Electronic Supplementary Information

Ordered Organization of Hydrogen-Bonded Organic Macrocycles into a Permanent Porosity Framework

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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. 1,8-Dibromoanthracene, (4-(methoxycarbonyl)phenyl)boronic acid, CsF, polysulfone, and $Pd(PPh_3)_4$ were purchased from MacLean Co., LTD.

1.1.1 Single Crystal X-ray Diffraction (SCXRD)

SCXRD data sets were measured on 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 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] Unless stated, all non-H atoms were refined anisotropically. Supplementary CIFs are available free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

1.1.2 Gas Sorption Analysis

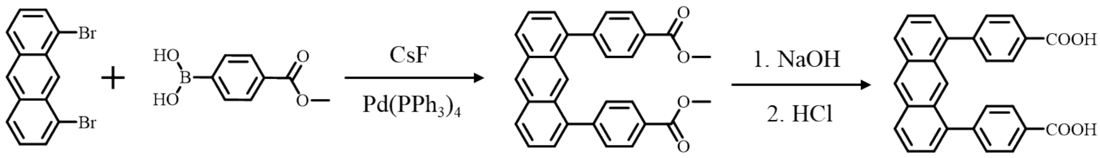
Surface areas were measured by nitrogen sorption at 77 K. Powder samples were degassed on the analysis port under vacuum. Isotherm measurements were performed using a Micromeritics 2420 surface characterization analyser, equipped with a Cold-Edge technologies liquid helium cryostat chiller unit for temperature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

1.1.3 Nuclear Magnetic Resonance Spectroscopy

NMR spectra were recorded on a Bruker 400 NMR spectrometer at 400 MHz (^{1}H) and referenced against the residual ^{1}H signal of the solvent.

2.0 Supplementary Data

2.1 Synthesis of 4,4'-(anthracene-1,8-diyl)dibenzoic acid (ADBA)



1 **2**

1,8-Dibromoanthracene (101 mg, 0.3 mmol), (4-(methoxycarbonyl)phenyl)boronic acid (162 mg, 0.9 mmol), CsF (91 mg, 1.8 mmol), and $Pd(PPh_3)_4$ (3.5 mg, 0.03 mmol) were added into two-neck round bottom flask. The system was evacuated air with dynamic pump for 15 mins and filled with nitrogen. The operation was executed by three pump-refilling cycles. Then 1,4-dioxane (120 mL) and H_2O (20 mL) were injected and bubbled with nitrogen for 15 mins to obtain clear yellow solution. After refluxing at 110 °C for 2 days, the orange solution was filtered immediately at a high temperature to remove the insoluble compounds. The orange solution was stood at room temperature to get the product (**1**, dimethyl 4,4'-(anthracene-1,8-diyl)dibenzoate). ^{1}H NMR ($CDCl_3$): δ 3.9 (s, 6H), 7.35 (d, 2H), 7.47 (d, 6H), 8.01 (d, 6H), 8.34 (s, 1H), 8.5 (s, 1H).

100 mg **1** was dispersed in THF/ethanol/H_2O (120 mL, ratio 5/2/2) and NaOH (2g) was added in the mixture. The system was stirred under reflux at 90 °C for 12 h and then concentrated with rotated evaporation. The pH value was adjusted to 1 with HCl and the resulting light-yellow solid was collected with filtration. The product was dried under vacuum to obtain **2**, 4,4'-(anthracene-1,8-diyl)dibenzoic acid (**ADBA**). ^{1}H NMR (DMSO-d_6): δ 7.51 (d, 2H), 7.64 (d, 2H), 7.70 (d, 4H), 8.03 (d, 4H), 8.20 (d, 2H), 8.50 (s, 1H), 8.80 (s, 1H).

