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Electronic Supplemental information

for

Statically and Dynamically Flexible Hydrogen-bonded Frameworks Based on 4,5,9,10-Tetrakis(4-carboxyphenyl)pyrene

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Contents

1. General

All reagents and solvents were used as received from commercial suppliers. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV400M (400 MHz) spectrometer. Residual proton and carbon of deuterated solvents were used as internal standards for the measurements: δ = 7.26 ppm ($CDCl_3$) and δ = 2.50 ppm (DMSO-d_6) for ^{1}H NMR, δ = 77.16 ppm ($CDCl_3$) and δ = 39.52 ppm (DMSO-d_6) for ^{13}C NMR. HR-MS analyses were conducted on a JEOL JMS-700 instrument. Thermo gravimetric (TG) analyses were performed on Rigaku Thermo plus EVO2 (TG-DTA8122) under an N_2 purge (300 mL/min) at a heating rate of 5 °C min^{-1}. Crystal structures were drawn using Mercury[S1] software. Powder X-ray diffraction (PXRD) data were collected on PANalytical XPert PRO X'Celerator (45 kV, 40 mA) using Cu-Kα radiation at room temperature with a scan rate of 1.2°min^{-1} or on Rigaku MiniFlex 600 (40 kV, 15 mA) using Cu-Kα radiation at room temperature with a scan rate of 4°min^{-1}.

Single crystal X-ray or electron diffraction measurement and analysis. CP-Py-1(DCB), **CP-Py-1**(TCB), **CP-Py-2**(DCB), **CP-Py-2**(TCB) and **CP-Py-1**(MeNaph) were collected at 113 K with a two-dimensional X-ray detector (PILATUS 200K/R) equipped on a Rigaku XtaLAB P200 diffractometer by using Mo-Kα radiation monochromated with multilayer mirror (λ = 0.71073 Å). Diffraction data of **CP-Py-1**(DMAni), **CP-Py-2**(DMAni) and **CP-Py-3** was collected with a two-dimensional X-ray detector (Pilatus 100K) at SPring-8 (BL40XU) by using synchrotron radiation (λ = 0.81106 Å). Diffraction Data collection, cell refinement, and data reduction were carried out with CrysAlis PRO.[S2] SHELXT[S3] was used for the structure solution of the crystals. These calculations were performed with the observed reflections [$I > 2\sigma(I)$] with the program OLEX-2 crystallographic software.[S4] Structural refinement was performed by SHELXL.[S5] 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. For structural analysis of **CP-Py-1**(TCB), **CP-Py-1**(DMAni) and **CP-Py-3**, SQUEEZE function equipped in the PLATON program was used to treat severely disordered solvent molecules in voids.[S6]

Gas sorption experiments. The activated bulk sample of **CP-Py-3** was used for gas sorption measurements, which were performed on BELSORP-max (BEL, Japan) or Micromeritics 3Flex. The adsorption isotherms of N_2, CO_2 were corrected at 77K and 195 K, respectively. Brunauer–Emmett–Teller (BET) specific surface area: $S_{A(BET)}$ was based on CO_2 absorption isotherms.

2. Experimental data

Table S1. Crystal data for **CP-Py-1**(DCB), **CP-Py-1**(TCB), **CP-Py-1**(DMAni), **CP-Py-2**(DCB), **CP-Py-2**(TCB), **CP-Py-2**(DMAni), **CP-Py-3** and **CP-Py-1**(MeNaph)

	CP-Py-1(DCB)	**CP-Py-2**(DCB)	**CP-Py-3**
Formular	$C_{44}H_{26}O_8 \cdot 4(C_6H_4Cl_2)$	$C_{44}H_{26}O_8 \cdot 2(C_6H_4Cl_2)$	$C_{44}H_{26}O_8$
Fw	1270.61	976.63	682.65
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1
a / Å	7.3723(2)	7.5511(4)	7.5864(17)
b / Å	15.6634(4)	11.4435(8)	9.404(3)
c / Å	25.1288(6)	26.3091(16)	13.016(3)
α / °	90	90	78.06 (2)
β / °	94.144(2)	92.902(5)	86.453 (17)
γ / °	90	90	67.84 (2)
V / Å^3	2894.17(13)	2270.5(2)	841.3 (4)
d / g·cm^{-3}	1.458	1.429	1.348
T / K	113	113	100
Crystal size / mm	0.49 × 0.15 × 0.058	0.13 × 0.07 × 0.03	0.10 × 0.08 × 0.02
No. of measured reflections	35154	21812	8327
No. of independent reflections	7651	5753	3644
R_1 ($I > 2\sigma(I)$)	0.0568	0.0720	0.2112
wR_2(all)	0.1237	0.1916	0.597
GOF	1.022	1.036	2.114
CCDC Nos.	2206159	2255738	2255739
Ref.	Ref. S7	This work	This work

Table S1. Continued.

	CP-Py-1(TCB)	**CP-Py-2**(TCB)
Formular	$C_{44}H_{26}O_8$	$C_{44}H_{26}O_8 \cdot 2(C_6H_3Cl_3)$
Fw	682.65	1045.51
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/m$
a / Å	6.7428(3)	27.5399(14)
b / Å	15.8023(9)	11.8206(8)
c / Å	27.6306(12)	7.2355(4)
α / °	90	90
β / °	93.044(4)	92.898(5)
γ / °	90	90
V / Å^3	2939.9(2)	2352.4(2)
d / g·cm^{-3}	0.771	1.476
T / K	113	113
Crystal size / mm	0.29 × 0.16 × 0.07	0.18 × 0.10 × 0.04
No. of measured reflections	30394	17520
No. of independent reflections	7603	3735
R_1 ($I > 2\sigma(I)$)	0.0957	0.0609
wR_2(all)	0.3294	0.1434
GOF	1.044	1.047
CCDC Nos.	2255740	2255741
Ref.	This work	This work

Table S1. Continued.

