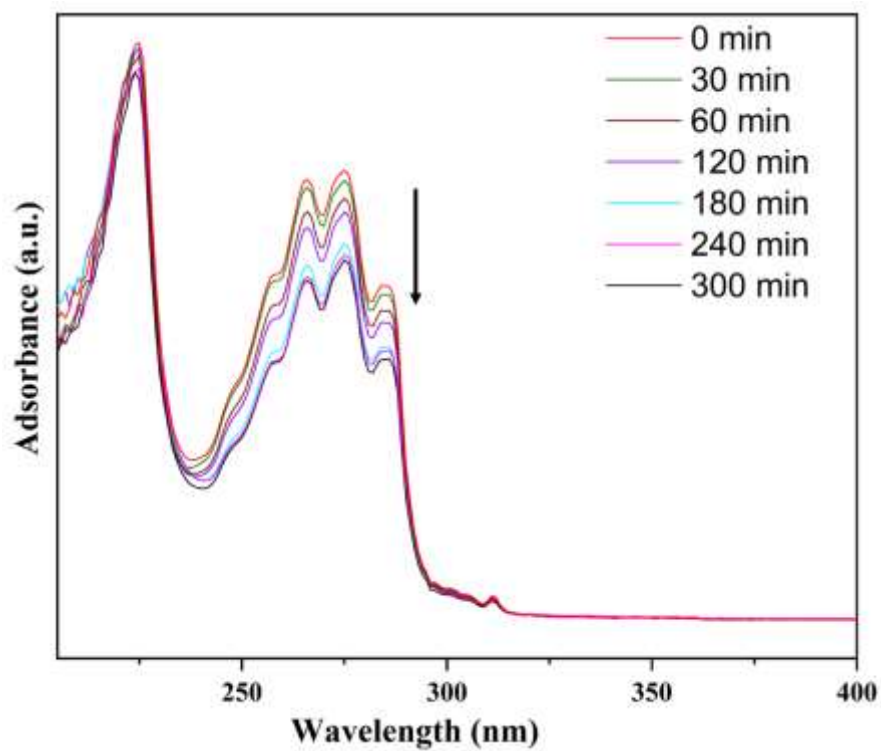


Figure S14. The UV spectrum of **NA** immersed in **BPTCA-2** from the start of the measurement to 300 mins.

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