2.2 Crystallization of ADBA-1:

ADBA (2 mg) was dissolved in THF (2 mL) at RT. Then 1,3-dimethoxybenzene (2 mL) was added into THF. The solvent mixtures were left to evaporate at RT for 5 days. The light yellow rodlike crystals were crystalized from THF/1,3-dimethoxybenzene solvent system and named as **ADBA-1**.

Crystal data for **ADBA-1** (200 K): Formula $C_{28}H_{18}O_4$ (0.2 $C_8H_{10}O_2$, 0.3 C_4H_8O); M = 467.69, monoclinic $P2_1/c$, light yellow block shape crystals; a = 10.1808(15) Å, b = 31.852(3) Å, c = 7.4992(13) Å, β = 107.560(7) °; V = 2318.5(6) Å^3; ρ = 1.340 g/cm^3; Z = 4; μ(Cu-Kα) = 0.090 mm^{-1}; F (000) = 979; crystal size = 0.18 × 0.1 × 0.04 mm; T = 200 K. 1912 reflections measured (4.386 < 2θ < 54.15 °), 5055 unique (R_{int} = 0.0855), 2691 ($I > 2\sigma(I)$); R_1 = 0.0971 for observed and R_1 = 0.1676 for all reflections; wR_2 = 0.2444 for all reflections; max/min difference electron density = 0.270 and -0.232 e·Å^{-3}; data/restraints/parameters = 5055/2/297; GOF = 1.046. CCDC No. 2537965.

Due to the presence of highly disordered solvent molecules (a mixture of 1,3-dimethoxybenzene and tetrahydrofuran) in the crystal channels, the solvent masking procedure as implemented in Olex2 (equivalent to PLATON-SQUEEZE) was applied to remove their contribution to the structure factors. The mask removed approximately 108 electrons per unit cell, corresponding to ca. 27 electrons per asymmetric unit. This electron count is consistent with a disordered mixture of 1,3-dimethoxybenzene (74 e^-) and THF (40 e^-) in non-integer occupancies, e.g. 0.2 [$C_8H_{10}O_2$], 0.3 [C_4H_8O].

2.3 Formation of ADBA-2:

Following the above the crystallization of **ADBA-1**, the residual THF and 1,3-dimethoxybenzene 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, **ADBA-2**.

Crystal data for **ADBA-2** (293 K): Formula $C_{28}H_{18}O_4$; M = 418.42, monoclinic $P2_1/c$, light yellow block shape crystals; a = 10.2492(5) Å, b = 32.0207(17) Å, c = 7.5196(3) Å, β = 108.043(4) °; V = 2346.5(2) Å^3; ρ = 1.184 g/cm^3; Z = 4; $\mu(\lambda=0.6889)$ = 0.074 mm^{-1}; F (000) = 872; crystal size = 0.22 × 0.06 × 0.03 mm; T = 293 (2) K. 4039 reflections measured (2.46 < 2θ < 48.41 °), 4107 unique (R_{int} = 0.1025), 1409 ($I > 2\sigma(I)$); R_1 = 0.1157 for observed and R_1 = 0.1720 for all reflections; wR_2 = 0.3235 for all reflections; max/min difference electron density = 0.530 and -0.274 e·Å^{-3}; data/restraints/parameters = 4107/2/294; GOF = 0.921. CCDC No. 2537966.

