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Electronic Supplemental Information

for

Hydrogen-bonded organic frameworks of twisted polycyclic aromatic hydrocarbon

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1. General

All reagents and solvents were used as received from commercial suppliers. ¹H NMR spectra were measured by JEOL 400 YH (400 MHz) spectrometer. ¹³C NMR spectra were measured by Bruker Avance III-400 spectrometers. Residual proton and carbon of deuterated solvents were used as internal standards for the measurements (for ¹H NMR, CDCl₃, $\delta = 7.26$ ppm; DMSO-*d*₆, $\delta = 2.75$ ppm: for ¹³C NMR, CDCl₃, $\delta = 77.00$ ppm; DMSO-*d*₆, $\delta = 29.76$ ppm). Mass spectrum data were obtained from a JEOL JMS-700 instrument. Thermo gravimetric (TG) analysis were performed on Rigaku TG8120 under an N₂ purge (100 mL/min) at a heating rate of 5 °C min⁻¹. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Ultima-IV (40 kV, 44 mA) using graphite-monochromatized Cu-K α radiation ($\lambda = 1.54187$ Å) at room temperature. A scan rate is 2.0 °/min.

Single crystal X-ray measurement and analysis. Diffraction data of **CPDBC-1** was collected at SPring-8 (BL02B1) with monochromated synchrotron radiation ($\lambda = 0.42860$ Å) and **CPDBC-2** was collected at Spring-8 (BL40XU) with synchrotron radiation ($\lambda = 0.81106$ Å). The cell refinements were performed with softwares RapidAuto or CrysAlisPro. SHELXT^[S1] were used for the structure solution of the crystals. All calculations were performed with the observed reflections [I > 2 σ (I)] with the program CrystalStructure crystallographic software. Structural refinement was performed by SHELXL.^[S2] All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters. SQUEEZE function equipped in the PLATON program was used to remove severely disordered solvent molecules in voids.^[S3]

Variable temperature (VT) PXRD measurement. Crystalline bulk of **CPDBC-1** placed on an aluminum substrate was subjected to VT-PXRD measurement under the air atmosphere. PXRD data were collected on a Rigaku Ultima-IV using graphite-monochromatized Cu-K α radiation ($\lambda = 1.54187$ Å) with a temperature control unit. Temperature of the sample was increased from room temperature to 633 K with a rate of 1 K/min. During temperature increasing, XRD patterns ranged from 2° to 19.8° was repeatedly recorded with a scan rate of 3 °/min. Therefore, each PXRD scan has a temperature width of about 6 K.

Sorption/desorption experiment. Gas sorption measurements on activated HOF **CPDBC-1a** were performed on BELSORP-max (BEL, Japan). The adsorption isotherms of N₂, O₂, CO₂, and H₂ were corrected at 77K, 77 K, 195 K and 77 K, respectively.

TRMC was performed for the powder samples placed on an adhesive tape on a quartz substrate. The microwave frequency and its power were ~9 GHz and ~3 mW, respectively. The third harmonic generation (355 nm) of a Nd:YAG laser (Continuum Inc., Surelite II, 5–8 ns pulse duration, 10 Hz) was used for the excitation (incident photon density $I_0 = 9.1 \times 10^{15}$ photons cm⁻² pulse⁻¹). The photoconductivity ($\Delta \sigma = A^{-1} \Delta P_r P_r^{-1}$ where A is the sensitivity factor, P_r is the reflected microwave power, and ΔP_r is the change in P_r upon exposure to light) was converted into the product of the quantum yield (φ) and sum of the charge carrier mobilities $\Sigma \mu$ (= $\mu_+ + \mu_-$) using the relationship $\varphi \Sigma \mu$ = $\Delta \sigma (eI_0 F_{\text{light}})^{-1}$, where e and F_{Light} are the electron charge and correction (or filling) factor, respectively. The experiments were performed at room temperature in the air.

