Electronic Supplementary Information

Highly Crystalline Covalent Organic Frameworks From Flexible Building Blocks

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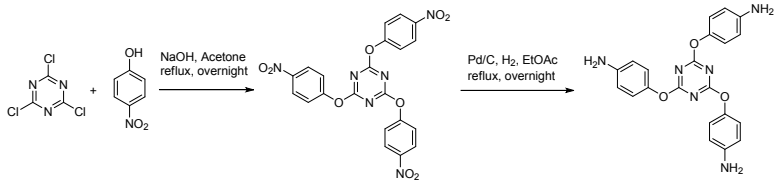
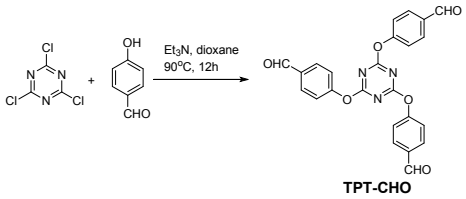
Experimental section

1. Materials and measurement

IR Spectra were recorded on a Thermo-Nicolet 6700 spectrometer using KBr discs. ^{13}C CP-MAS NMR Spectra data were collected on a BRUKER AVANCE Ⅲ 400MHz solid state NMR spectrometer. Thermogravimetric analysis was performed on SDT Q600 V20.9 Build 20 with a temperature ramping 10°C min^{-1} from room temperature to 700 °C. Scanning electron microscopy(SEM) was performed on S-4300 scanning electron microscope at 15.0 KV. Powder X-ray diffraction(PXRD) data were recorded on X-ray powder diffractometer, from 2θ=2° up to 50°. Nitrogen adsorption isotherms were carried out with a Micrometrics ASAP 2020 instrument at 77 K, hydrogen adsorption isotherms were measured at 77 K from 0 to 1 bar on Micrometric ASAP 2020 instrument. Carbon dioxide adsorption isotherms were measured at 273 K from 0 to 1 bar on Belsorp-HP. Geometry optimization of hexagonal pore structure was performed at Forcite Module in Material Studio 8.0. All chemicals were used as received without further purification unless stated otherwise.

2. Synthesis



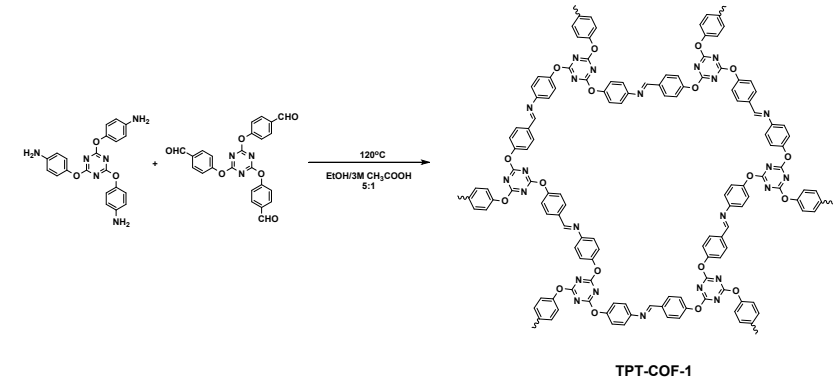


2,4,6-tris(4-nitrophenoxy)-1,3,5-triazine, 2,4,6-tris(4-aminophenoxy)-1,3,5- triazine and 2,4,6-tris (4-formylphenoxy)-1,3,5-triazine were synthesized according to previous reported procedures.[1,2]

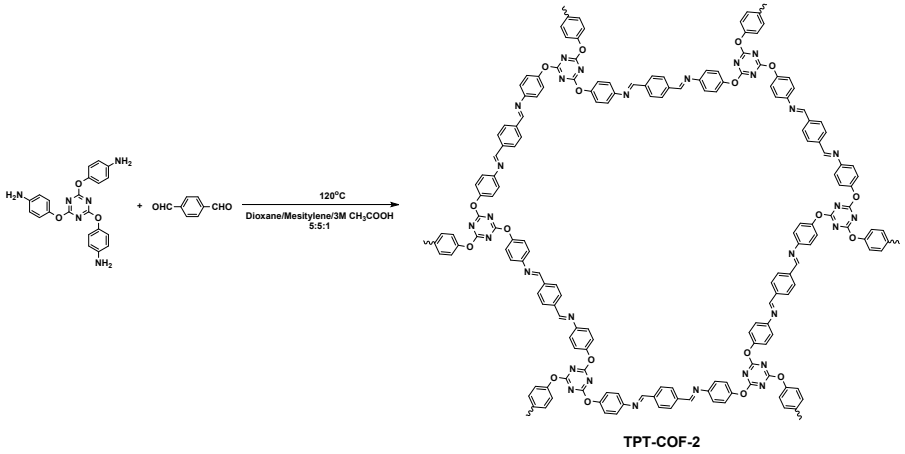
TPT-NO_2: 3.55g, 86%; ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, 6H, J=9.2 Hz), 7.34 (d, 6H, J=9.2 Hz); ^{13}C NMR (100 MHz, DMSO-d^6) δ 172.6, 155.9, 145.3, 125.5, 122.9.

TPT-NH_2: 2.04g, 79%; ^1H NMR (400 MHz, DMSO-d^6) δ 6.84 (d, 6H, J=8.4 Hz), 6.54 (d, 6H, J=8.4 Hz); ^{13}C NMR (100 MHz, DMSO-d^6) δ 173.7, 146.7, 141.7, 121.7, 114.0.

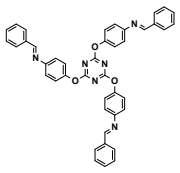
TPT-CHO: 5.70g, 86%; ^1H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 3H, J=8.4 Hz), 7.92 (d, 6H, J=8.4 Hz), 7.32 (d, 6H, J=8.4 Hz); ^{13}C NMR (100 MHz, DMSO-d^6) δ 192.0, 172.8, 155.7, 134.2, 131.2, 122.4.



TPT-COF-1



TPT-COF-2



MC

Model Compound (MC): To a 50 mL flask was charged 2,4,6-tris(4-aminophenoxy)-1,3,5-triazine (TPT-NH_2, 201 mg, 0.5 mmol), 20 mL EtOH, then benzaldehyde (175 mg, 1.65 mmol) was added. The mixture was heated to reflux for overnight. After cooled to room temperature, white powder was obtained after filtration. Wash the powder with EtOH, then dried in vacuum, 303 mg white solid product was obtained with 91% yield. FTIR (KBr) ν 3060, 1597, 1571, 1499, 1367, 1211, 1187, 839, 804, 757, 691 cm^{-1}; ^1H NMR (400 MHz, DMSO-d^6) δ 8.61 (s, 3H), 7.89 (d, 6H, J=7.0Hz), 7.57-7.45 (m, 9H), 7.35-7.26 (m, 12H); ^{13}C NMR (100 MHz, DMSO-d^6) δ 173.3, 161.2, 149.6, 149.4, 135.9, 131.6, 128.9, 128.8, 122.3, 122.0; HRMS (ESI) 667.2448 ($[M+H]^+$).

TPT-COF-1: A 350 mL Schlenk tube was charged with 2,4,6-tris(4-aminophenoxy)-1,3,5-triazine (TPT-NH_2, 604 mg, 1.5 mmol), 2,4,6-tris(4-formylphenoxy)-1,3,5-triazine (TPT-CHO,

662 mg, 1.5 mmol), and 43.2 mL of a 5:1 (v/v) solution of EtOH/3M CH_3COOH. The tube was evacuated to vacuum at 77 K (LN_2 bath) and sealed. The mixture was heated at 120 ^oC for 3 days. The product was isolated by filtration, washed with acetone and then soaked in HPLC acetone for overnight. After filtration, the powder was dried under vacuum at 100 ^oC for 12h. 1079 mg white powder was obtained with 91% yield. FTIR (KBr) *v* 1627, 1571, 1504, 1359, 1205, 1164, 1077, 846, 805, 533 cm^{-1};^{13}C CP-MAS NMR (100 MHz, solid state) δ 173.6, 157.0, 153.8, 150.6, 149.7, 134.7, 128.9, 121.8. Anal. calcd. for $(C_{15}H_9N_3O_2)n$: C, 68.44; H, 3.45; N, 15.96. Found: C, 66.19; H, 3.62; N 15.81.

TPT-COF-2: The procedure is similar to above: 2,4,6-tris(4-aminophenoxy)-1,3,5-triazine (TPT-NH_2, 1207 mg, 3 mmol), terephthalic aldehyde (604 mg, 4.5 mmol) and 67.2 mL of a 5:5:1 (v/v/v) solution of Dioxane/Mesitylene/3M CH_3COOH. 1332 mg yellow powder was obtained with 81% yield. FTIR (KBr) *v* 1624, 1605, 1565, 1494, 1366, 1210, 1186, 1075, 1012, 972, 841, 812, 551 cm^{-1}; ^{13}C CP-MAS NMR (100 MHz, solid state) δ 173.6, 158.1, 150.7, 148.9, 138.9, 128.8, 121.5. Anal. calcd. for $(C_{11}H_7N_2O)n$: C, 72.12; H, 3.85; N, 15.29. Found: C, 69.94; H, 3.92; N, 15.37.

3. NMR spectra for MC

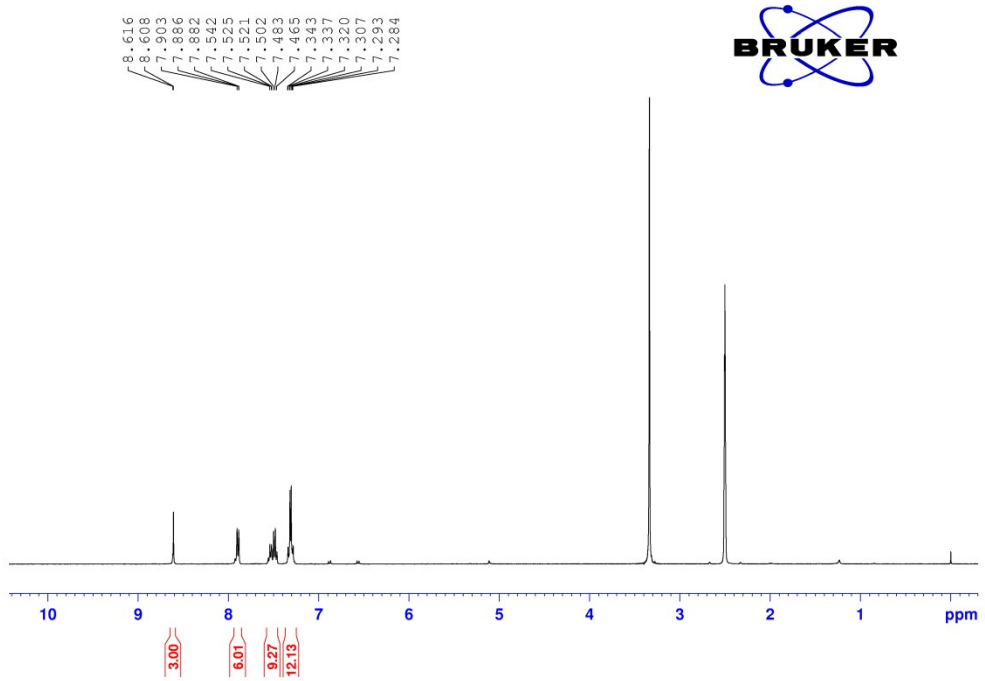


Fig. S1 [1]HNMR for Model Compound (MC).

