

Aggregated Structures of Two-Dimensional Covalent Organic Frameworks

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Experimental Details

1. Materials and Methods

1.1 Materials

1,3,5-Tris(4-aminophenyl)benzene (> 93%), terephthalaldehyde (> 98%), 1,4-dimethoxybenzene (> 97%), 4-aminobenzonitrile (> 98%), trifluoromethanesulfonic acid (> 98%), p-xylene (> 99%), paraformaldehyde (95%), zinc chloride (98%), hexamethylenetetramine (> 99%), and 1,4-dioxane (> 99%) were obtained from Tokyo Chemical Industry CO., LTD. Other reagents and solvents were obtained from commercial sources and used as received.

1.2 Methods

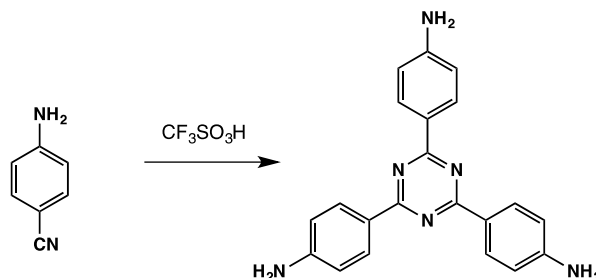
Instruments and methods. Powder X-ray diffraction (PXRD) patterns were obtained on a Bruker D8 Advance X-ray powder diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178 \text{ \AA}$) at a scan rate of 3° min^{-1} . Before PXRD measurements, each sample was prepared by pressing 15 mg of COF powders with 5 kN force into a round flake with 1 cm in diameter. Fourier-transform infrared spectroscopy (FTIR) was performed with a Bio-Rad FTS-3500 ARX FTIR spectrometer. Solution-based nuclear magnetic resonance spectroscopy (NMR) was conducted on a Bruker Avance 400 MHz NMR spectrometer (DRX400) with chemical shifts being quoted in parts-per-million (ppm) relative to tetramethylsilane. Solid-state NMR experiments were completed on a 14.1 T Bruker Avance III HD 600 MHz spectrometer utilising a 1.9 mm Bruker HXY probe at an MAS frequency of 30 kHz. All spectra were processed using the Topspin software package and referenced to the unified scale using IUPAC recommended frequency ratios relative to the ^{13}C adamantane_(s) methylene resonance ($\delta = 37.77 \text{ ppm}$).^{1,2} The $^{13}\text{C}[^1\text{H}]$ NMR ($\nu_0 = 150.93 \text{ MHz}$) CP experiment employed a $6000 \mu\text{s}$ contact pulse length, a $2.05 \mu\text{s } ^1\text{H } \pi/2$ pulse and high power proton decoupling. Recycle delays of 4-5 s were employed throughout. In order to measure the SSNMR spectra of the TAPB-OMeTA COF in CDCl_3 , 0.2 mL of CDCl_3 was added to 50 mg of COF sample, such that the sample was fully wetted without free liquid inside the tube. **Great care should be taken during the wet sample measurement to avoid any accident due to the presence of liquid in a high-speed spinning tube!** Field-emission scanning electron microscopy (FESEM) images were taken on a JEOL JSM-7610F SEM. Samples were coated with Pt sputtering for 120 s before imaging. Brunauer-Emmett-Teller (BET) surface area measurements were performed at 77 K on a Micromeritics ASAP 2020 instrument equipped with commercial software for data calculation and analysis. Before each measurement, the sample (50–80 mg) was degassed at 373 K for 12 h. The N_2 isotherms were collected with a pressure range of 0–0.95 bar.

Structural modeling of COFs. Structural modeling of COFs was carried out in the software package of *Materials Studio* (2018 version, Accelrys Software Inc.). Theoretical models were initially optimized by the *Forcite* module, then Pawley refinements of the PXRD patterns were conducted in the *Reflex* module using 2 theta data from 1.5 to 40° . The integrated intensities were extracted with the Pseudo-Voigt profile. As for the dried COFs, the unit cell parameters a, b, c, FWHM parameters, U, V, W, profile parameters NA, NB, and

zero point were refined based on previous studies.^{3,4} As for the solvated TAPB-OMeTA-H, in addition to the above parameters, alpha, beta, and gamma parameters were also refined. The background was refined with 20th order polynomial. The simulation of TAPB-OMeTA was reported previously,³ and the simulation data of N-TAPB-OMeTA, TAPB-MeTA, N-TAPB-MeTA, and TAPB-OMeTA-H are provided in Tables S1-4.