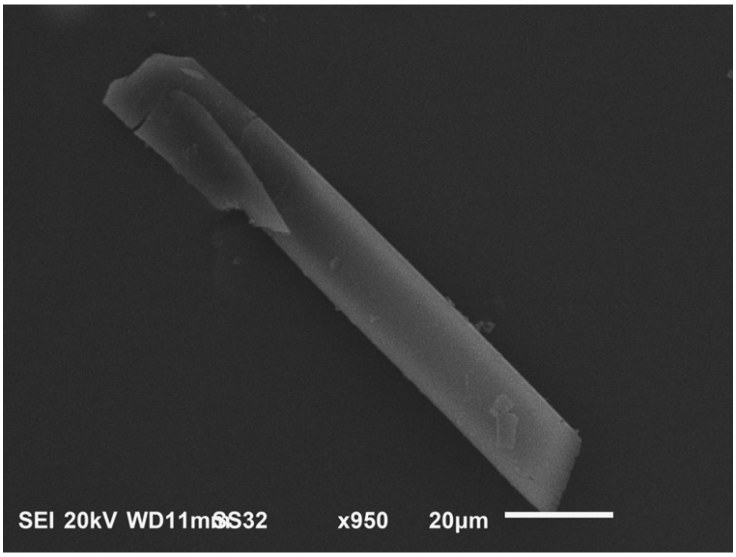


Figure S1. SEM image of **ADBA-1**.

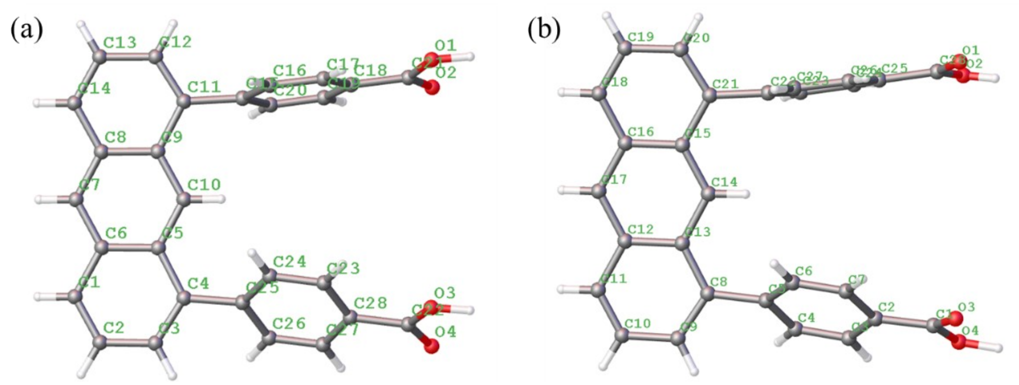


Figure S2. The structure of **ADBA** molecule in (a) **ADBA-1** and (b) **ADBA-2**; C: grey, O: red, H: white.

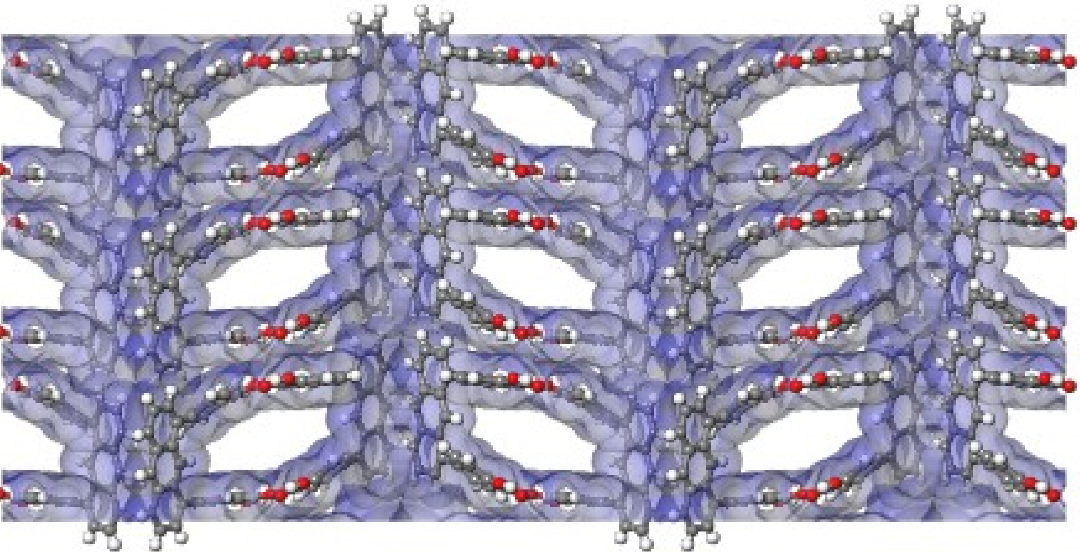


Figure S3. The single crystal structure of **ADBA-2** viewed along c axis.