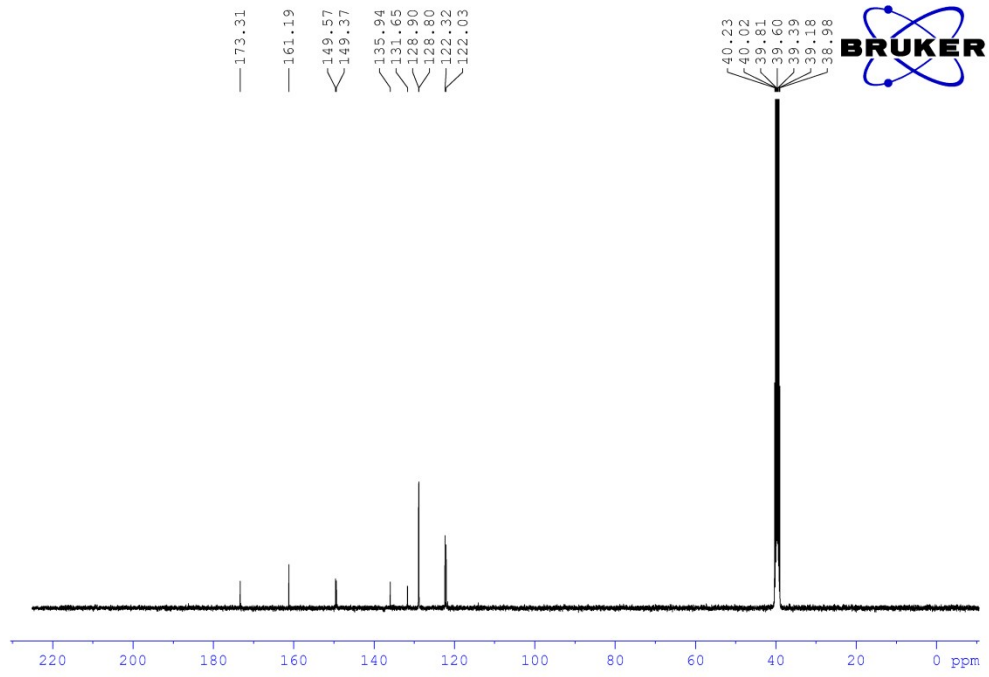


Fig. S2 [13]CNMR for Model Compound (MC).

4. FTIR spectra

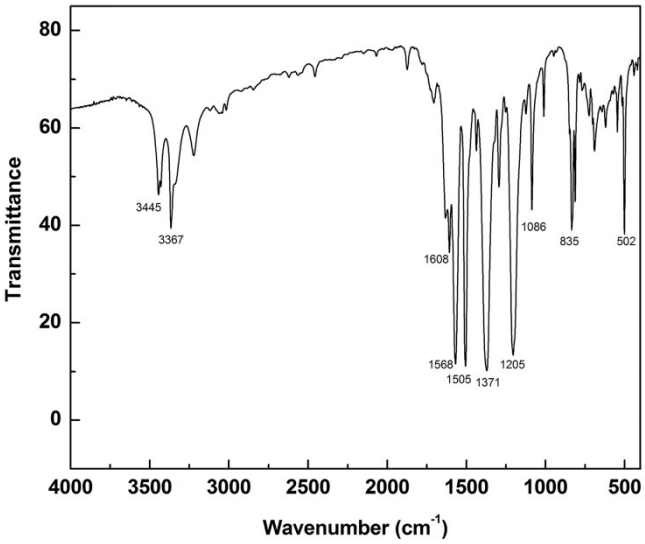


Fig. S3 The FTIR spectra of TPT-NH_2.

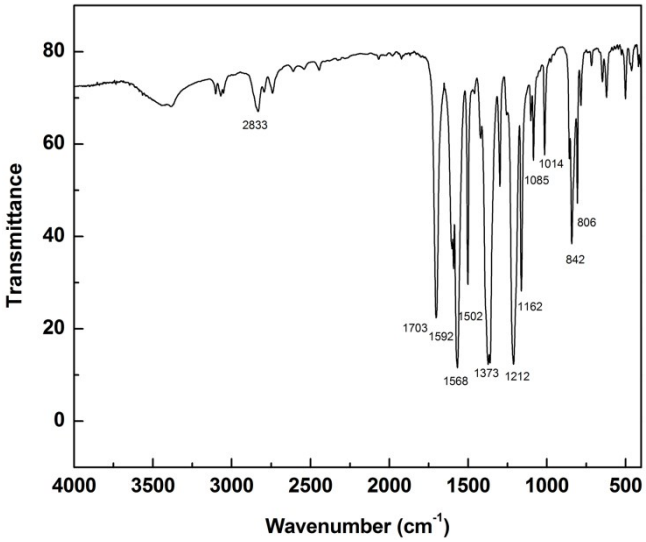


Fig. S4 The FTIR spectra of TPT-CHO.

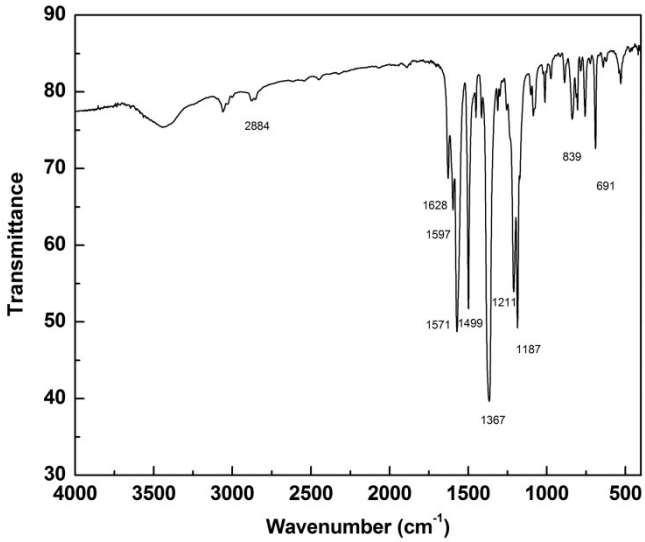


Fig. S5 The FTIR spectra of MC.

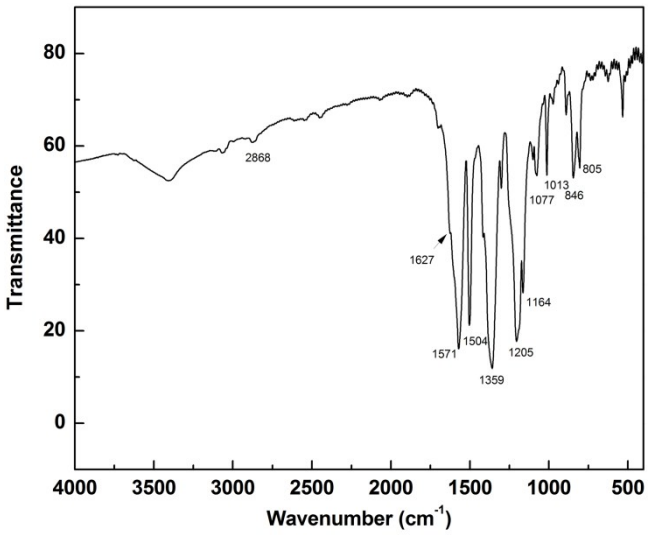


Fig. S6 The FTIR spectra of TPT-COF-1.

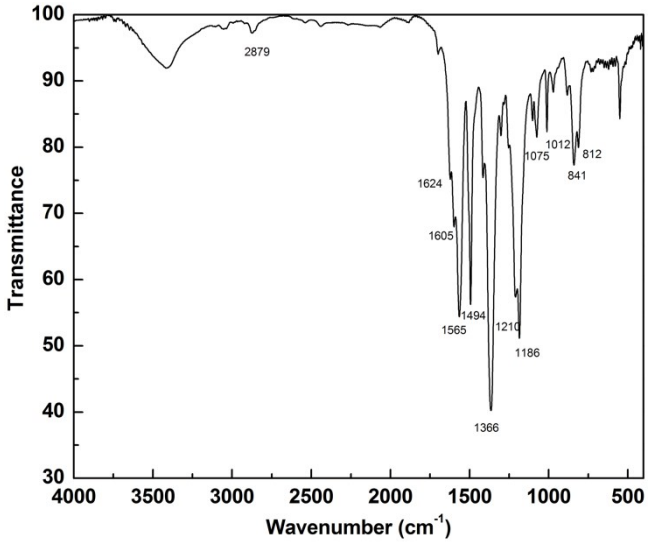


Fig. S7 The FTIR spectra of TPT-COF-2.

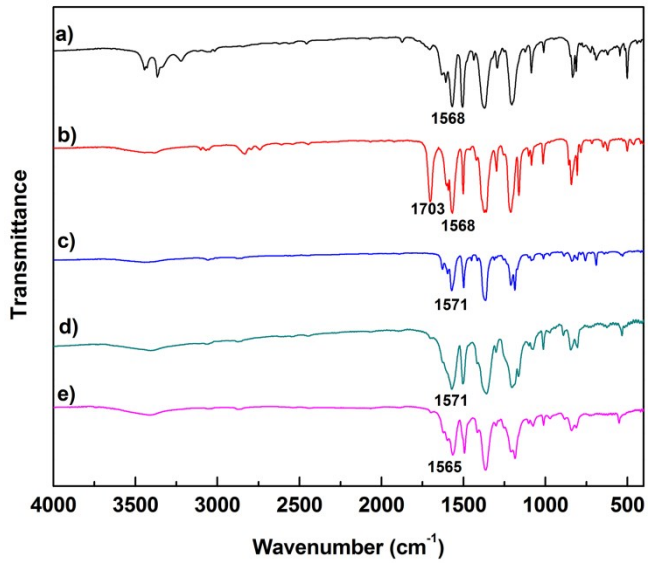


Fig. S8 The FTIR spectra for a) TPT-NH_2 (black); b) TPT-CHO (red); c) MC (blue); d) TPT-COF-1 (green); e) TPT-COF-2 (pink).

5. ^{13}C CP-MAS NMR spectra for TPT-COFs

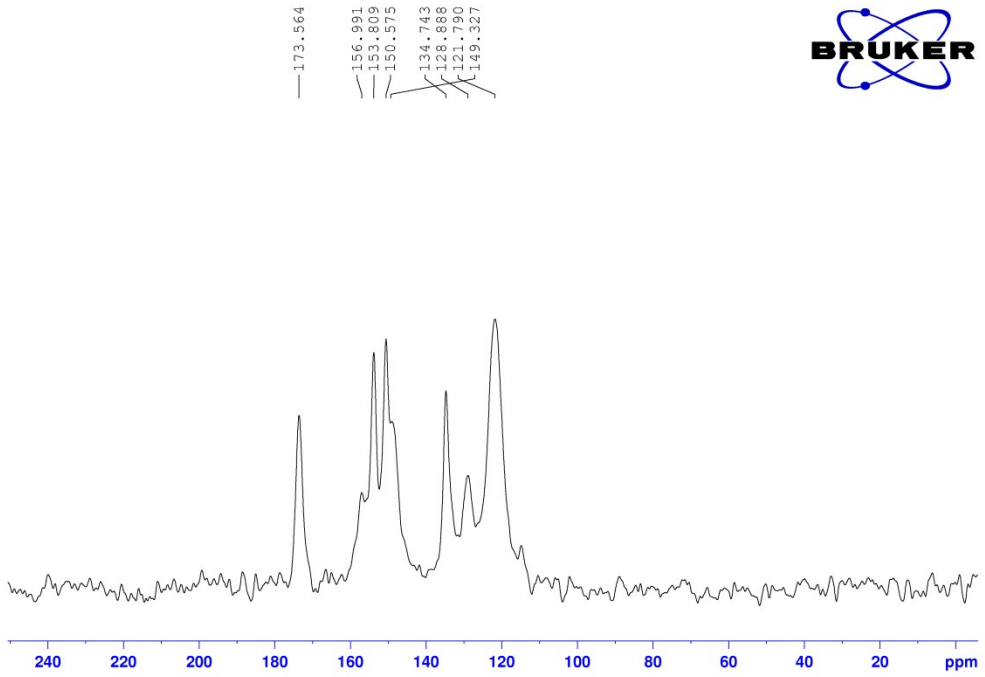


Fig. S9 ^{13}C CP-MAS NMR spectra for TPT-COF-1.