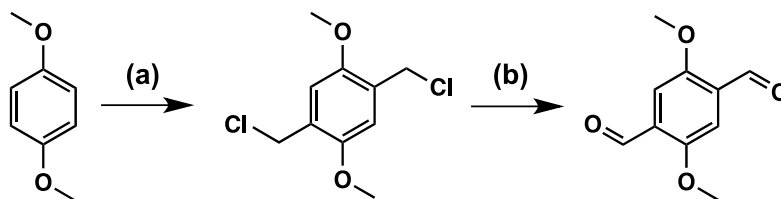
2. Synthesis of Building Blocks and 2D COFs

2.1 Synthesis of 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline (N-TAPB)⁵



4-Aminobenzonitrile (386.0 mg, 3.3 mmol) and CHCl_3 (10 mL) were added into a 50.0 mL flask, then $\text{CF}_3\text{SO}_3\text{H}$ (1.0 mL, 11.1 mmol) was added to the above mixture drop wisely in an ice-water bath with gentle stirring. The mixture was stirred for 24 h at room temperature. After that, distilled water (10.0 mL) was added and neutralized by 2M NaOH solution. Light yellow product was collected by filtration and extensively washed with deionized water (yield: 82%). $^1\text{H NMR}$ (400 MHz, DMSO): δ 8.36 (6 H), 6.70 (6 H), 5.92 (6 H).

2.2 Synthesis of 2,5-dimethoxyterephthalaldehyde⁶



(a) Synthesis of 1,4-bis(chloromethyl)-2,5-dimethoxybenzene

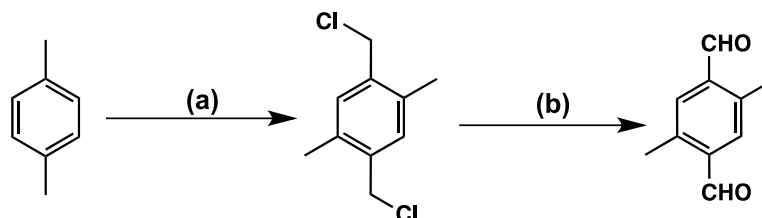
1,4-Dioxane (15 mL) was added to a mixture of formaldehyde solution (2.5 mL, 37 wt%), 1,4-dimethoxybenzene (5.0 g, 36.2 mmol), and paraformaldehyde (1.5 g, 50 mmol). The mixture was heated to 90 °C, and concentrated HCl (5 mL, 37 wt%) was added in 5 min. After heating at 90 °C for another 1 h, HCl (15 mL, 37 wt%) was added. Then, the mixture was allowed to cool at room temperature with white precipitate obtained. The crude product was separated by filtration, washed with water, and then purified by recrystallization from acetone. The pure product was obtained as a white powder (yield: 86%). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ : 6.86 (2 H), 4.57 (4 H), 3.79 (6 H).

(b) Synthesis of 2,5-dimethoxyterephthalaldehyde

Chloroform (25 mL) was added to a mixture of 1,4-bis(chloromethyl)-2,5-dimethoxybenzene (2.5 g, 10.6 mmol) and hexamethylenetetramine (3.0 g, 21.3 mmol). The mixture was heated at 90 °C with stirring for 24 h. Then, a pale yellowish precipitate was obtained as the mixture cooled to room temperature. The precipitate was collected by filtration and washed with CHCl_3 , then dried under vacuum and redissolved in deionized water. Acetic acid (5 mL) was added to the aqueous mixture, heated to 90 °C, and stirred for another 24 h.

After cooling to room temperature, the mixture was extracted with dichloromethane (DCM) and dried by anhydrous MgSO_4 . DCM was removed by rotary evaporation, and the crude product was purified by recrystallization from ethanol. The purified product was obtained as a yellow solid (yield: 34%). $^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ : 10.4 (2 H), 7.46 (2 H), 3.95 (6 H).