	CP-Py-1(DMAni)	**CP-Py-2**(DMAni)	**CP-Py-1**(MeNaph)
Formular	$C_{44}H_{26}O_8$	$C_{44}H_{26}O_8 \cdot 3(C_8H_{11}N)$	$C_{44}H_{26}O_8 \cdot 3(C_{11}H_{10})$
Fw	682.65	1046.18	1109.21
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2/*m*	$P2_1/c$	$P2_1/c$
a / Å	23.4820(13)	7.4693 (4)	7.6554(13)
b / Å	17.2143(10)	14.233 (2)	15.342(3)
c / Å	7.5294(3)	24.1720 (16)	24.524(5)
α / °	90	90	90
β / °	94.013(5)	94.080 (6)	94.763(18)
γ / °	90	90	90
V / Å^3	3036.1(3)	2563.2 (4)	2870.4(10)
d / g·cm^{-3}	0.747	1.356	1.283
T / K	100	100	113
Crystal size / mm	0.20 × 0.09 × 0.04	0.12 × 0.09 × 0.03	0.08 × 0.07 × 0.01
No. of measured reflections	18358	32342	43799
No. of independent reflections	3692	6267	7579
R_1 ($I > 2\sigma(I)$)	0.0911	0.1210	0.1408
wR_2(all)	0.3094	0.4120	0.3606
GOF	1.232	1.255	1.020
CCDC Nos.	2255742	2255743	2262072
Ref.	This work	This work	This work

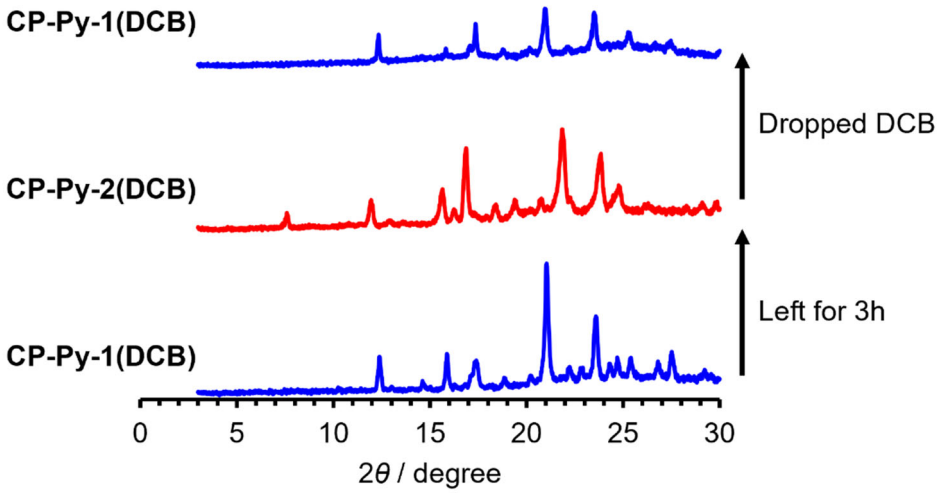


Fig. S1 PXRD pattern of **CP-Py-2**(DCB) after added DCB.

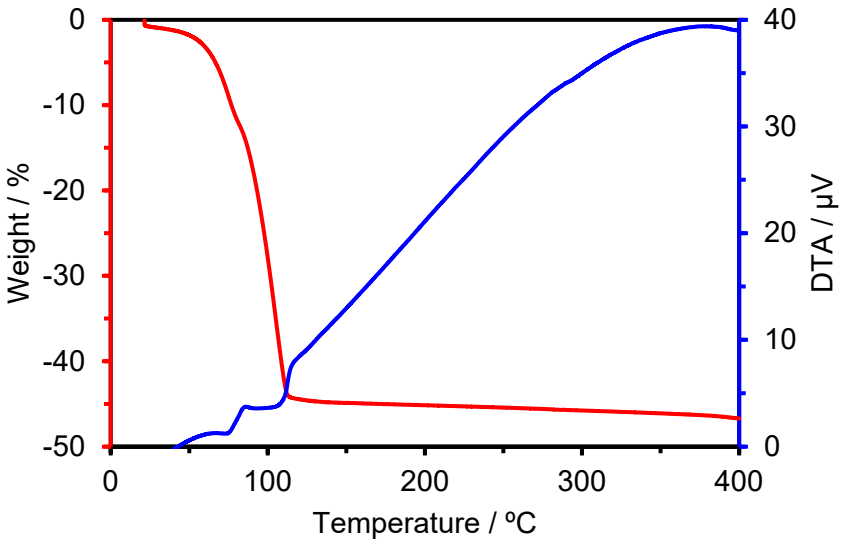


Fig. S2 TGA-DTA curves of **CP-Py-1**(DCB).