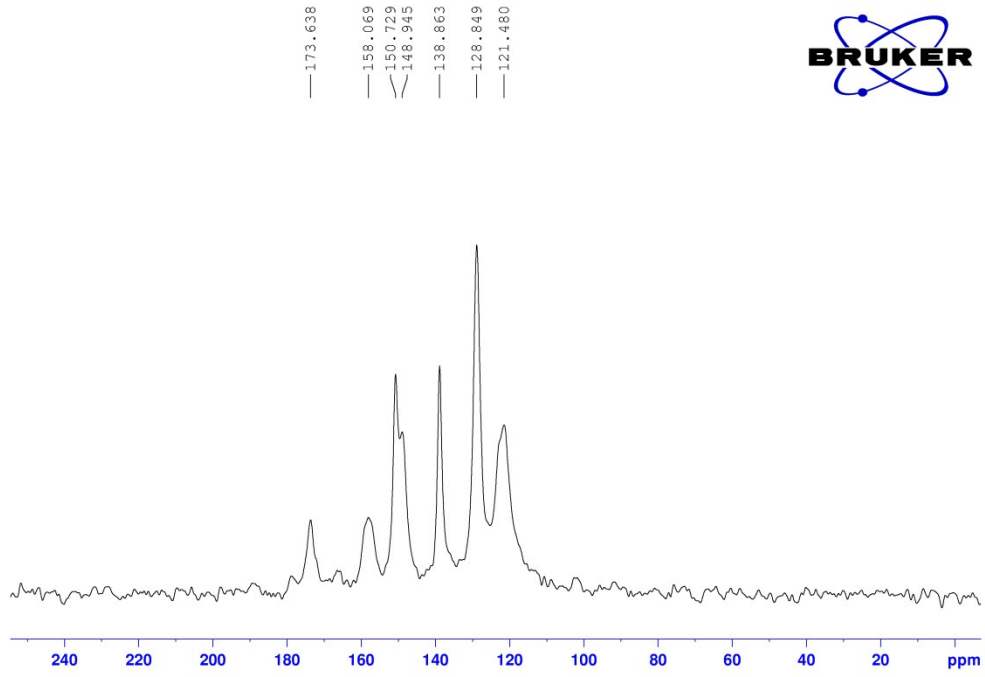


Fig. S10 ^{13}C CP-MAS NMR spectra for TPT-COF-2.

6. TGA measurement for TPT-COFs

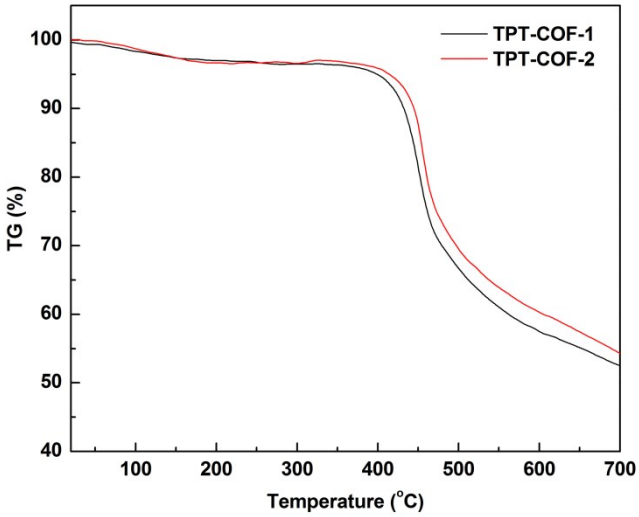


Fig. S11 TGA measurement for TPT-COF-1 (black) and TPT-COF-2 (red).

7. Variable temperature XRD for TPT-COFs

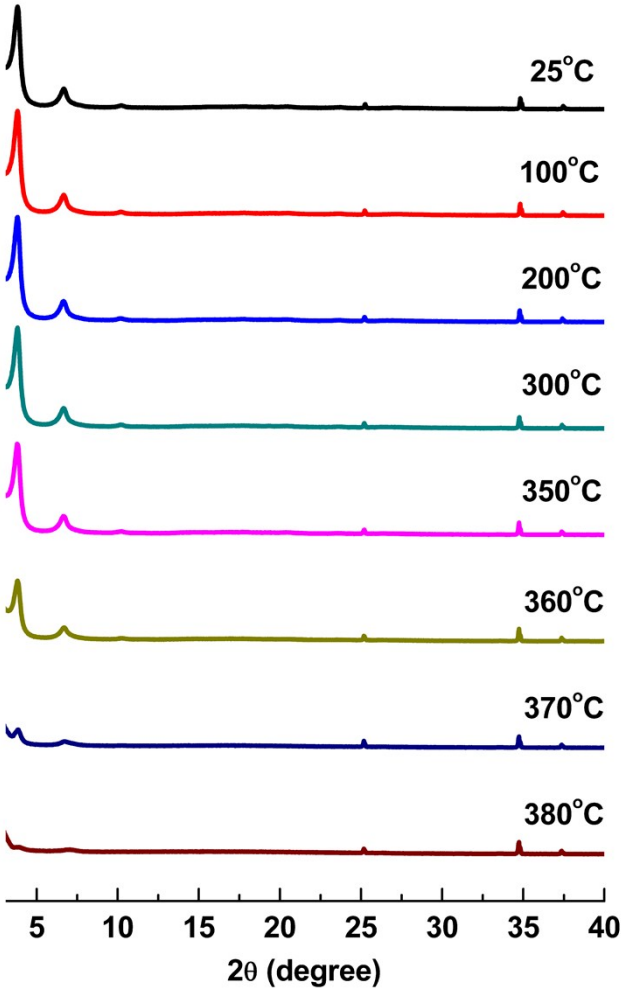


Fig. S12 Variable temperature XRD for TPT-COF-1.

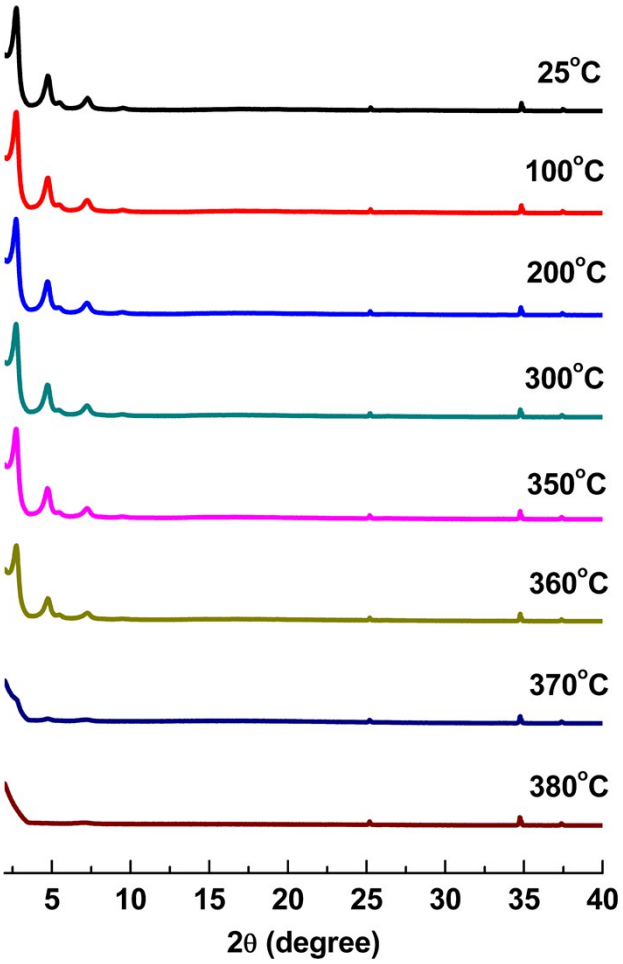


Fig. S13 Variable temperature XRD for TPT-COF-2.

8. SEM images for TPT-COFs

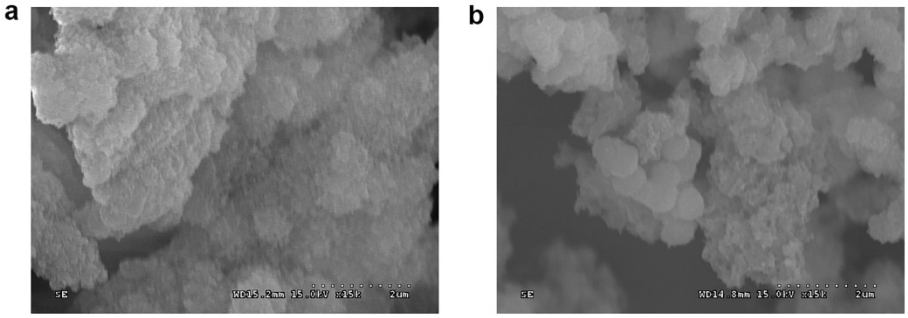


Fig. S14 SEM image for a) TPT-COF-1; b) TPT-COF-2.

9. BET plot for TPT-COFs

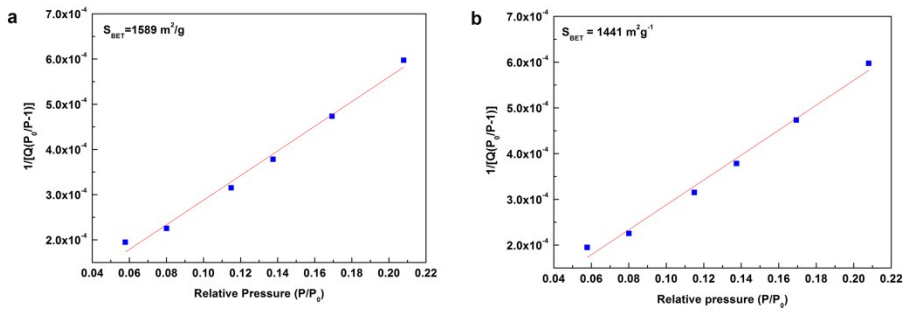


Fig. S15 BET plot for a) TPT-COF-1; b) TPT-COF-2.

10. Gas uptake

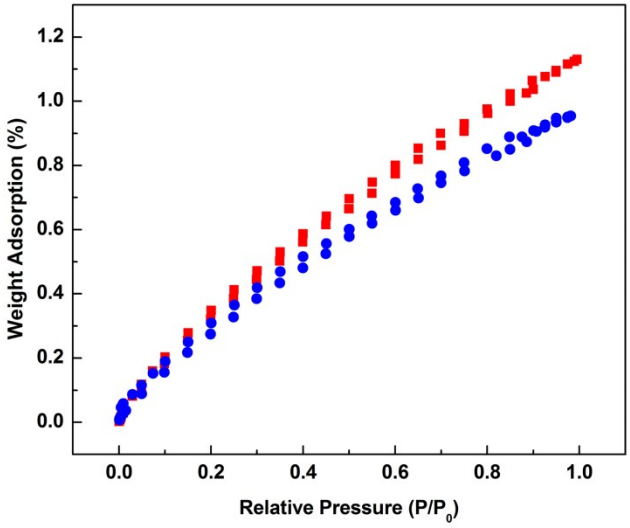


Fig. S16 Hydrogen uptake (squares: TPT-COF-1; circles: TPT-COF-2).

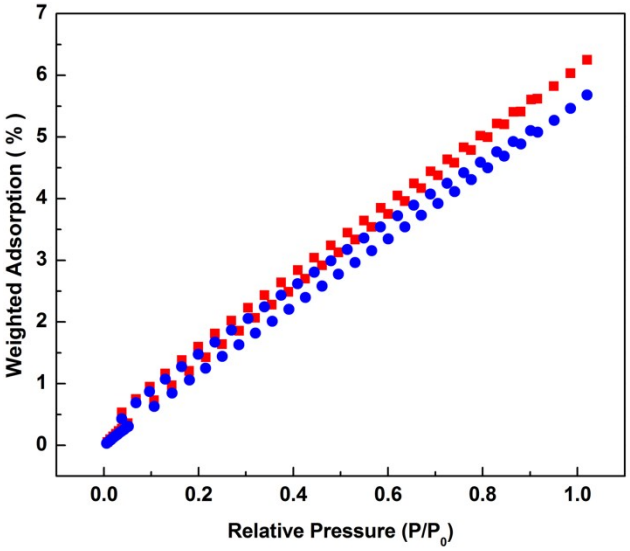


Fig. S17 Carbon dioxide uptake (squares: TPT-COF-1; circles: TPT-COF-2).