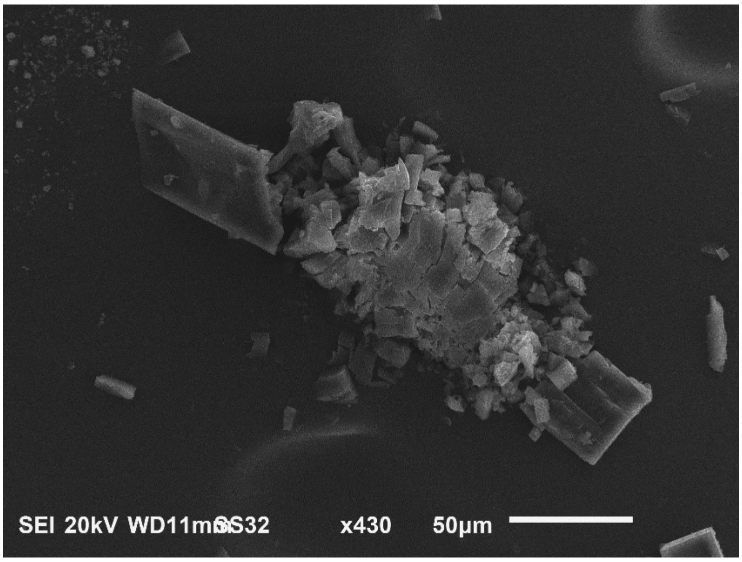


Figure S4. SEM image of **ADBA-2** after adsorption of naphthalene. Scale bars are included on bottom right corner of the SEM image.

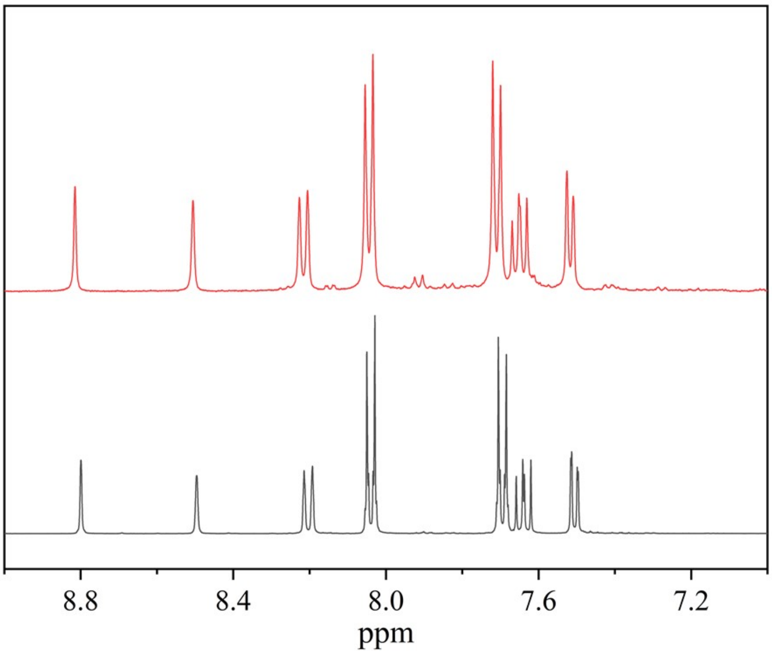


Figure S5. The ^{1}H-NMR of **ADBA-2** before (black) and after adsorption of naphthalene (red).