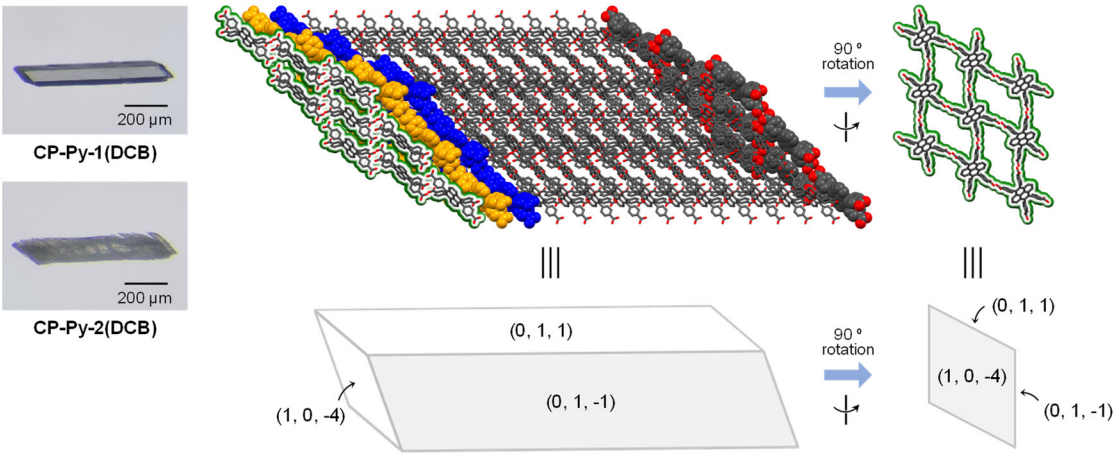


Fig. S3 Morphology of a single crystal and the corresponding molecular arrangements of **CP-Py-1**(DCB).

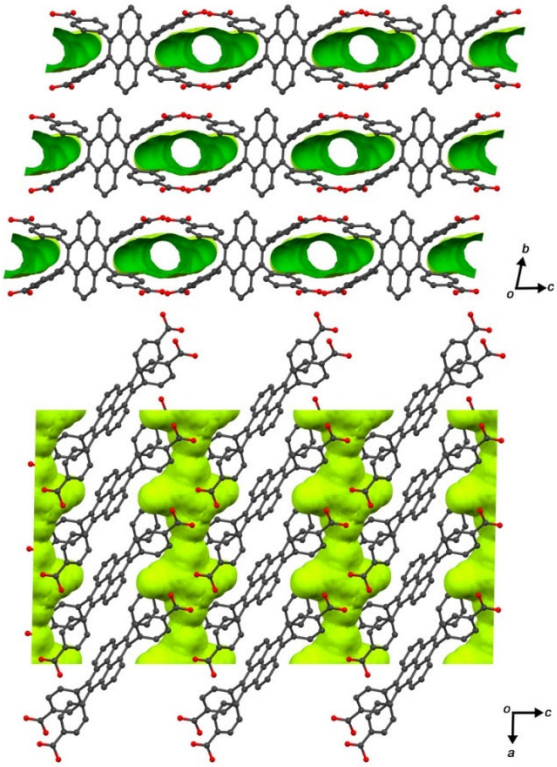


Fig. S4 Visualized void surface of **CP-Py-3**. Projection from the *a* axis (top) and the *b* axis (bottom). The surface was generated by Mercury software with probe radius of 1.2 Å and grid spacing of 0.2 Å.

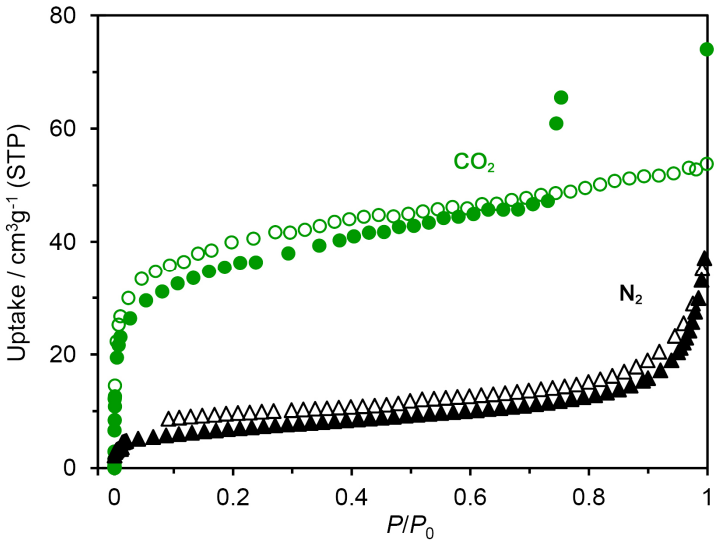
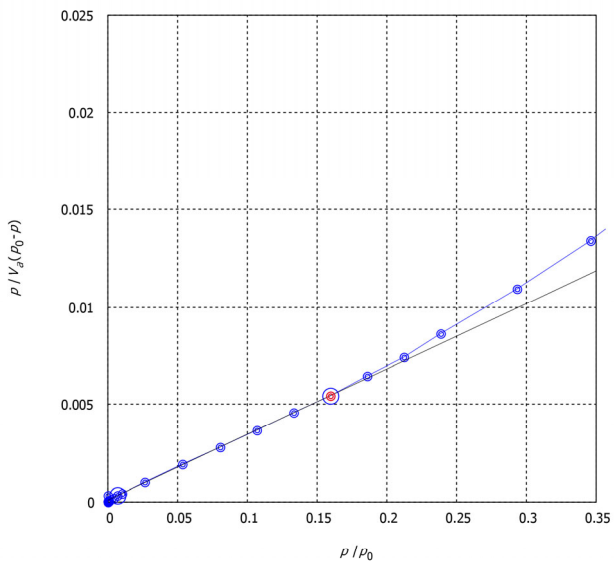


Fig. S5 CO_2 (green circle) and N_2 (black triangle) sorption isotherms of **CP-Py-3** recorded at 195 K and 77 k, respectively. Solid and open symbols correspond to adsorption and desorption processes, respectively.