2. Synthesis of CPDBC



2,7,10,15-tetrabromodibenzo[g,p]chrysene (1) was synthesized by bromination of tetraphenylethene, followed by the one-electron oxidation cyclization with DDQ, as reported in literature.^[S4]

Synthesis of ester precursor 3. A suspension of tetrabromochrysene 1 (1.47 g, 2.29 mmol), boronic acid pinacol ester 2, K_2CO_3 (3.00 g, 21.7 mmol), and $Pd(PPh_3)_4$ (0.577 g, 0.500 mmol) in a deoxygenated toluene (30 mL), dioxane (70 mL), and H_2O (8 mL) was stirred for 48 h at 110 °C. The solvent was removed in vacuum. To the residual reaction mixture methanol (50 mL) and water (50 mL) were added, followed by being sonicated. The precipitate was filtered by a filter paper and carefully rinsed with water and methanol. The product was purified by reprecipitation with CHCl₃ and acetone, followed by passing through a bet of silica gel with CHCl₃ to give 3 (917 mg, 0.801 mmol) in 35% yield as yellow solid.

3. Mp. 179 °C. ¹H NMR (400 MHz, CDCl₃) : δ 8.11 (d, 2H, J = 8.8 Hz) , 7.70 (d, 2H, J = 8.0 Hz) , 7.63 (d, 2H, J = 7.2 Hz) , 7.50 (d, 2H, J = 7.2 Hz), 4.34 (t, 2H, J = 6.8 Hz), 1.74–1.84 (m, 2H), 1.30–1.52 (m, 6H), 0.941 (t, 2H, J = 7.6 Hz) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 166.27, 144.43, 137.45, 130.60, 130.10, 129.50, 128.86, 128.30, 127.02, 126.82, 125.28, 121.59, 65.20, 31.49, 28.73, 25.70, 22.56, 14.00 ppm. HR-MS (FAB+): calcd. For C₇₈H₈₀O₈ [M]⁺ 1144.5853; found: 1144.5847.

Hydrolysis of 3. Hexyl ester derivative **3** (340 mg, 297 μmol) in THF (25 mL) and 5% aqueous solution of KOH (30 mL) was stirred for 48 h at 80 °C. After removing THF in vaccuo, 3M-HCl was added till further precipitate did not form. The precipitate was collected by centrifuge and washed with water, methanol, and acetone, and dried to give CPDBC (248 mg, 283 μmol) in 95% yield as a yellow solid.

CPDBC. Mp: >300 °C. ¹H NMR (400 MHz, DMSO- d_6) : δ 9.02 (s, 4H), 8.23 (d, 4H, J = 8.4 Hz) , 8.04 (d, 8H, J = 8.4 Hz) , 7.94 (d, 8H, J = 8.4 Hz) , 7.73 (d, 4H, J = 8.4 Hz) ppm. ¹³C NMR (100 MHz, DMSO- d_6): δ 167.18, 143.71, 137.11, 130.52, 129.81, 129.76, 128.62, 127.68, 127.25, 126.45, 125.55, 122.07 ppm. HR-MS (FD+): calcd. For C₅₄H₃₂O₈ [M]⁺ 808.2097; found: 808.2092

3. Crystallography of CPDBC

CPDBC-1 was obtained by slow evaporation of a mixed solution of DMF and 5-*tert*-butyl-*m*-xylene at 80 °C for 2 days, yielding single crystals of HOF. Other aromatic solvents such as methyl benzoate and 1,2,4-trichlorobenzene instead of 5-*tert*-butyl-*m*-xylene also resulted in formation of **CPDBC-1**.

CPDBC-2 was obtained by low evaporation of a mixed solvent of DMF and 3-carene for 2 days at 80 °C. During crystallization, the liquid gradually changed into relatively viscus liquid with color changes from yellow to brown.



Figure S1. Photographs of crystals CPDBC-1(left) and CPDBC-2(right).