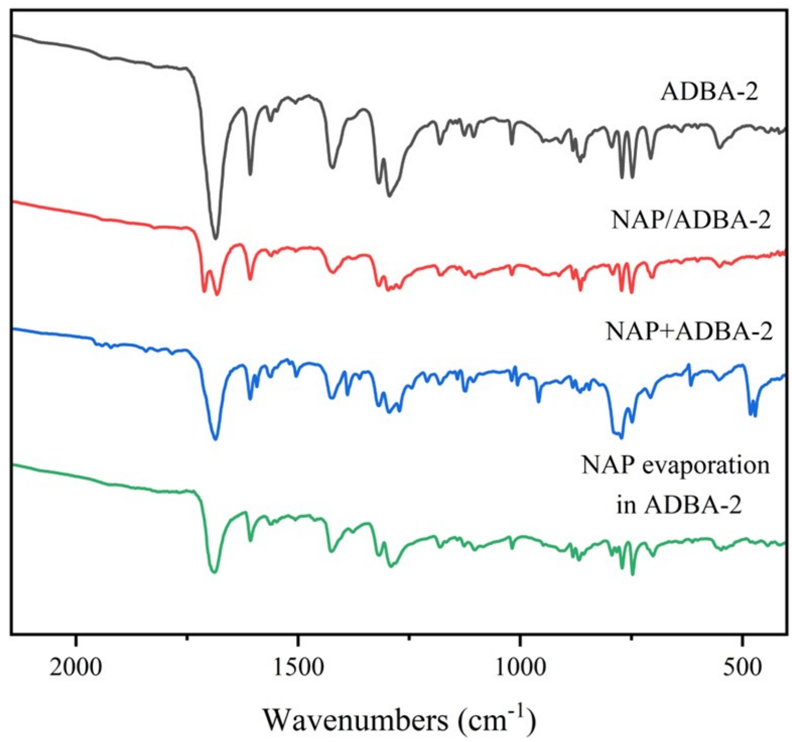


Figure S6. The FTIR spectrums of ADBA-2 (black), after adsorption of naphthalene (red), mixed with naphthalene (blue) and evaporation of naphthalene in ADBA-2 (green).