BET range limit	21th point (p/p_0=0.1596)				
$V_a(p_0-p)$ Max value	2953.5		V_m	29.674	[cm^3(STP) g^{-1}]
$a_{s,BET}$	1.7221E+02	[m^2 g^{-1}]	C	301.64	
Total pore volume (p/p_0=0.9900)	0.2398	[cm^3 g^{-1}]	Average pore diameter	5.5699	[nm]

Fig. S6 BET plot of **CP-Py-3** based on CO_2 adsorption isotherm.

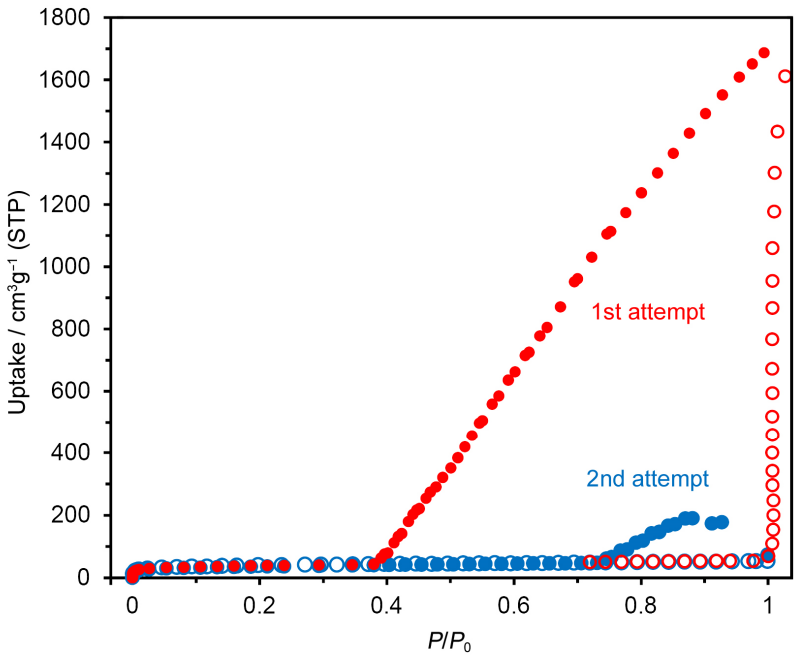


Fig. S7 Anomalous absorption behavior of **CP-Py-3** in CO_2 adsorption experiments.

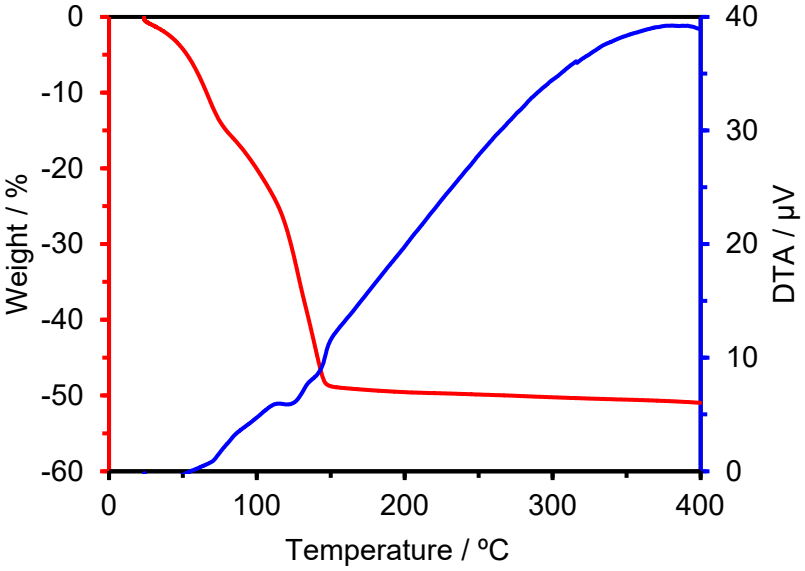


Fig. S8 TGA-DTA curves of **CP-Py-1**(TCB).