2.3 Synthesis of 2,5-dimethylterephthalaldehyde (MeTA)⁷



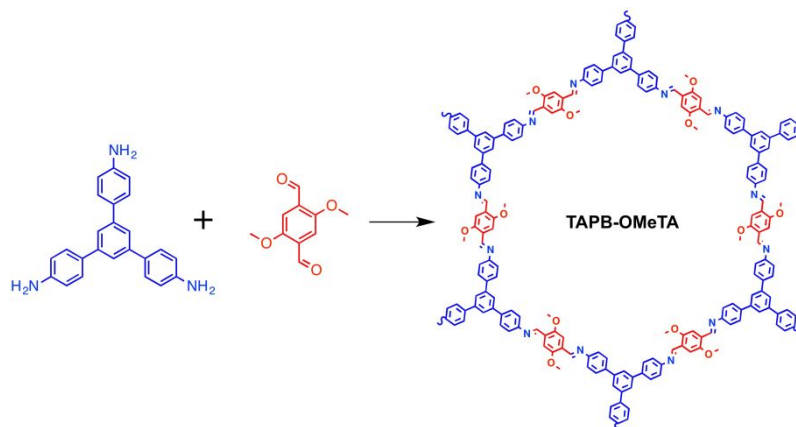
(a) Synthesis of 1,4-bis(chloromethyl)-2,5-dimethylbenzene

To a 100 mL flask, *p*-xylene (10 mL, 0.08 mol), paraformaldehyde (6.3 g, 1.3 eq), and ZnCl_2 (6.8 g, 0.05 mol) were added; then, HCl (50 mL, 37%) was added to the mixture. The mixture was refluxed at 110 °C for 2 days. After the reaction, the mixture was cooled down to room temperature, and white needle crystals were obtained and filtered, washed by water, and dried under vacuum (yield: 80.6%). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.12 (2 H), 4.56 (2 H), 2.35 (6 H).

(b) Synthesis of MeTA

1,4-Bis(chloromethyl)-2,5-dimethylbenzene (2.9 g, 14.2 mmol), hexamethylenetetramine (5.2 g, 39.2 mmol), and acetic acid solution (20 mL, 50% (v/v)) were added into a 50 mL flask. The mixture was refluxed at 110 °C for 1 h, then HCl (10 mL, 37%) was added, and the mixture was refluxed for an additional 1 h. After that, the mixture was cooled down in ice-cold water. White crystals were precipitated out, filtered, and washed with water (yield: 73.9%). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ : 10.39 (2 H), 7.72 (2 H), 2.71 (6 H).

2.4 Synthesis of TAPB-OMeTA-M and -H COF⁸



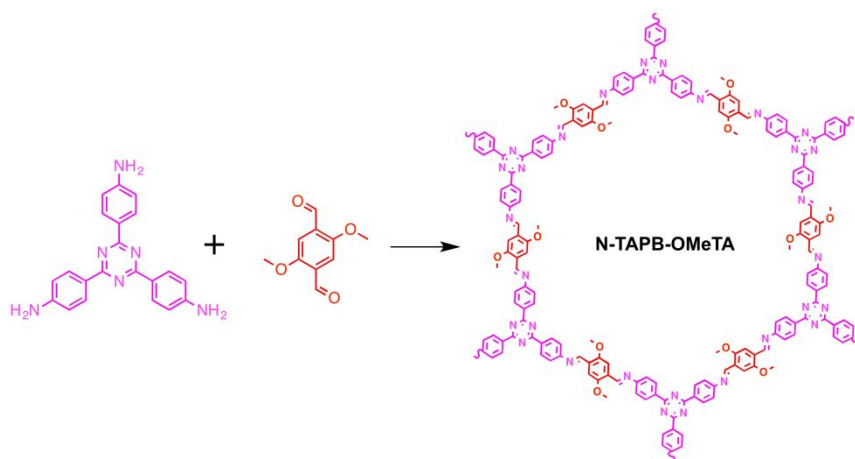
1,3,5-Tris(4-aminophenyl)benzene (55.0 mg, 0.16 mmol) and 2,5-dimethoxyterephthalaldehyde (45.6 mg,

0.27 mmol) were dispersed in a mixture of 1,2-dioxane (2.65 mL) and mesitylene (0.65 mL). The mixture was sonicated for 2 min and heated at 65 °C for 10 min to obtain a clear solution. Then, acetic acid (1.66 mL, 6 M) was added to the mixture. The mixture was heated at 65 °C for 5 min and 4 h to obtain M- and H-TAPB-OMeTA, respectively. The precipitate was collected by filtration, washed with THF and ethanol, and immersed in THF and ethanol, respectively, for three days. After being dried under vacuum, the final COF was obtained as a yellow powder (yield: 89%).