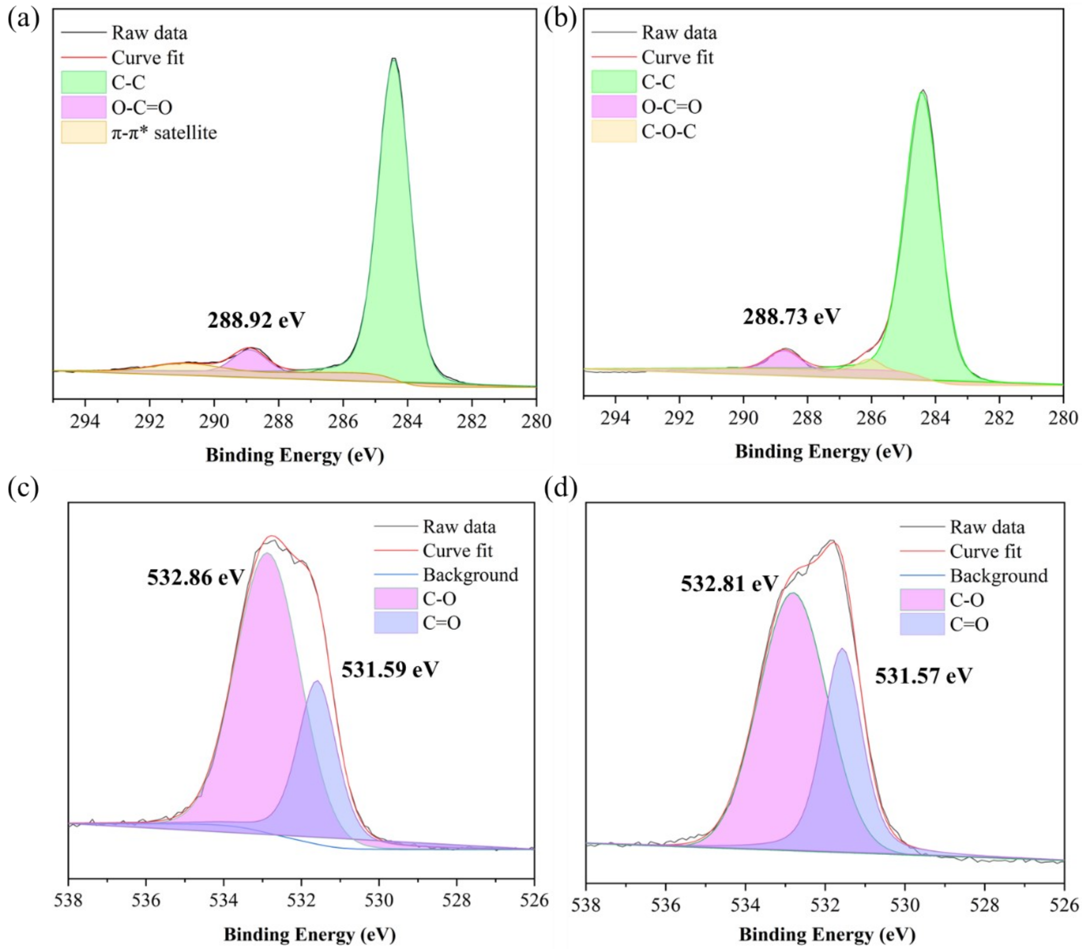


Figure S7. The XPS spectrums of (a) C 1s in ADBA-2; (b) C1s after adsorption of naphthalene; (c) O 1s in ADBA-2; (b) O1s after adsorption of naphthalene.

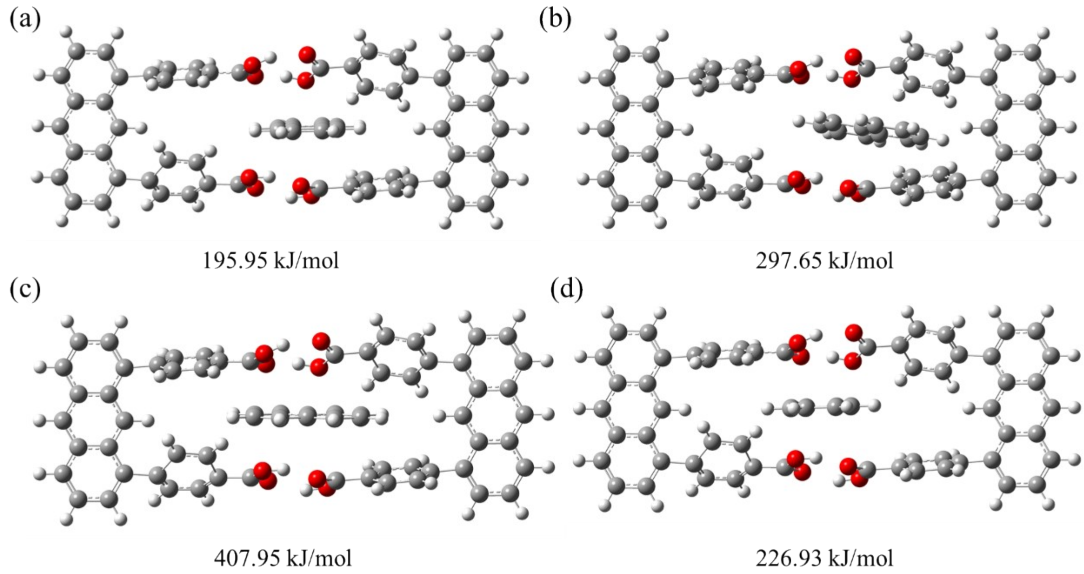


Figure S8. The four different positions of naphthalene in **ADBA-2** with the relative energy.

Reference

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