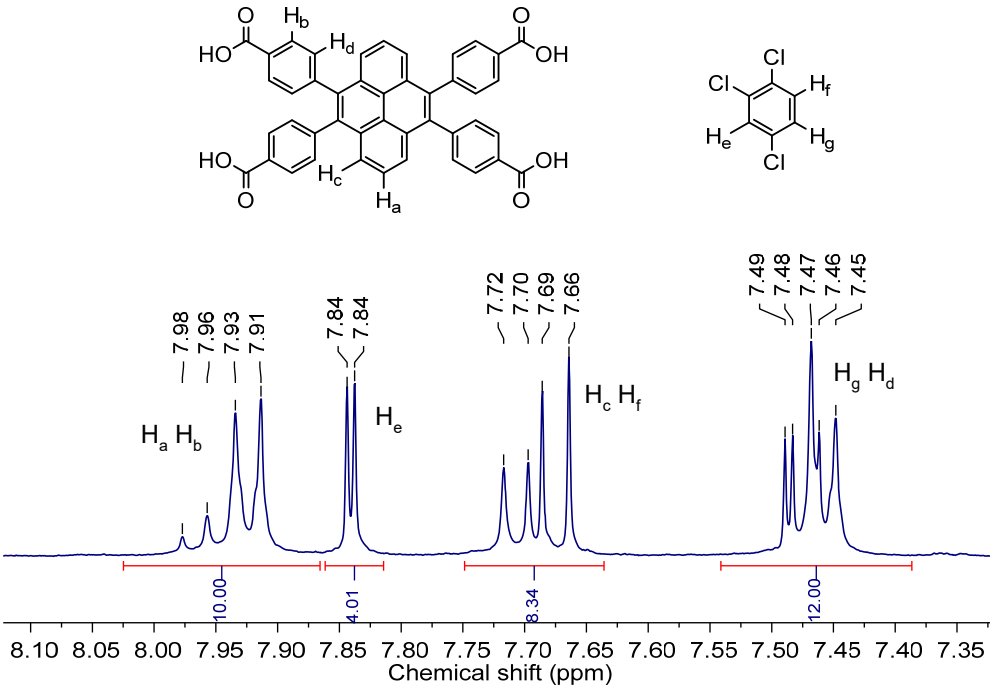


Fig. S9 ^{1}H NMR (400 MHz) spectrum of **CP-Py-1**(TCB) dissolved in DMSO-d_6.

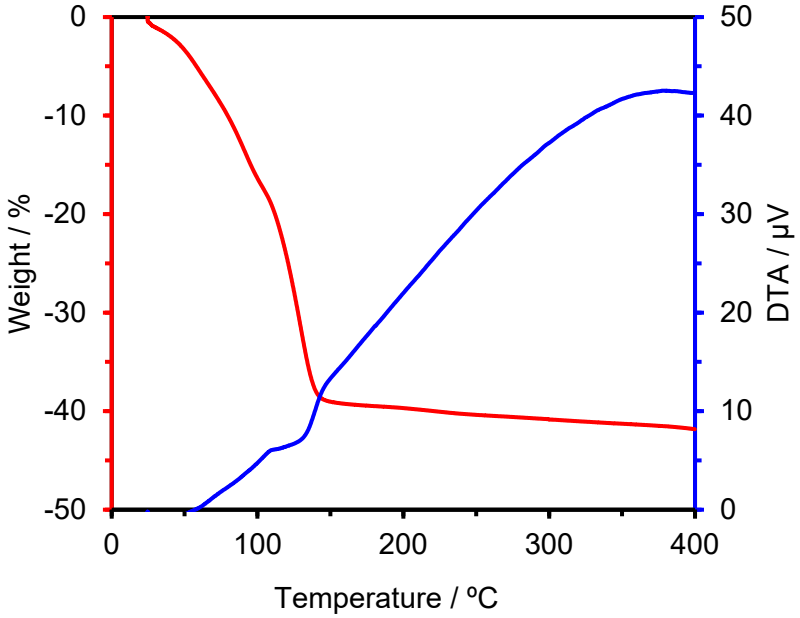


Fig. S10 TGA-DTA curves of **CP-Py-1**(DMAni).

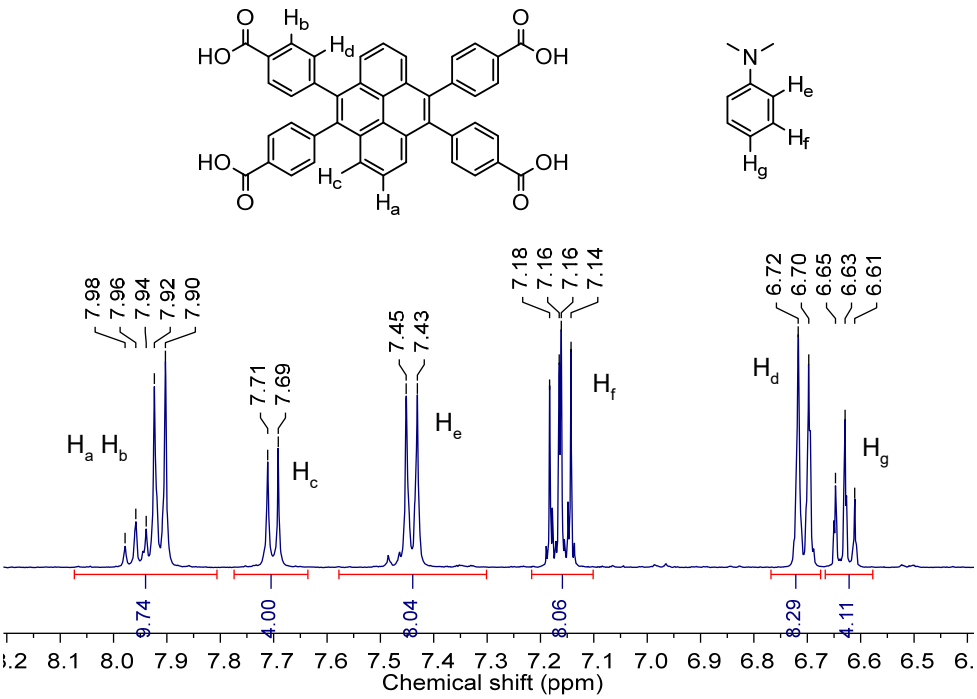


Fig. S11 ^{1}H NMR (400 MHz) spectrum of **CP-Py-1**(DMAni) dissolved in DMSO-d_6.