11. PRXD

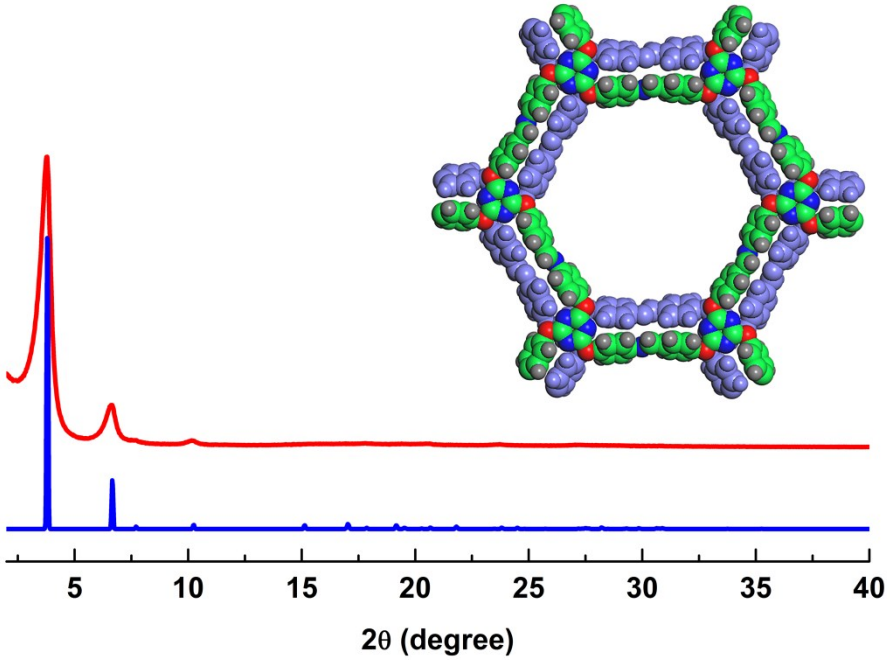


Fig. S18 Comparison of the experimentally observed PXRD pattern with the simulated eclipsed **AA-1** pattern for TPT-COF-1.

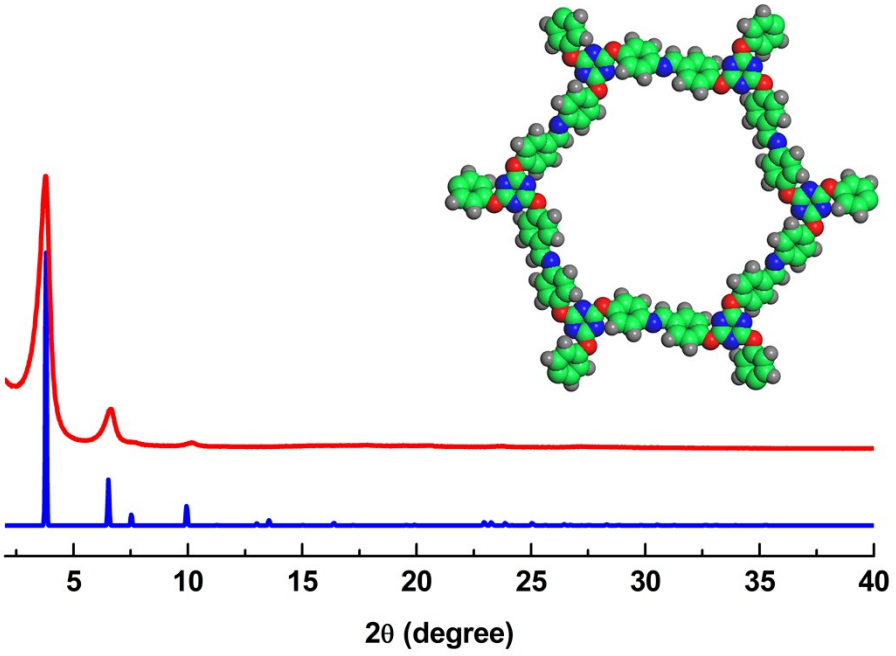


Fig. S19 Comparison of the experimentally observed PXRD pattern with the simulated eclipsed **AA-2** pattern for TPT-COF-1.

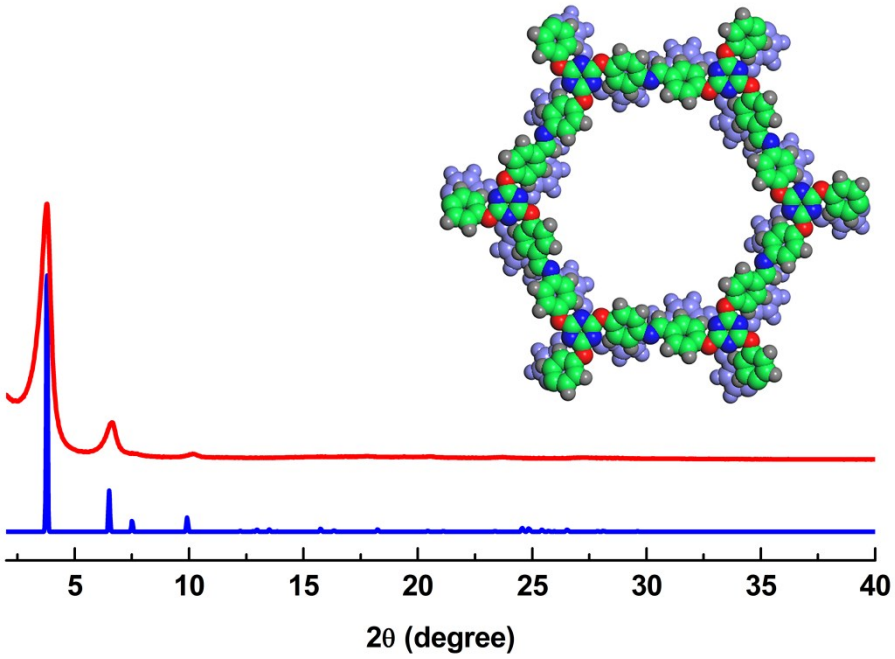


Fig. S20 Comparison of the experimentally observed PXRD pattern with the simulated eclipsed **AA-3** pattern for TPT-COF-1.

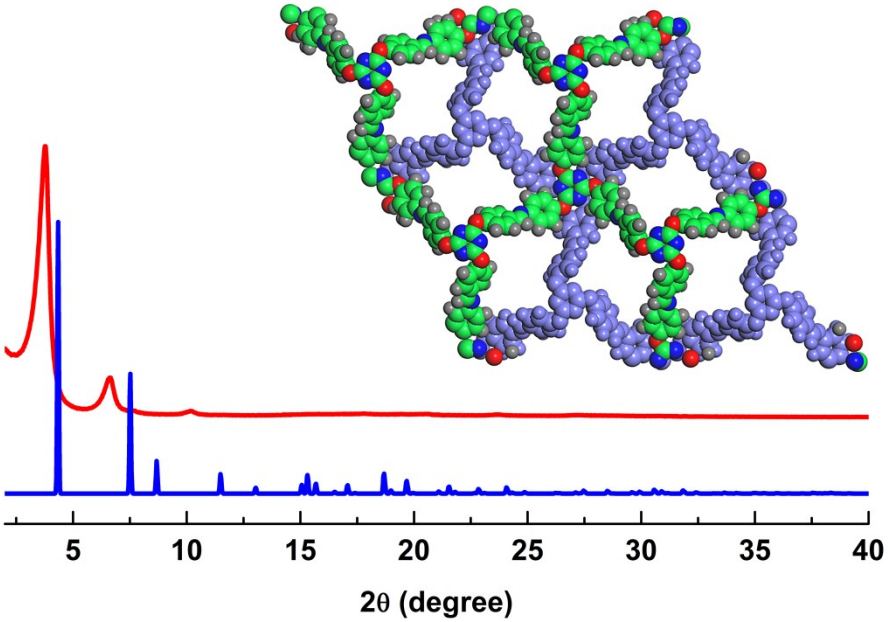


Fig. S21 Comparison of the experimentally observed PXRD pattern with the simulated staggered **AB-1** pattern for TPT-COF-1.

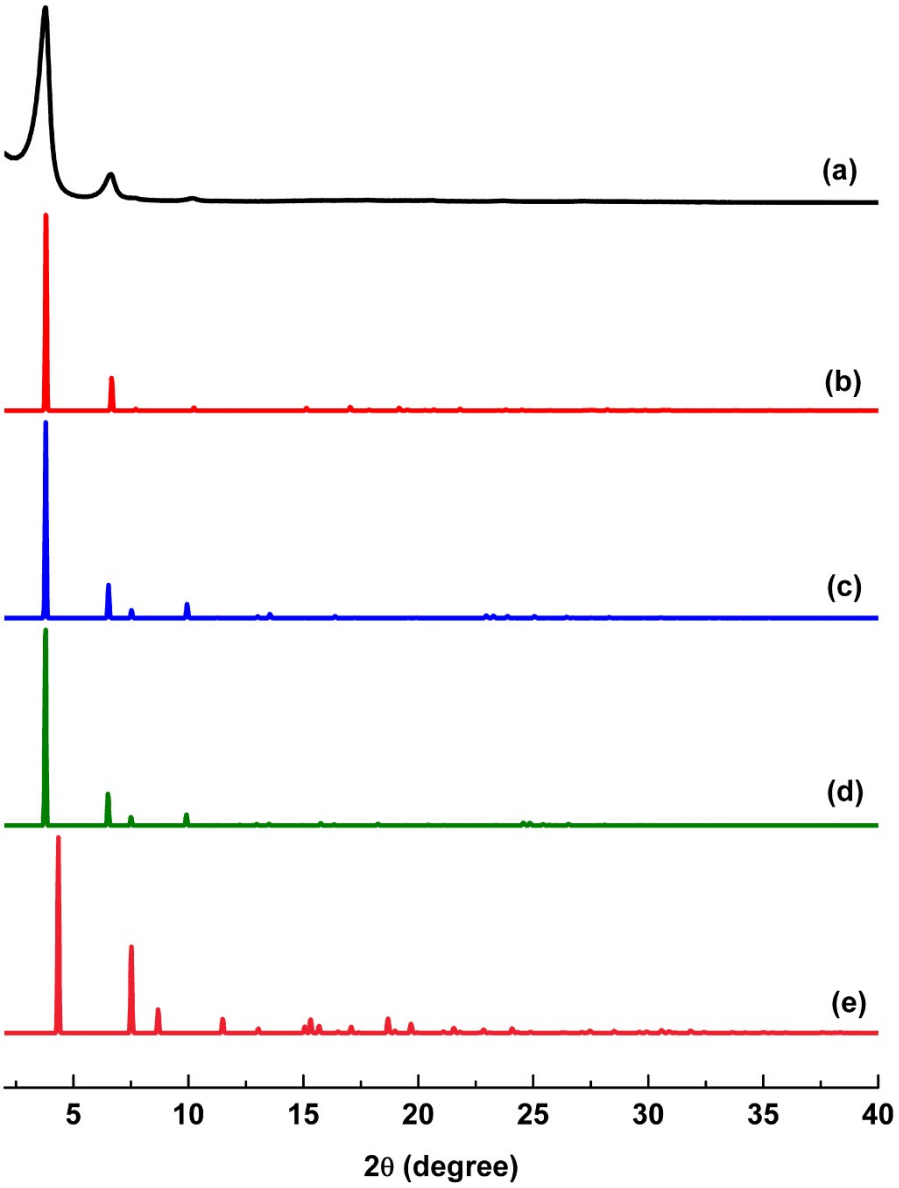


Fig. S22 Comparison of PXRD patterns for TPT-COF-1: experimentally observed (a, black) pattern as well as calculated based on the eclipsed AA-1 (b, red), eclipsed AA-2 (c, blue), eclipsed AA-3 (d, olive) and staggered AB-1 (e, pink) patterns.

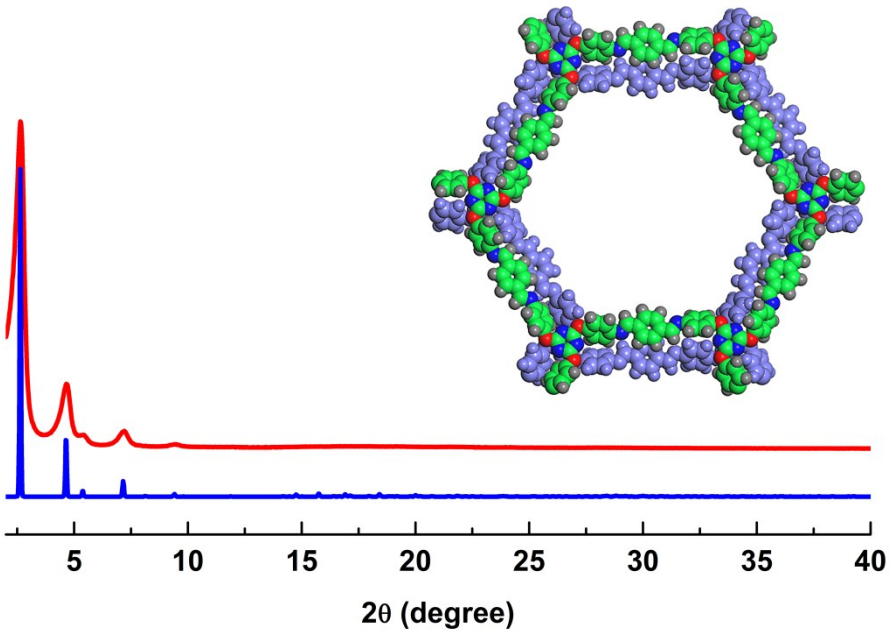


Fig. S23 Comparison of the experimentally observed PXRD pattern with the simulated eclipsed **AA-1** pattern for TPT-COF-2.

