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.

1.2.2. 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 = 0.6889 Å), data reduction and absorption corrections were performed with xia2. Structures were solved with SHELXT, or by direct methods using SHELXS, and refined by full-matrix least-squares on |F|^2 by SHELXL, interfaced through the programme OLEX2. 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 × 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, CHCl₃, 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/CHCl₃ system, but no particles were found in the other vials.

Crystal data for BPTCA-1 (100 K): Formula C₁₆H₁₀O₈; M = 330.24, orthorhombic Pnna, colorless block shape crystals; a = 15.2243(19) Å, b = 7.1637(13) Å, c = 17.5962(19) Å; V = 1919.1(5) Å³; ρ = 1.143 g/cm³; 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 (Rint = 0.0922), 1529 (I > 2σ(I)); R₁ = 0.0919 for observed and R₁ = 0.1190 for all reflections; wR₂ = 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) Å³; ρ = 1.073 g/cm³; 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 < 2θ < 60.11 °), 6797 unique (R_{int} = 0.028), 6259 (I > 2σ(I)); R₁ = 0.0699 for observed and R₁ = 0.1078 for all reflections; wR² = 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 CHCl₃. 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 C₂₂H₁₄O₈; 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) Å³; ρ = 0.950 g/cm³; 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 (Rint = 0.0378), 3176 (I > 2σ(I)); R₁ = 0.0482 for observed and R₁ = 0.0568 for all reflections; wR₂ = 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, \( \beta = 92.149(4) ^{\circ} \); V = 2961.8(2) Å³; \( \rho = 0.902 \) g/cm³; Z = 4; \( \mu(\text{Mo-K}\alpha) = 0.070 \) mm⁻¹; \( F(000) = 840 \); crystal size = 0.05 × 0.032 × 0.019 mm; \( T = 291 \) (2) K. 10816 reflections measured (5.35 < 2\( \theta < 58.79 \) °), 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 eÅ⁻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, $\beta = 116.60(5)$ °; $V = 2290.3(18)$ Å$^3$; $\rho = 1.178$ g/cm$^3$; $Z = 4; \mu(\lambda = 0.6889$ 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 < 2$\theta$ < 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\textsubscript{2} sorption isotherms of TPTCA-2\textunderscore 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-$2\supset$NA and TPTCA-$2\supset$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.
References

1 G. M. Sheldrick, 2008.