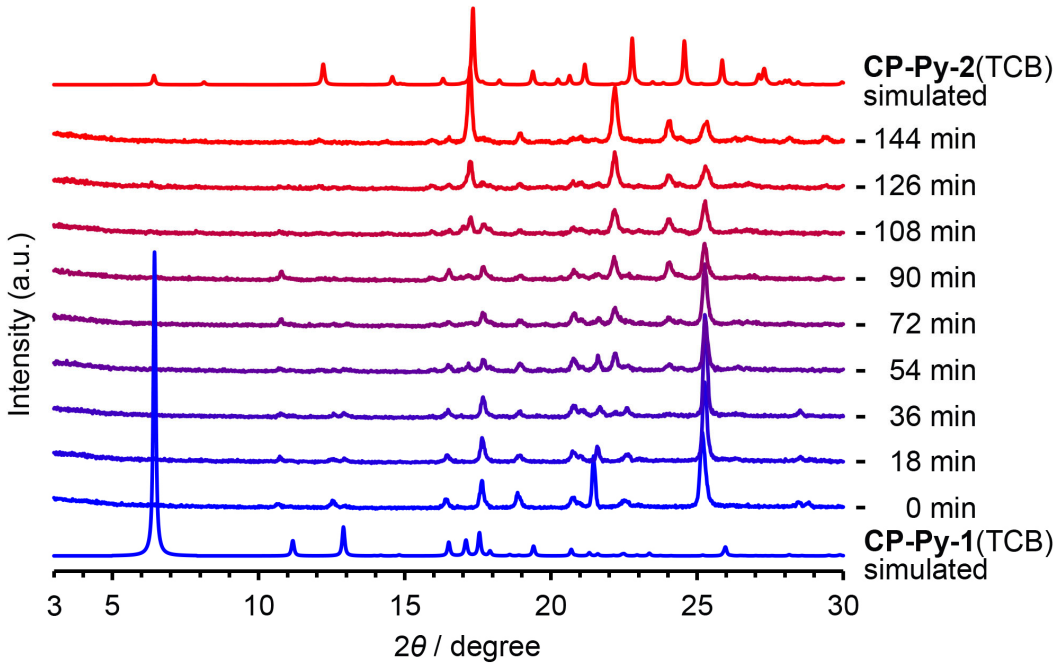


Fig. S12. PXRD pattern changes from **CP-Py-1**(TCB) to **CP-Py-2**(TCB).

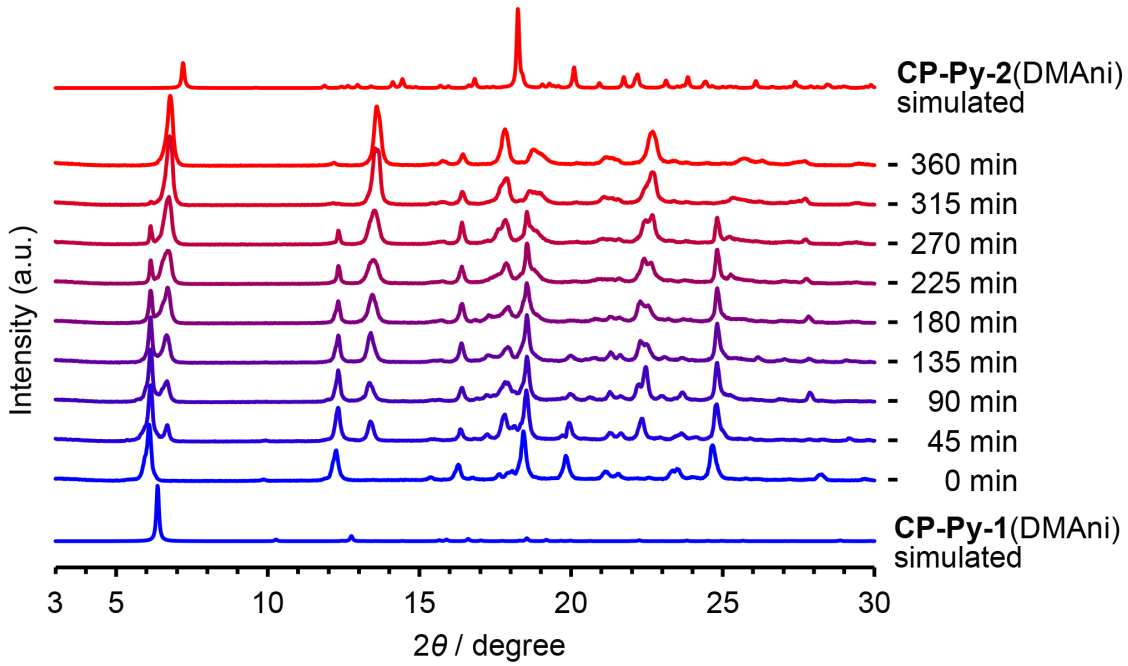


Fig. S13. PXRD pattern changes from **CP-Py-1**(DMAni) to **CP-Py-2**(DMAni).