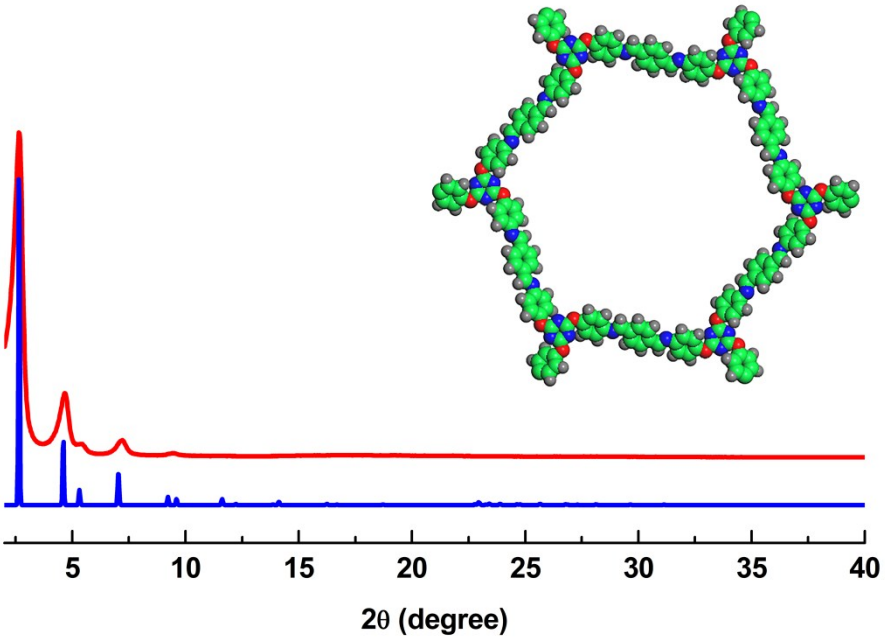


Fig. S24 Comparison of the experimentally observed PXRD pattern with the simulated eclipsed **AA-2** pattern for TPT-COF-2.

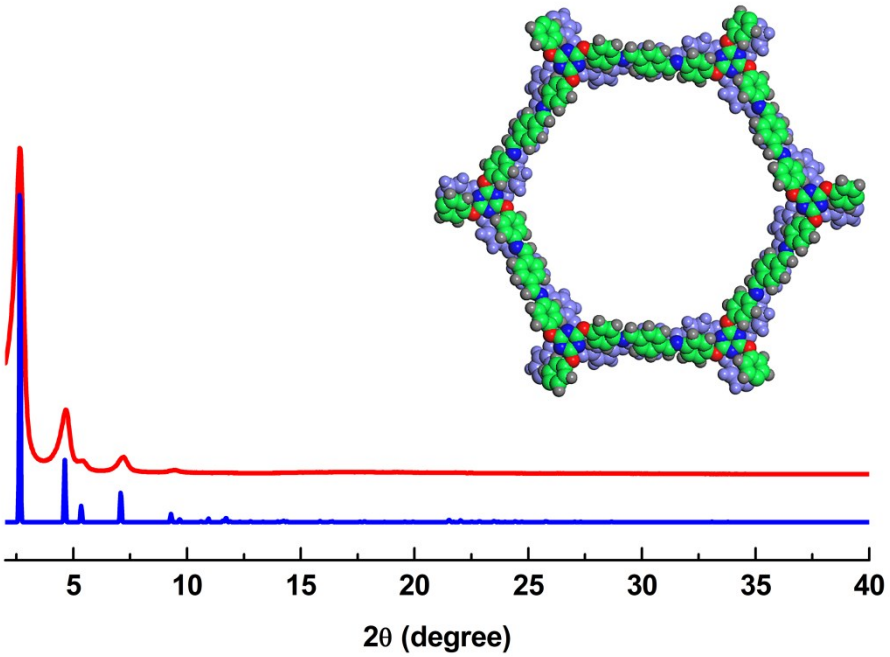


Fig. S25 Comparison of the experimentally observed PXRD pattern with the simulated eclipsed **AA-3** pattern for TPT-COF-2.

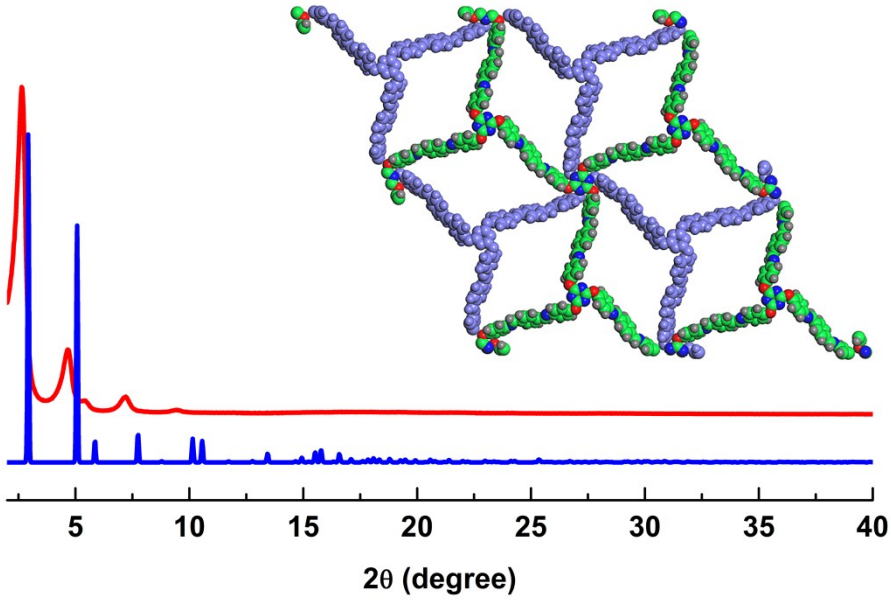


Fig. S26 Comparison of the experimentally observed PXRD pattern with the simulated staggered **AB-1** pattern for TPT-COF-2.

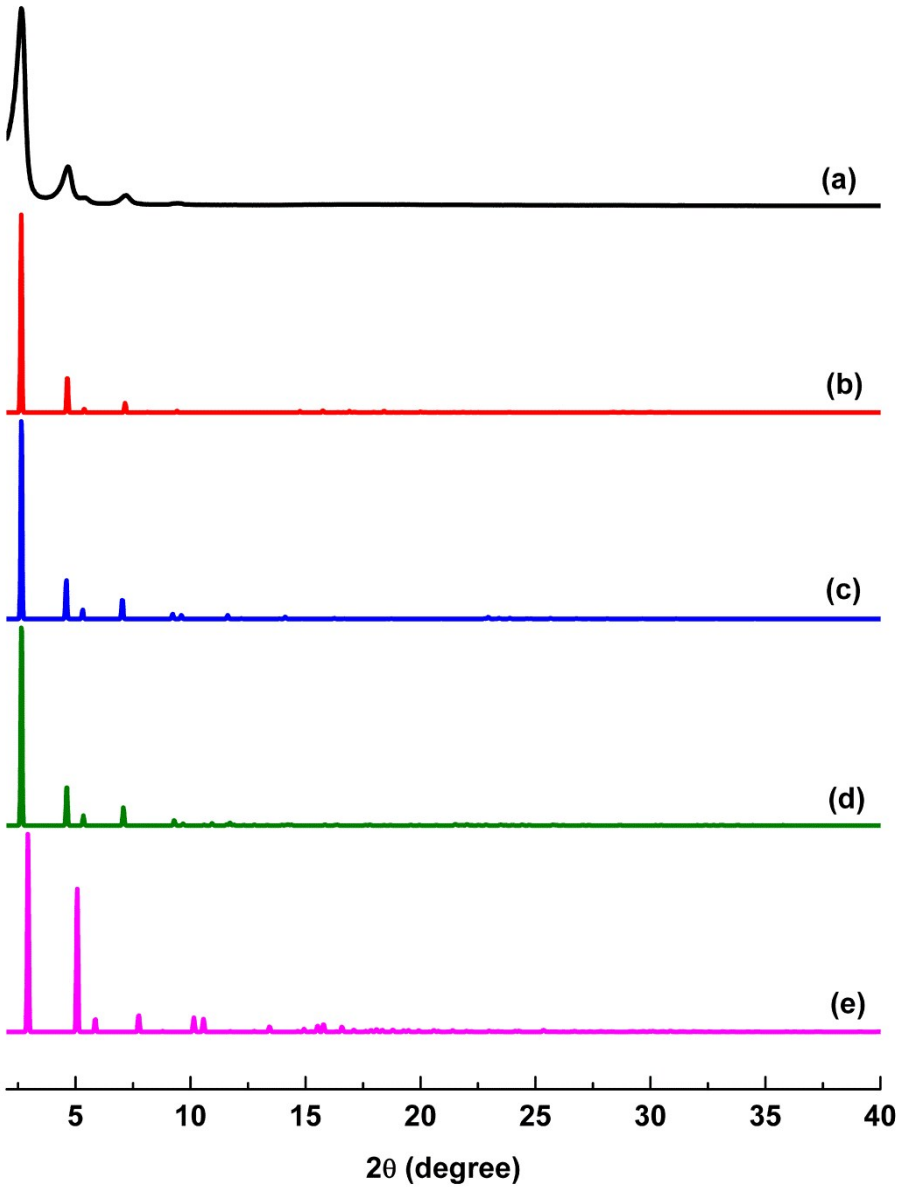


Fig. S27 Comparison of PXRD patterns for TPT-COF-2: experimentally observed (a, black) pattern as well as calculated based on the eclipsed AA-1 (b, red), eclipsed AA-2 (c, blue), eclipsed AA-3 (d, olive) and staggered AB-1 (e, pink) patterns.

12. Models of TPT-COFs

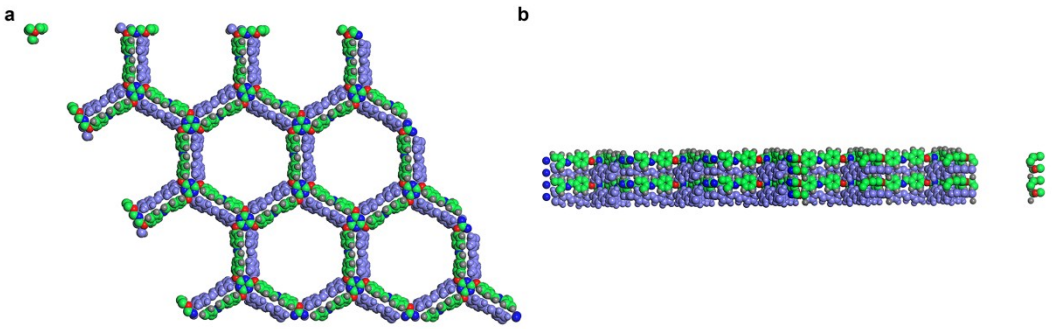


Fig. S28 Top view (a) and side view (b) of eclipsed **AA-1** pattern for TPT-COF-1. C green, O red, N blue, H grey. Another layer is coloured by purple.

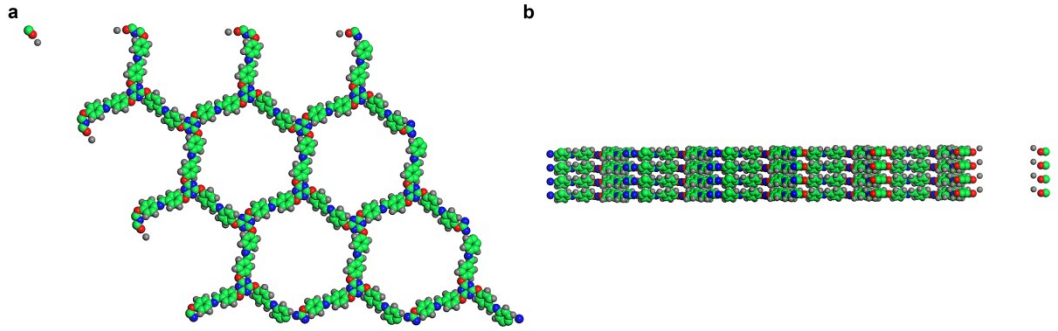


Fig. S29 Top view (a) and side view (b) of eclipsed **AA-2** pattern for TPT-COF-1. C green, O red, N blue, H grey.