2.5 Synthesis of TAPB-OMeTA-A COF

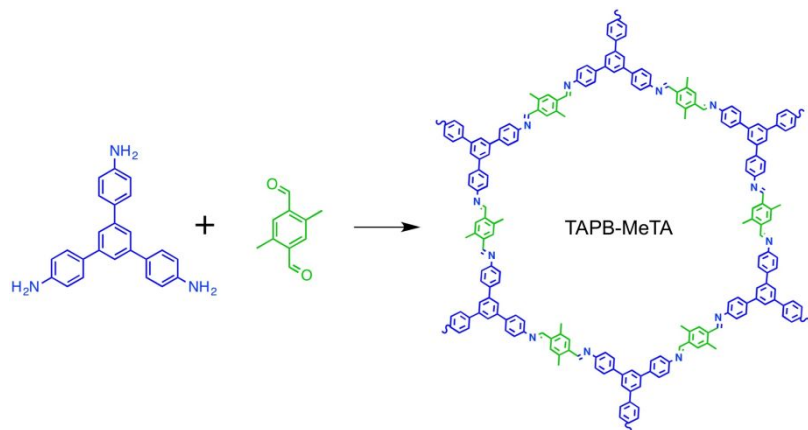
1,3,5-Tris(4-aminophenyl)benzene (55.0 mg, 0.16 mmol) and 2,5-dimethoxyterephthalaldehyde (45.6 mg, 0.27 mmol) were dispersed in 1,2-dioxane (3.0 mL). The mixture was frozen in liquid nitrogen to obtain a solid, to which acetic acid (1.66 mL, 6 M) was added. The mixture was frozen again in liquid nitrogen for another 5 min and then warmed up to room temperature under vigorous stirring. After 4 h of reaction at room temperature, the precipitate was collected by filtration, washed with THF and ethanol, and immersed in THF and ethanol respectively for three days. After being dried under vacuum, the final COF was obtained as a yellow powder (yield: 92%).

2.6 Synthesis of N-TAPB-OMeTA



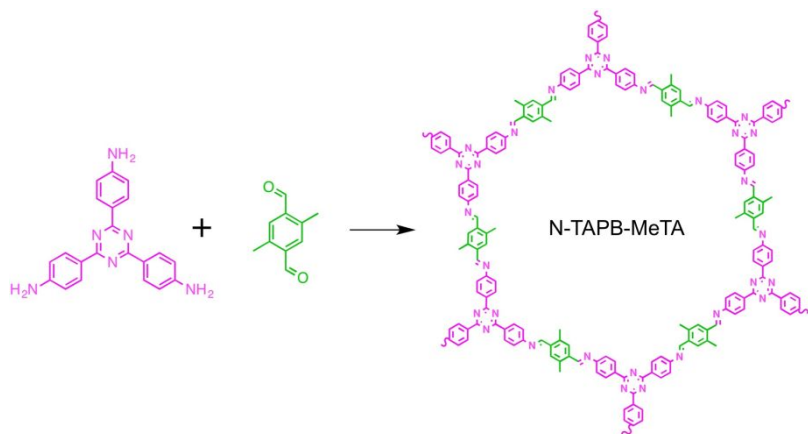
4,4',4''-(1,3,5-Triazine-2,4,6-triyl)trianiline (56.7 mg, 0.16 mmol) and 2,5-dimethoxyterephthalaldehyde (45.6 mg, 0.27 mmol) were dispersed in a mixture of 1,2-dioxane (2.65 mL) and mesitylene (0.65 mL). The mixture was sonicated for 2 min and heated at 65 °C for 10 min to obtain a clear solution. Then, acetic acid (1.66 mL, 6 M) was added to the mixture. After gentle shaking, additional 1 mL acetic acid was added to the mixture. The mixture was heated at 65 °C, and red solids gradually grew from the solution. After 24 h, red N-TAPB-OMeTA was obtained. The precipitate was collected by filtration, washed with THF and ethanol, and immersed in THF and ethanol, respectively, for three days. After being dried under vacuum, the final COF was obtained as a yellow powder (yield: 91%).