	CPDBC-1	CPDBC-2
System	Orthorombic	Tetragonal
Space group	<i>Pnnn</i> (no. 48)	I41/acd (no.142)
Fourmula	$C_{54}H_{32}O_8$	$C_{54}H_{32}O_8$
Fourmula weight	808.80	808.80
<i>a</i> / Å	3.7618(5)	47.5006(10)
<i>b</i> / Å	24.323(3)	47.5006(10)
<i>c</i> / Å	41.416(6)	7.4170(2)
α/°	90	90
β/°	90	90
γ / °	90	90
$V(Å^3)$	3789.5(9)	16735.0(7)
Ζ	2	8
$D / \mathrm{g} \mathrm{cm}^3$	0.709	0.661
Crystal size (mm)	$0.5\times0.03\times0.03$	$0.1 \times 0.02 \times 0.02$
crystal color	yellow	yellow
<i>R1</i> ($I > 2.0\sigma(I)$)	0.0763	0.0917
<i>wR2</i> (all)	0.2556	0.2920
Completeness	0.999	0.950
GOF	1.010	1.053
λ / Å	0.42860 (synchrotron)	0.81106 (synchrotron)
T/K	93	93
CCDC no.	2027309	2027310

 Table S1. Crytal data of CPDBC-1 and CPDBC-2.



Figure 2. PXRD pattern of as-formed crystalline bulk of **CPDBC-1** obtained from a mixed solution of methyl benzoate (MeBz) and DMF [labeled as **CPDBC-1**(MeBz)], together with the simulated patterns of **CPDBC-1** and **CPDBC-2** based on single-crystalline X-ray diffraction data. The pattern of **CPDBC-1**(MeBz) is in good agreement with the simulated pattern based on the single crystal of **CPDBC-1** obtained from a mixed solution of 5-*tert*-butyl-*m*-xylen and DMF.

4. Theoretical calculation



Figure S3. Optimized structure of **CPDBC** by the DFT method at the B3LYP/6-31G* level. (a) Side and (b) top views.