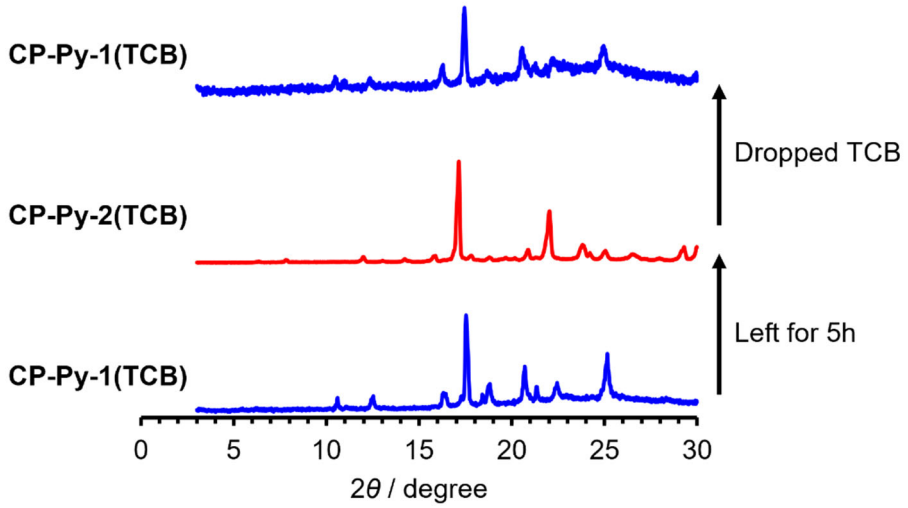


Fig. S14 PXRD pattern of **CP-Py-2**(TCB) after added TCB.

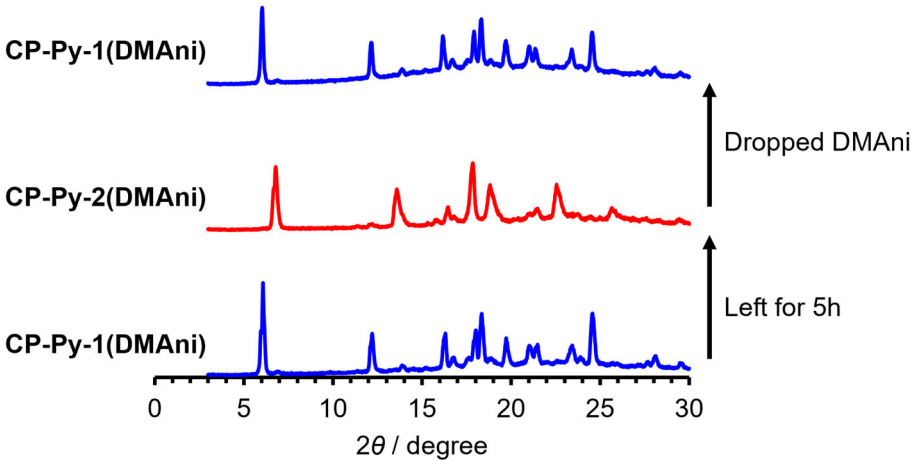


Fig. S15 PXRD pattern of **CP-Py-2**(DMAni) after added DMAni.

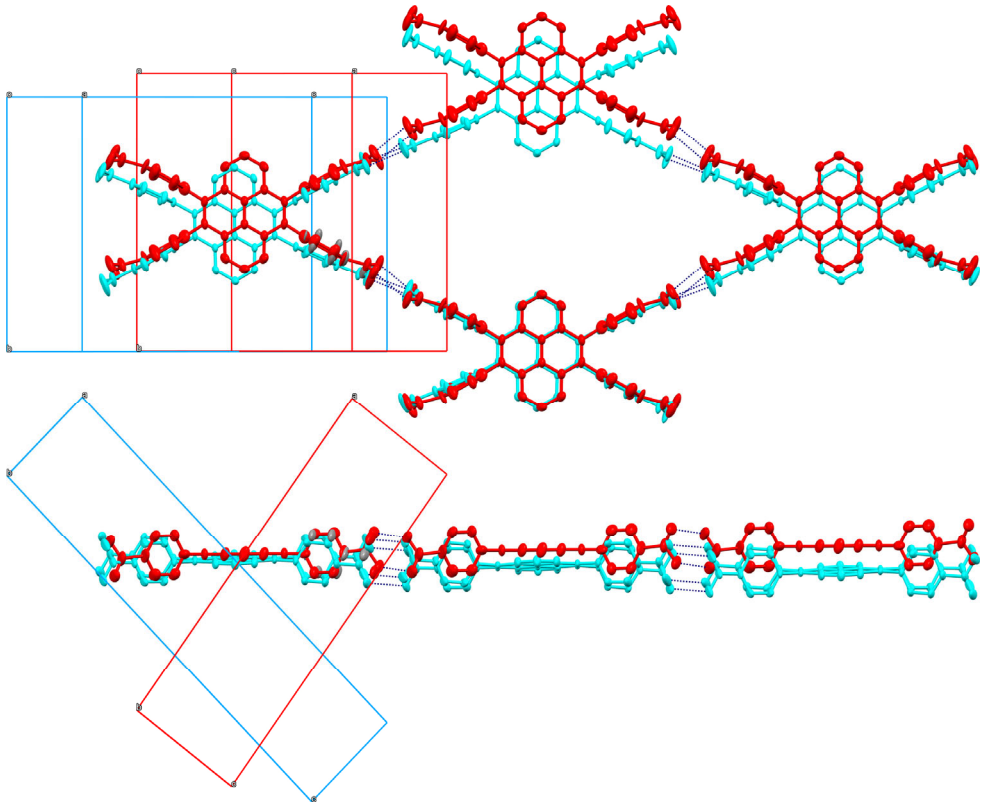


Fig. S16 Structural similarity of **CP-Py-1(**TCB) (cyan) and **CP-Py-1**(DMAni) (red). The framework shown in top corresponds to one layer allowed in the side view at the bottom.