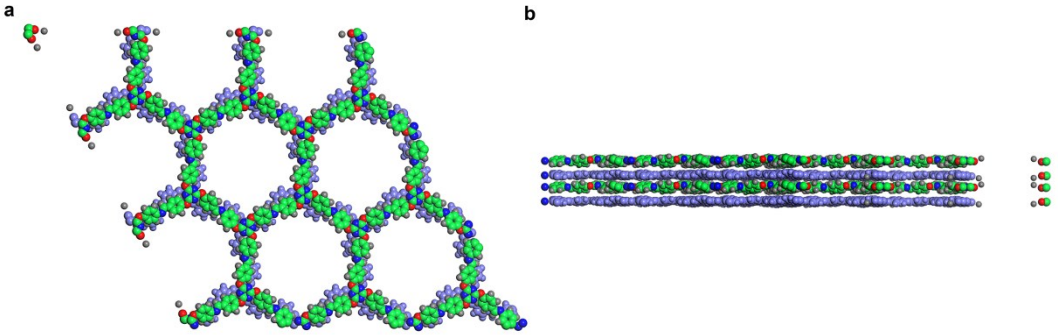


Fig. S30 Top view (a) and side view (b) of eclipsed **AA-3** pattern for TPT-COF-1. C green, O red, N blue, H grey. Another layer is coloured by purple.

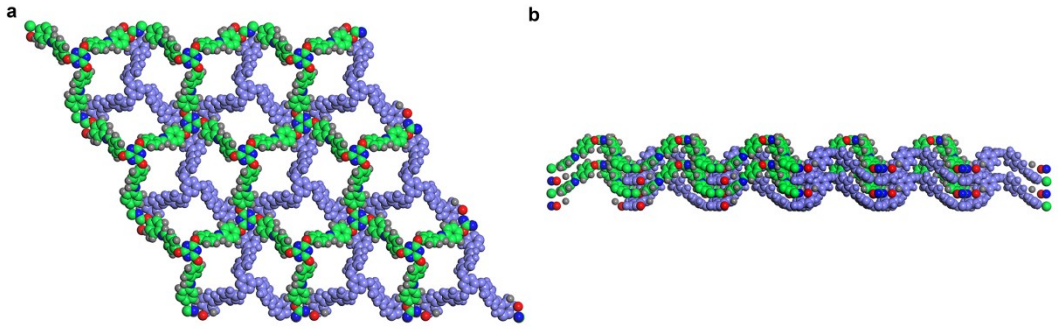


Fig. S31 Top view (a) and side view (b) of staggered **AB-1** pattern for TPT-COF-1. C green, O red, N blue, H grey. Another layer is coloured by purple.

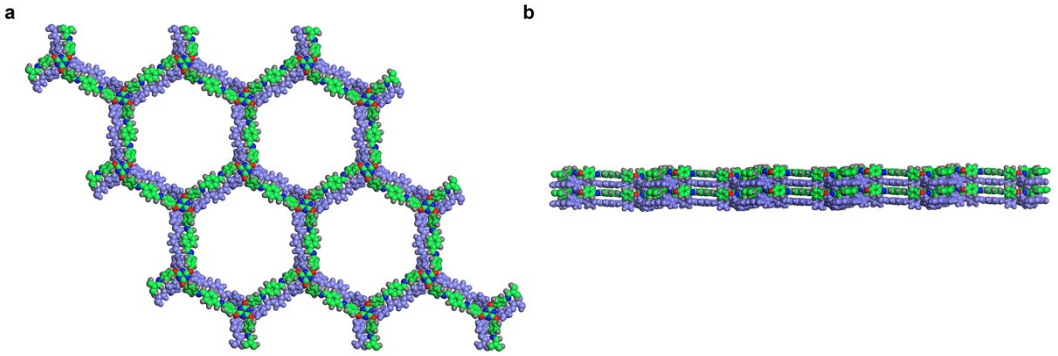


Fig. S32 Top view (a) and side view (b) of eclipsed **AA-1** pattern for TPT-COF-2. C green, O red, N blue, H grey. Another layer is coloured by purple.

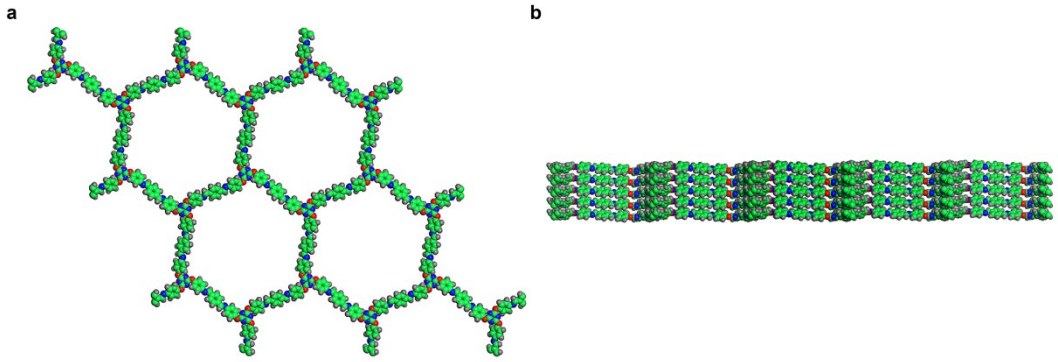


Fig. S33 Top view (a) and side view (b) of eclipsed **AA-2** pattern for TPT-COF-2. C green, O red, N blue, H grey.

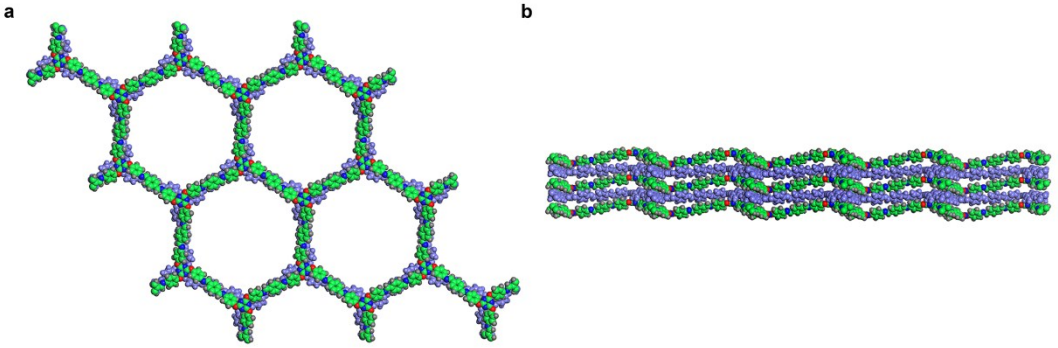


Fig. S34 Top view (a) and side view (b) of eclipsed **AA-3** pattern for TPT-COF-2. C green, O red, N blue, H grey. Another layer is coloured by purple.

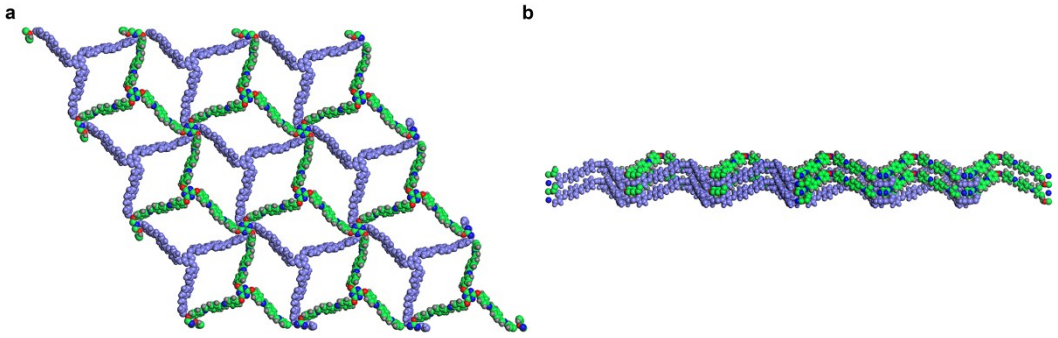


Fig. S35 Top view (a) and side view (b) of staggered **AB-1** pattern for TPT-COF-2. C green, O red, N blue, H grey. Another layer is coloured by purple.

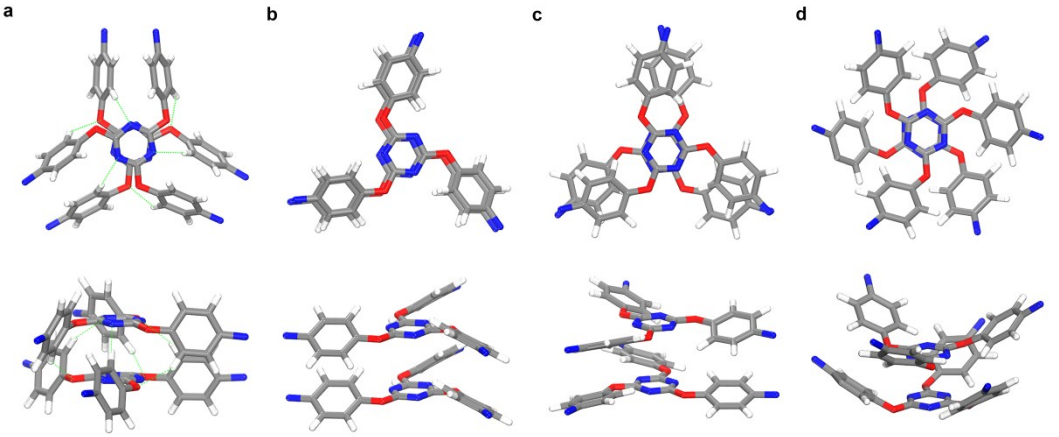


Fig. S36 Top view and side view of Piedfort units in simulated models of TPT-COF-1. C–H···N, C–H···O hydrogen bonds are indicated

as dashed lines. (a) Piedfort units in eclipsed AA-1 model, (b) Piedfort units in eclipsed AA-2 model, (c) Piedfort units in eclipsed AA-3 model, (d) Piedfort units in staggered AB-1 model

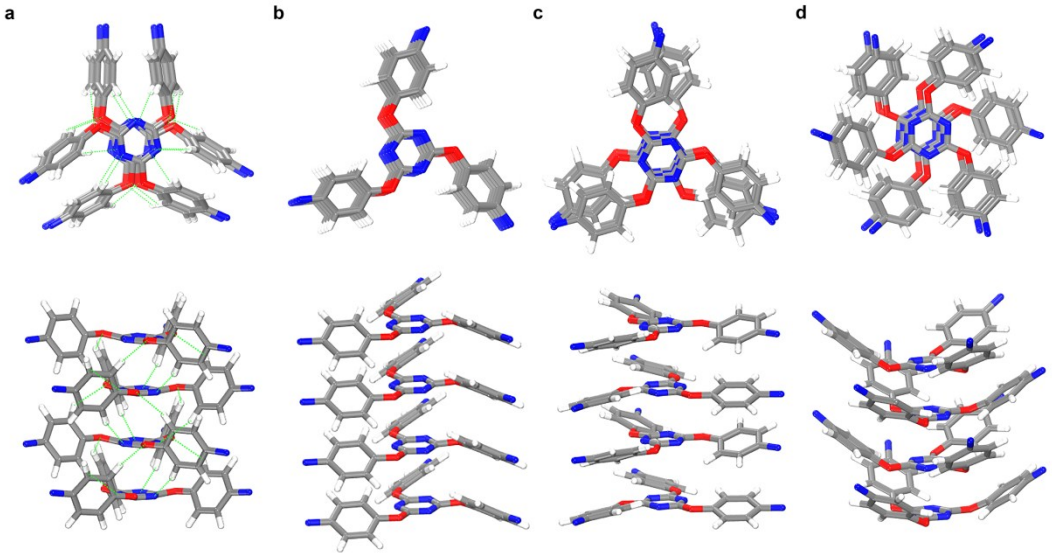


Fig. S37 Top view and side view of stacking Piedfort units in simulated models of TPT-COF-1. C–H···N, C–H···O hydrogen bonds are indicated as dashed lines. (a) stacking Piedfort units in eclipsed AA-1 model, (b) stacking Piedfort units in eclipsed AA-2 model, (c) stacking Piedfort units in eclipsed AA-3 model, (d) stacking Piedfort units in staggered AB-1 model