(A)-(A')	23.05°
(B)-(B')	41.75°
(A)-(B)	11.79°
(A)-(B')	11.63°
(B)-(C)	36.65°
RMSD	0.7842

Table S2. Selected dihedral angles of the optimized CPDBC

С	1.385028	0.33189	1.252313	С	-3.2804	-1.57058	4.950266
С	2.632469	1.154541	3.683238	С	-4.50555	-2.36422	7.372831
С	0.687441	0.24454	2.490375	С	-4.11691	-2.69854	5.000971
С	2.6848	0.893993	1.269536	С	-3.0833	-0.84043	6.137159
С	3.29363	1.289647	2.44441	С	-3.69139	-1.22453	7.325481
С	1.334387	0.648718	3.673474	С	-4.71847	-3.09107	6.193155
Н	3.204009	1.064686	0.33485	Н	-4.2825	-3.2862	4.10305
Н	4.296667	1.704435	2.409757	Н	-2.47096	0.056265	6.115957
Н	0.78745	0.625862	4.609125	Н	-3.55615	-0.64725	8.234155
С	-0.68744	-0.24454	2.490375	Н	-5.38159	-3.95359	6.18134
С	-3.29363	-1.28965	2.44441	С	-3.33213	1.46584	-4.93866
С	-1.38503	-0.33189	1.252313	С	-4.60204	2.224294	-7.34947
С	-1.33439	-0.64872	3.673474	С	-3.09803	0.763077	-6.13525
С	-2.63247	-1.15454	3.683238	С	-4.2074	2.564701	-4.97948
С	-2.6848	-0.89399	1.269536	С	-4.83392	2.937539	-6.16489
Н	-0.78745	-0.62586	4.609125	С	-3.71309	1.141348	-7.32206
Н	-3.20401	-1.06469	0.33485	Н	-2.44438	-0.10415	-6.12569
Н	-4.29667	-1.70443	2.409757	Н	-4.37183	3.154355	-4.08266
С	0.699397	0.013371	0.004058	Н	-5.46672	3.822768	-6.16192
С	-0.69572	0.219936	-2.48206	Н	-3.52742	0.600585	-8.24418
С	1.396495	-0.27975	-1.24415	С	3.332131	-1.46584	-4.93866
С	-0.6994	-0.01337	0.004058	С	4.602039	-2.22429	-7.34947
С	-1.3965	0.279752	-1.24415	С	4.207404	-2.5647	-4.97948
С	0.695717	-0.21994	-2.48206	С	3.098032	-0.76308	-6.13525
С	1.355118	-0.60472	-3.66471	С	3.713085	-1.14135	-7.32206
С	2.670486	-1.06398	-3.67423	С	4.833924	-2.93754	-6.16489
С	3.337541	-1.16984	-2.43574	Н	4.371827	-3.15435	-4.08266
С	2.716096	-0.7934	-1.26116	Н	2.444378	0.104146	-6.12569
Н	0.805807	-0.60575	-4.59923	Н	3.527416	-0.60058	-8.24418
Н	4.354739	-1.54863	-2.40106	Н	5.466724	-3.82277	-6.16192
Н	3.242099	-0.94291	-0.32665	С	5.138407	2.717393	8.684576
С	-2.7161	0.7934	-1.26116	С	-5.13841	-2.71739	8.684576
С	-3.33754	1.16984	-2.43574	С	-5.23083	2.580147	-8.66251
С	-2.67049	1.063975	-3.67423	С	5.230834	-2.58015	-8.66251
С	-1.35512	0.604716	-3.66471	О	4.77862	-2.23763	-9.72912
Н	-3.2421	0.942912	-0.32665	О	-4.77862	2.237634	-9.72912
Н	-4.35474	1.548634	-2.40106	О	-5.28423	-1.92536	9.585142
Н	-0.80581	0.605746	-4.59923	О	5.284226	1.925365	9.585142
С	3.2804	1.570581	4.950266	О	-5.56015	-4.00325	8.836534
С	4.505553	2.364218	7.372831	Н	-5.23083	-4.55148	8.106201
С	3.083302	0.840426	6.137159	0	-6.36789	3.328147	-8.61575
С	4.116912	2.698536	5.000971	Н	-6.69253	3.384827	-7.70268
С	4.71847	3.091074	6.193155	0	6.367886	-3.32815	-8.61575
С	3.691388	1.224527	7.325481	Н	6.692525	-3.38483	-7.70268
Н	2.470961	-0.05626	6.115957	0	5.560149	4.003253	8.836534
Н	4.2825	3.286196	4.10305	Н	5.230833	4.551478	8.106201
Н	5.381592	3.953587	6.18134				
Н	3.556151	0.647247	8.234155				

Table S3 Atomic coordinate of CPDBC for the DFT calculation

5. Activation of the framework



Figure S4. ¹H NMR (400 MHz) spectrum of the activated HOF CPDBC-1a dissolved in DMSO-d₆.



BET range limit	(p/p ₀ =5.0357E-02)		
Maximum Va(p ₀ -p) value	32390		
Vm [cm ³ (STP)g ⁻¹]	355.69		
as(BET) [m ² g ⁻¹]	1548.1		
С	177.94		
Total pore volume (p/p0=0.990) [cm ³ g ⁻¹]	0.6394		
Average pore size [nm]	1.6521		

Figure S5. BET surface area analysis of CPDBC-1a.



Figure S6. Chemical stability of **CPDBC-1a**. PXRD patterns of **CPDBC-1a** was recorded after immersing in conc. HCl and aqueous solution of NaOH (pH10) at r.t. for 24 h and then drying at 100 °C under vacuum condition. The resultant patterns are clearly different from the original ones, indicating structural transformation.

6. Spectroscopy



Figure S7. UV-vis absorption spectrum of ester derivative 3 in dichloromethane.



7. NMR spectra of the newly synthesized compound

Figure S8. ¹H NMR (400 MHz, CDCl₃) spectrum of ester derivative 3.



Figure S9. ¹³C NMR (100 MHz, CDCl₃) spectrum of ester derivative 3.



Fig. S10 ¹H NMR (400 MHz, DMSO- d_6) spectrum of CPDBC.



Fig. S11 ¹³C NMR (100 MHz, DMSO-*d*₆) spectrum of CPDBC.

8. Reference

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