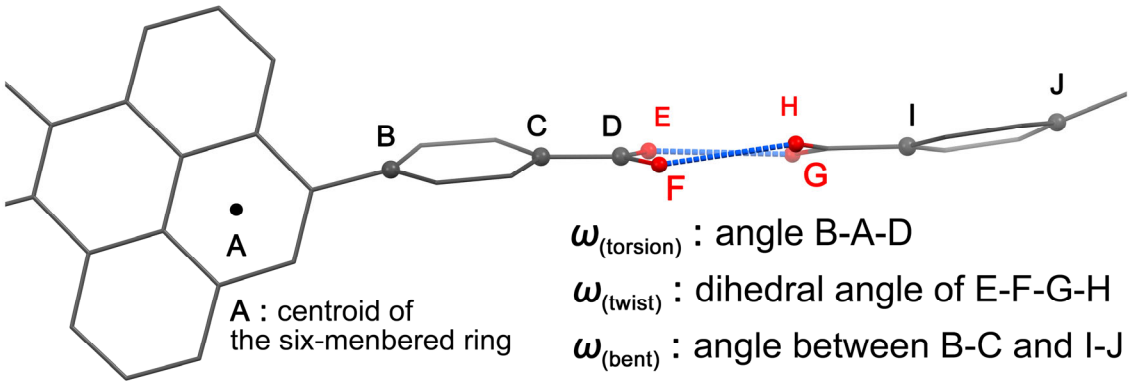


Fig. S17 Definition of the structural parameters: $\omega_{(torsion)}$, $\omega_{(twist)}$, and $\omega_{(bent)}$, which characterize versatile shapes of the framework.

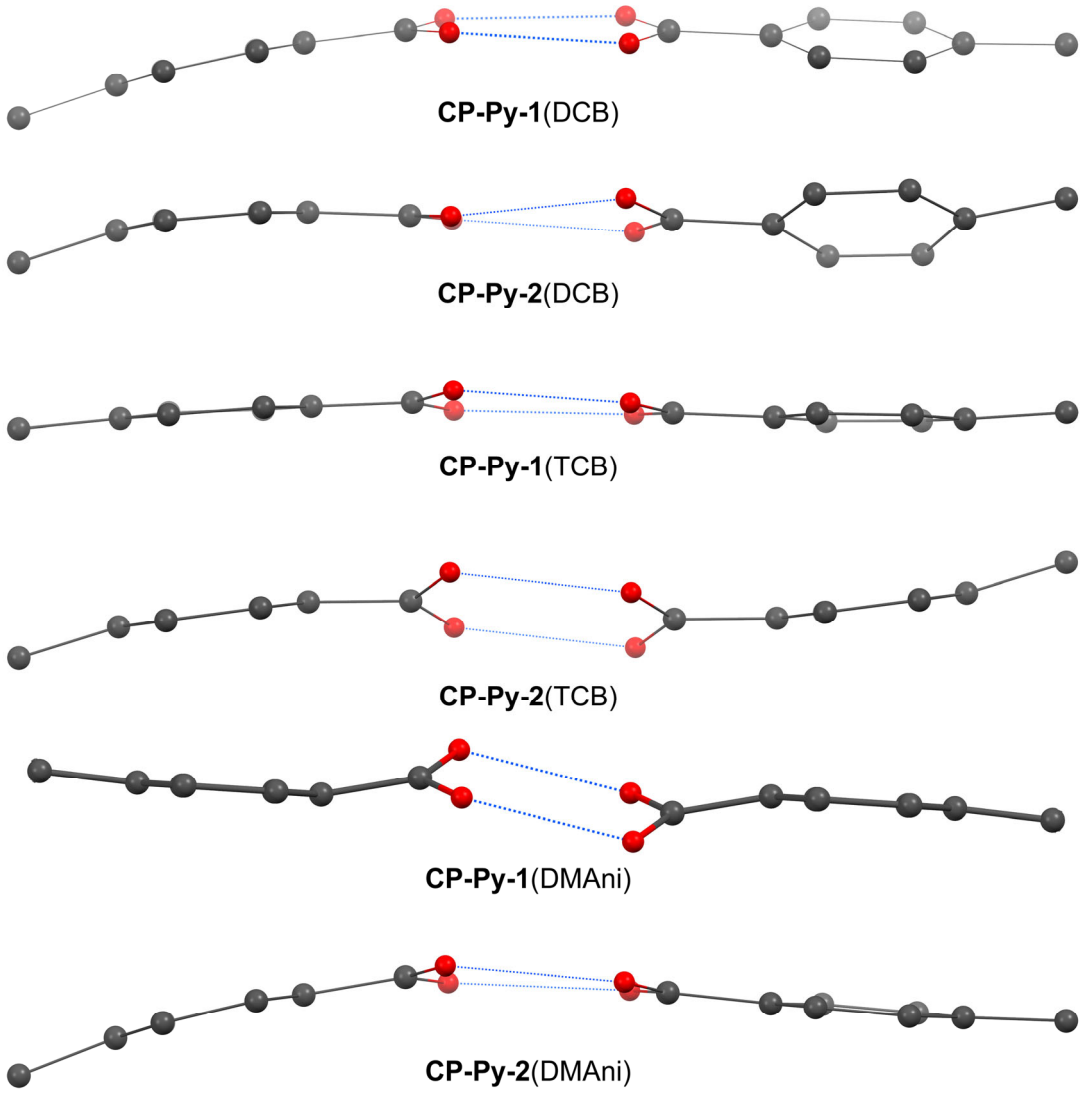


Fig. S18 Selected side views of the H-bonded dimer moieties of **CP-Py-1**(DCB), **CP-Py-2**(DCB), **CP-Py-1**(TCB), **CP-Py-2**(TCB), **CP-Py-1**(DMAni), and **CP-Py-2**(DMAni).

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