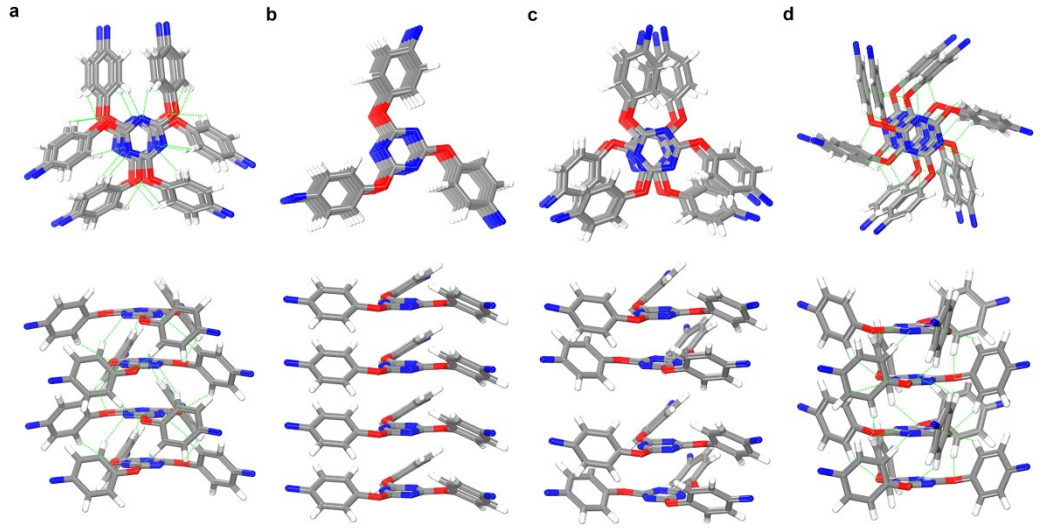


Fig. S38 Top view and side view of stacking Piedfort units in simulated models of TPT-COF-2. C–H···N, C–H···O hydrogen bonds are indicated as dashed lines. (a) stacking Piedfort units in eclipsed AA-1 model, (b) stacking Piedfort units in eclipsed AA-2 model, (c) stacking Piedfort units in eclipsed AA-3 model, (d) stacking Piedfort units in staggered AB-1 model

13. Tables

***Table S*1**. The space group, cell parameters, and relative total energies of the four simulated models of TPT-COF-1

Model	Space group	Cell parameters	Relative total energy (kcal/mol)
Eclipsed AA-1	*P*3	*a*=*b*=26.1241 Å, *c*=6.4920 Å, *α*=*β*=90°, *γ*=120°	0
Eclipsed AA-2	*P*3	*a*=*b*=27.3197 Å, *c*=3.8818 Å, *α*=*β*=90°, *γ*=120°	31.6
Eclipsed AA-3	*P*3	*a*=*b*=27.4023 Å, *c*=7.2613 Å, *α*=*β*=90°, *γ*=120°	50.8
Staggered AB-1	$P6_3$	*a*=*b*=23.5241 Å, *c*=6.0337 Å, *α*=*β*=90°, *γ*=120°	51.7

***Table S*2**. The space group, cell parameters, and relative total energies of the four simulated models of TPT-COF-2

Model	Space group	Cell parameters	Relative total energy (kcal/mol)
Eclipsed AA-1	*P***Error!**	*a*=*b*=37.1512 Å, *c*=6.2868 Å, *α*=*β*=90°, *γ*=120°	0
Eclipsed AA-2	*P***Error!**	*a*=*b*=38.2536 Å, *c*=3.8967 Å, *α*=*β*=90°, *γ*=120°	18.2
Eclipsed AA-3	*P***Error!**	*a*=*b*=37.8560 Å, *c*=8.3054 Å, *α*=*β*=90°, *γ*=120°	28.6
Staggered AB-1	$P6_3$	*a*=*b*=34.8717 Å, *c*=6.0482 Å, *α*=*β*=90°, *γ*=120°	38.7

***Table S*3**. The pore width of the four simulated models of TPT-COF-1

Model	Eclipsed AA-1	Eclipsed AA-2	Eclipsed AA-3	Staggered AB-1
Pore width	21.261 Å	23.559 Å	21.167 Å	6.963 × 10.070 Å

***Table S*4**. The pore width of the four simulated models of TPT-COF-2

Model	Eclipsed AA-1	Eclipsed AA-2	Eclipsed AA-3	Staggered AB-1
Pore width	29.907 Å	34.009 Å	32.130 Å	12.870 × 16.280 Å

***Table S*5**. Structure parameters of the simulated eclipsed AA-1 model of TPT-COF-1

Interaction	d/Å	D/Å	θ/°
C–H···N (C_3-PU1 TPT-NH_2)	2.40	3.449	159.3
C–H···O (C_3-PU1 TPT-NH_2)	2.38	3.284	138.5
C–H···N (C_3-PU2 TPT-NH_2)	2.46	3.509	158.8
C–H···O (C_3-PU2 TPT-NH_2)	2.46	3.382	140.5
C–H···N (C_3-PU3 TPT-CHO)	2.57	3.585	152.3
C–H···O (C_3-PU3 TPT-CHO)	2.55	3.429	136.2
C–H···N (C_3-PU4 TPT-CHO)	2.34	3.404	162.7
C–H···O (C_3-PU4 TPT-CHO)	2.34	3.267	141.3
π···π (C_3-PU1 TPT-NH_2)		3.258	
π···π (C_3-PU2 TPT-NH_2)		3.234	
π···π (C_3-PU3 TPT-CHO)		3.089	
π···π (C_3-PU4 TPT-CHO)		3.403	
Phenyl tilt (C_3-PU1 TPT-NH_2)			22.5
Phenyl tilt (C_3-PU2 TPT-NH_2)			20.2
Phenyl tilt (C_3-PU3 TPT-CHO)			17.9
Phenyl tilt (C_3-PU4 TPT-CHO)			23.9
C–C centroid (C_3-PU1 TPT-NH_2)		3.785	

C–C centroid (C_3-PU2 TPT-NH_2)	3.889
C–C centroid (C_3-PU3 TPT-CHO)	3.990
C–C centroid (C_3-PU4 TPT-CHO)	3.751

Table S6. Structure parameters of the simulated eclipsed AA-1 model of TPT-COF-2

Interaction	d/Å	D/Å	θ/°
C–H···N (C_3-PU1 TPT-NH_2)	2.43	3.475	159.4
C–H···O (C_3-PU1 TPT-NH_2)	2.48	3.229	124.6
C–H···N (C_3-PU2 TPT-NH_2)	2.47	3.506	157.0
C–H···O (C_3-PU2 TPT-NH_2)	2.45	3.224	126.4
π···π (C_3-PU1 TPT-NH_2)		3.158	
π···π (C_3-PU2 TPT-NH_2)		3.129	
Phenyl tilt (C_3-PU1 TPT-NH_2)			35.1
Phenyl tilt (C_3-PU2 TPT-NH_2)			33.7
C–C centroid (C_3-PU1 TPT-NH_2)		3.852	
C–C centroid (C_3-PU2 TPT-NH_2)		3.850	

Table S7. Fractional atomic coordinates for the unit cell of TPT-COF-1 calculated based on eclipsed **AA-1** model.

Space group	*P*3		
Calculated unit cell	$a = b = 26.1241$ Å, $c = 6.4920$ Å, $\alpha = \beta = 90^o$, $\gamma = 120^o$		
Measured unit cell	$a = b = 26.9733$ Å, $c = 6.3570$ Å, $\alpha = \beta = 90^o$, $\gamma = 120^o$		
Pawley refinement	$R_p = 7.18\%$, $R_{wp} = 9.13\%$		
atom	x	y	z
C1	0.13143	0.13411	0.07991
C2	0.16533	0.16439	-0.09205
C3	0.22631	0.19046	-0.08805
C4	0.25628	0.18812	0.08841
C5	0.22153	0.15699	0.25834
C6	0.16047	0.13036	0.2554
C7	0.35614	0.2497	-0.03598
C8	0.41891	0.28165	0.00964
C9	0.4573	0.32058	-0.14033
C10	0.51756	0.35355	-0.10843
C11	0.54276	0.3482	0.07429
C12	0.50552	0.3094	0.22586
C13	0.44496	0.27705	0.19343
C14	0.63361	0.35454	0.12588
C15	0.03639	0.05349	0.10754
C16	0.12407	-0.01398	0.56899

C17	0.15681	0.02201	0.73379
C18	0.21771	0.05645	0.71973
C19	0.24846	0.05648	0.54202
C20	0.21495	0.01991	0.37898
C21	0.15411	-0.01495	0.39197
C22	0.34754	0.12434	0.66121
C23	0.41045	0.15032	0.6256
C24	0.44919	0.18055	0.78835
C25	0.50965	0.20521	0.76929
C26	0.5344	0.20081	0.58411
C27	0.49671	0.17144	0.41873
C28	0.43614	0.14708	0.43918
C29	0.65018	0.37019	0.60275
C30	0.03275	-0.02152	0.60921
O1	0.07174	0.11234	0.07664
O2	0.60239	0.38285	0.10185
O3	0.06411	-0.04949	0.58003
O4	0.59368	0.22151	0.56687
N1	0.3184	0.21624	0.10251
N2	0.59368	0.22151	0.56687
N3	-0.01799	0.03818	0.10038
N4	0.31033	0.09045	0.52251
N5	0.61065	0.31601	0.59526
N6	-0.02257	-0.05692	0.60228
H1	0.14324	0.16823	-0.2306
H2	0.25064	0.21423	-0.2268
H3	0.24308	0.15447	0.40034
H4	0.13521	0.10756	0.39384
H5	0.3431	0.25787	-0.18821
H6	0.44007	0.32634	-0.28784
H7	0.54595	0.38455	-0.22785
H8	0.52426	0.30494	0.37197
H9	0.41737	0.24729	0.31727
H10	0.13438	0.02273	0.87608
H11	0.24141	0.08367	0.85376
H12	0.23708	0.01803	0.23743
H13	0.12922	-0.04385	0.26251
H14	0.33414	0.13233	0.81301
H15	0.43197	0.1844	0.93854
H16	0.53783	0.2273	0.90273
H17	0.51565	0.16754	0.27223
H18	0.4083	0.12408	0.30528

***Table S*8.** Fractional atomic coordinates for the unit cell of TPT-COF-1calculated based on eclipsed **AA-2** model.

Space group	*P*3		
Calculated unit cell	$a = b = 27.3197$ Å, $c = 3.8818$ Å, $\alpha = \beta = 90^o$, $\gamma = 120^o$		
atom	x	y	z
C1	0.13878	0.11582	0.17139
C2	0.17947	0.16576	0.01224
C3	0.23624	0.18192	0.02077
C4	0.25506	0.14889	0.18932
C5	0.21407	0.09966	0.35351
C6	0.15724	0.0835	0.35049
C7	0.35551	0.20618	0.06395
C8	0.41132	0.213	0.10803
C9	0.45825	0.25926	-0.04406
C10	0.5125	0.26786	-0.01373
C11	0.52254	0.23068	0.18144
C12	0.47609	0.18377	0.33
C13	0.422	0.17526	0.29475
C14	0.66668	0.37864	0.2369
C15	0.04157	0.04826	0.14217
O1	0.08358	0.10315	0.15595
O2	0.57472	0.23577	0.22127
N1	0.31217	0.16316	0.20271
N2	0.61918	0.33334	0.23854
N3	0.0506	0.00704	0.14071
H1	0.16562	0.19204	-0.12448
H2	0.26617	0.2212	-0.11149
H3	0.22702	0.07295	0.49337
H4	0.12762	0.04529	0.49376
H5	0.35254	0.23841	-0.08994
H6	0.45267	0.28983	-0.19919
H7	0.54685	0.304	-0.1498
H8	0.4832	0.15382	0.48111
H9	0.38731	0.13807	0.4213

***Table S*9.** Fractional atomic coordinates for the unit cell of TPT-COF-1 calculated based on eclipsed **AA-3** model.

Space group	*P*3		
Calculated unit cell	$a = b = 27.4023$ Å, $c = 7.2613$ Å, $\alpha = \beta = 90^o$, $\gamma = 120^o$		
atom	x	y	z
C1	0.1454	0.03545	0.02337
C2	0.16378	0.09158	0.0705
C3	0.22098	0.13108	0.07281
C4	0.26244	0.11699	0.02995
C5	0.24341	0.06072	-0.01644

C6	0.18656	0.02113	-0.02001
C7	0.34567	0.21041	0.01953
C8	0.40685	0.24394	0.02437
C9	0.4331	0.3024	-0.00132
C10	0.49103	0.33639	0.00591
C11	0.52656	0.31423	0.03901
C12	0.50127	0.25588	0.06207
C13	0.44302	0.22216	0.05465
C14	0.62426	0.33868	0.05332
C15	0.0452	-0.00018	0.02157
C16	0.14359	0.10639	0.56247
C17	0.18657	0.15863	0.62595
C18	0.24215	0.17135	0.62677
C19	0.25721	0.13215	0.56539
C20	0.21414	0.08018	0.50168
C21	0.15852	0.06753	0.49661
C22	0.35566	0.19244	0.52894
C23	0.41211	0.20191	0.55348
C24	0.45767	0.25216	0.48826
C25	0.5127	0.26368	0.5034
C26	0.52489	0.22593	0.59387
C27	0.4798	0.17544	0.65963
C28	0.42477	0.16358	0.63899
C29	0.66452	0.37741	0.62645
C30	0.04477	0.04553	0.57369
O1	0.09053	-0.00797	0.02384
O2	0.58311	0.35273	0.05207
O3	0.09007	0.09825	0.56237
O4	0.57806	0.2339	0.6143
N1	0.32083	0.15594	0.03283
N2	0.67234	0.38319	0.05271
N3	0.04744	0.04716	0.0208
N4	0.31304	0.14355	0.56756
N5	0.61834	0.3311	0.62701
N6	0.04764	0.00081	0.57376
H1	0.13438	0.10594	0.11072
H2	0.23346	0.17447	0.1127
H3	0.27399	0.04733	-0.05147
H4	0.17296	-0.02282	-0.05676
H5	0.32248	0.23327	0.0019
H6	0.40784	0.3227	-0.0269
H7	0.51023	0.38218	-0.01355
H8	0.52571	0.23496	0.09048

H9	0.4253	0.17666	0.07648
H10	0.17545	0.18974	0.67607
H11	0.27447	0.21267	0.67903
H12	0.22442	0.04859	0.45074
H13	0.12769	0.02682	0.43663
H14	0.35136	0.22812	0.47967
H15	0.45035	0.28355	0.41843
H16	0.54565	0.30282	0.44066
H17	0.4888	0.14512	0.72898
H18	0.39094	0.12348	0.6939

***Table S*10.** Fractional atomic coordinates for the unit cell of TPT-COF-1 calculated based on staggered **AB-1** model.

Space group	$P6_3$		
Calculated unit cell	$a = b = 23.5241$ Å, $c = 6.0337$ Å, $\alpha = \beta = 90^o$, $\gamma = 120^o$		
atom	x	y	z
C1	0.16395	0.1254	-0.39391
C2	0.20299	0.18701	-0.29521
C3	0.25845	0.20066	-0.1745
C4	0.27853	0.15393	-0.15312
C5	0.24262	0.09492	-0.2692
C6	0.18643	0.08051	-0.38687
C7	0.34988	0.19643	0.16285
C8	0.40496	0.20051	0.28467
C9	0.42222	0.23185	0.49195
C10	0.47436	0.23696	0.6144
C11	0.51253	0.21152	0.53117
C12	0.49589	0.17963	0.326
C13	0.44336	0.17432	0.20606
C14	0.66138	1.38293	0.6588
C15	1.05304	1.05267	-0.4884
O1	0.10674	0.11387	-0.49281
O2	0.56524	0.21641	0.64332
N1	0.33225	0.16417	-0.02231
N2	0.60877	1.32779	0.65673
N3	1.0548	0.99965	-0.4909
H1	0.18716	0.22377	-0.3053
H2	0.28589	0.24865	-0.09241
H3	0.25738	0.05741	-0.26089
H4	0.15954	0.0324	-0.467
H5	0.32379	0.21971	0.23707
H6	0.39416	0.25344	0.56242
H7	0.48656	0.26208	0.77579
H8	0.52535	0.15904	0.25968

H9	0.43271	0.14912	0.04497

***Table S*11.** Fractional atomic coordinates for the unit cell of TPT-COF-2 calculated based on eclipsed **AA-1** model.

Space group	*P***Error!**		
Calculated unit cell	$a = b = 37.1512$ Å, $c = 6.2868$ Å, $\alpha = \beta = 90^o$, $\gamma = 120^o$		
Measured unit cell	$a = b = 37.3065$ Å, $c = 6.6266$ Å, $\alpha = \beta = 90^o$, $\gamma = 120^o$		
Pawley refinement	$R_p = 7.36\%$, $R_{wp} = 8.82\%$		
atom	x	y	z
C1	0.7515	0.31789	0.17189
C2	0.7762	0.34826	0.02261
C3	0.81914	0.36901	0.04019
C4	0.83909	0.36011	0.2043
C5	0.814	0.3292	0.35044
C6	0.77112	0.30844	0.33482
C7	0.90803	0.4199	0.20235
C8	0.95237	0.43545	0.2168
C9	0.98028	0.47825	0.23973
C10	0.02276	0.49406	0.25356
C11	0.68867	0.31701	0.13228
C12	0.75933	0.42731	0.67136
C13	0.78232	0.45438	0.8365
C14	0.82496	0.4711	0.84787
C15	0.84647	0.46189	0.6937
C16	0.82309	0.43482	0.52923
C17	0.78045	0.41802	0.51607
C18	0.91559	0.51723	0.74748
C19	0.95979	0.5319	0.7577
C20	0.9877	0.57468	0.78133
C21	0.03016	0.59052	0.79219
C22	0.6785	0.30755	0.63455
O1	0.70908	0.2956	0.15878
O2	0.71746	0.41248	0.66193
N1	0.88254	0.38034	0.22266
N2	0.64956	0.2932	0.13919
N3	0.88976	0.47872	0.70115
N4	0.70606	0.34573	0.64155
H1	0.76179	0.35566	-0.11029
H2	0.83776	0.3925	-0.08006
H3	0.82834	0.32104	0.48083
H4	0.75212	0.28419	0.4513
H5	0.89778	0.4427	0.17597
H6	0.96881	0.50037	0.24792
H7	0.76622	0.46237	0.95832

H8	0.84184	0.49196	0.98104
H9	0.83886	0.42705	0.40493
H10	0.76347	0.39753	0.38214
H11	0.90565	0.54015	0.77826
H12	0.97615	0.5967	0.79098
H13	0.48523	0.95735	0.2716
H14	0.57415	0.94986	0.81076

***Table S*12.** Fractional atomic coordinates for the unit cell of TPT-COF-2 calculated based on eclipsed **AA-2** model.

Space group	*P***Error!**		
Calculated unit cell	$a = b = 38.2536$ Å, $c = 3.8967$ Å, $\alpha = \beta = 90^o$, $\gamma = 120^o$		
atom	x	y	z
C1	-0.23538	-0.58248	0.14718
C2	-0.20569	-0.54618	0.29261
C3	-0.16508	-0.53366	0.25807
C4	-0.1522	-0.55684	0.07567
C5	-0.18217	-0.59273	-0.0733
C6	-0.22286	-0.60527	-0.04411
C7	-0.07964	-0.51343	0.14603
C8	-0.03986	-0.50731	0.06883
C9	-0.00538	-0.47238	0.18731
C10	0.03316	-0.46528	0.12101
C11	0.69579	0.36814	1.20245
O	-0.27489	-0.5924	0.18626
N1	-0.11135	-0.54549	0.03287
N2	0.70317	0.33931	1.20399
H1	-0.21509	-0.52766	0.43904
H2	-0.14313	-0.50512	0.3801
H3	-0.17342	-0.61154	-0.22303
H4	-0.24461	-0.6331	-0.17718
H5	-0.08103	-0.49006	0.30011
H6	-0.00843	-0.44997	0.34104
H7	0.05868	-0.4375	0.22452

***Table S*13.** Fractional atomic coordinates for the unit cell of TPT-COF-2 calculated based on eclipsed **AA-3** model.

Space group	*P***Error!**		
Calculated unit cell	$a = b = 37.8560$ Å, $c = 8.3054$ Å, $\alpha = \beta = 90^o$, $\gamma = 120^o$		
atom	x	y	z
C1	0.7664	0.41568	0.19279
C2	0.79839	0.44953	0.26927
C3	0.83865	0.46111	0.23731
C4	0.84878	0.43939	0.12733
C5	0.81647	0.40496	0.05505

C6	0.77612	0.39345	0.0845
C7	0.92226	0.48408	0.12301
C8	0.96102	0.4914	0.05939
C9	0.99689	0.52785	0.09775
C10	0.0346	0.53622	0.04044
C11	0.69682	0.36807	0.22311
C12	0.763	0.34246	0.56646
C13	0.78284	0.37905	0.65302
C14	0.82406	0.406	0.62971
C15	0.84734	0.39756	0.52123
C16	0.82691	0.36108	0.43387
C17	0.78574	0.33404	0.45594
C18	0.91376	0.45798	0.56776
C19	0.95705	0.47863	0.53155
C20	0.98348	0.51636	0.60408
C21	0.02498	0.53701	0.57385
C22	0.69489	0.32575	0.59633
O1	0.72735	0.40754	0.21936
O2	0.72302	0.31355	0.59075
N1	0.8891	0.45077	0.08522
N2	0.70311	0.33814	0.22339
N3	0.88952	0.42346	0.49841
N4	0.6587	0.29576	0.59518
H1	0.79111	0.46723	0.35458
H2	0.8626	0.48809	0.2996
H3	0.82307	0.3868	-0.03029
H4	0.7521	0.36684	0.02059
H5	0.92275	0.50808	0.19939
H6	0.99568	0.55051	0.17684
H7	0.76599	0.38679	0.7405
H8	0.83835	0.43425	0.70089
H9	0.84381	0.35326	0.3468
H10	0.77041	0.30543	0.38671
H11	0.90345	0.47253	0.65628
H12	0.97162	0.53014	0.68925
H13	0.50389	0.93865	1.07618
H14	0.52238	0.9562	0.63616

***Table S*14.** Fractional atomic coordinates for the unit cell of TPT-COF-2 calculated based on staggered **AB-1** model.

Space group	$P6_3$		
Calculated unit cell	$a = b = 34.8717$ Å, $c = 6.0482$ Å, $\alpha = \beta = 90^o$, $\gamma = 120^o$		
atom	x	y	z
C1	0.09514	0.10275	-0.467

C2	0.11147	0.11905	-0.25603
C3	0.15589	0.1364	-0.20791
C4	0.186	0.13796	-0.36657
C5	0.16939	0.12278	-0.57942
C6	0.12509	0.10628	-0.63006
C7	0.2517	0.17388	-0.13964
C8	0.29518	0.18003	-0.09214
C9	0.31564	0.19923	0.11013
C10	0.3567	0.20518	0.16632
C11	0.3802	0.1924	0.02346
C12	0.36001	0.17373	-0.18017
C13	0.31887	0.16769	-0.23625
C14	0.42311	0.1976	0.07708
C15	0.48241	0.22269	0.34893
C16	0.49742	0.24384	0.55387
C17	0.53789	0.25306	0.64126
C18	0.56528	0.24163	0.52365
C19	0.55044	0.21973	0.32101
C20	0.50988	0.21054	0.23561
C21	1.0406	1.01475	-0.01426
C22	1.65759	1.3633	1.6121
O1	0.05117	0.08548	-0.51231
O2	0.60573	0.2506	0.60116
N1	0.23081	0.15304	-0.31736
N2	0.44128	0.2146	0.26609
N3	1.02701	1.04248	-0.01323
N4	1.6255	1.32378	1.61061
H1	0.08887	0.11747	-0.12538
H2	0.16682	0.14827	-0.03894
H3	0.19174	0.12353	-0.70983
H4	0.11299	0.09528	-0.7984
H5	0.23714	0.18535	-0.01261
H6	0.29904	0.20972	0.23045
H7	0.37053	0.22019	0.32792
H8	0.37661	0.16318	-0.3001
H9	0.3049	0.15258	-0.39748
H10	0.43853	0.18667	-0.04787
H11	0.47693	0.25386	0.64858
H12	0.54894	0.27022	0.80109
H13	0.57151	0.21003	0.22913
H14	0.49985	0.19345	0.07551

14. Supporting References

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