2.7 Synthesis of TAPB-MeTA



1,3,5-Tris(4-aminophenyl)benzene (55.0 mg, 0.16 mmol) and 2,5-dimethylterephthalaldehyde (43.8 mg, 0.27 mmol) were dispersed in a mixture of 1,2-dioxane (2.65 mL) and mesitylene (0.65 mL). The mixture was sonicated for 2 min and heated at 65 °C for 10 min to obtain a clear solution. Then, acetic acid (1.66 mL, 6 M) was added to the mixture. The mixture was heated at 65 °C for 24 h to obtain TAPB-MeTA. The yellowish precipitate was collected by filtration, washed with THF and ethanol, and immersed in THF and ethanol, respectively, for three days. After being dried under vacuum, the final COF was obtained (yield: 81%).

2.8 Synthesis of *N*-TAPB-MeTA



4,4',4''-(1,3,5-Triazine-2,4,6-triyl)trianiline (56.7 mg, 0.16 mmol) and 2,5-dimethylterephthalaldehyde (43.8 mg, 0.27 mmol) were dispersed in a mixture of 1,2-dioxane (2.65 mL) and mesitylene (0.65 mL). The mixture was sonicated for 2 min and heated at 65 °C for 10 min to obtain a clear solution. Then, acetic acid (1.66 mL, 6 M) was added to the mixture. The mixture was heated at 65 °C for 24 h to obtain N-TAPB-MeTA. The yellowish precipitate was collected by filtration, washed with THF and ethanol, and immersed in THF and ethanol, respectively, for three days. After being dried under vacuum, the final COF was obtained (yield: 65%).

3. Additional Figures and Tables

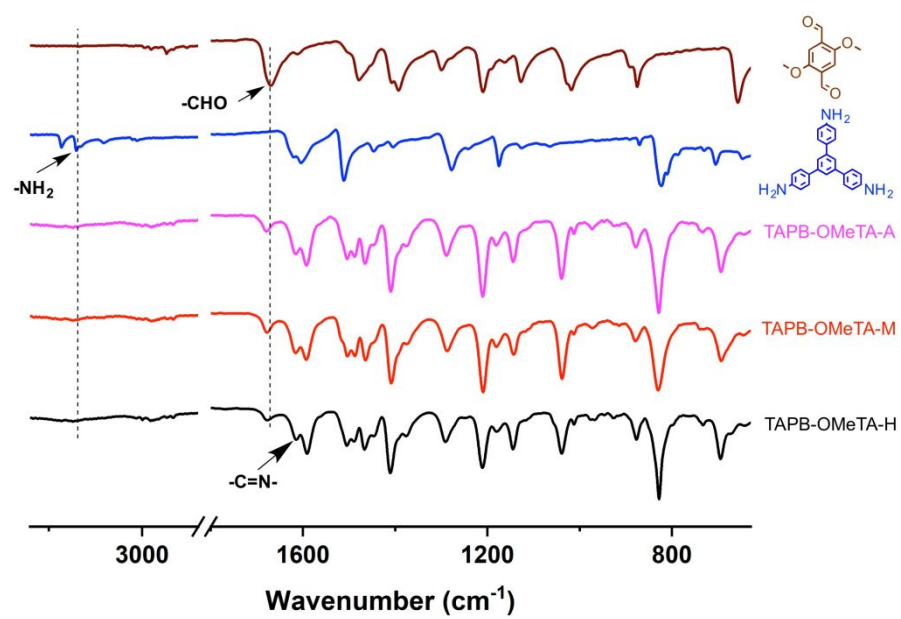


Figure S1. FTIR spectra of monomers and TAPB-OMeTA COF with different crystallinity.

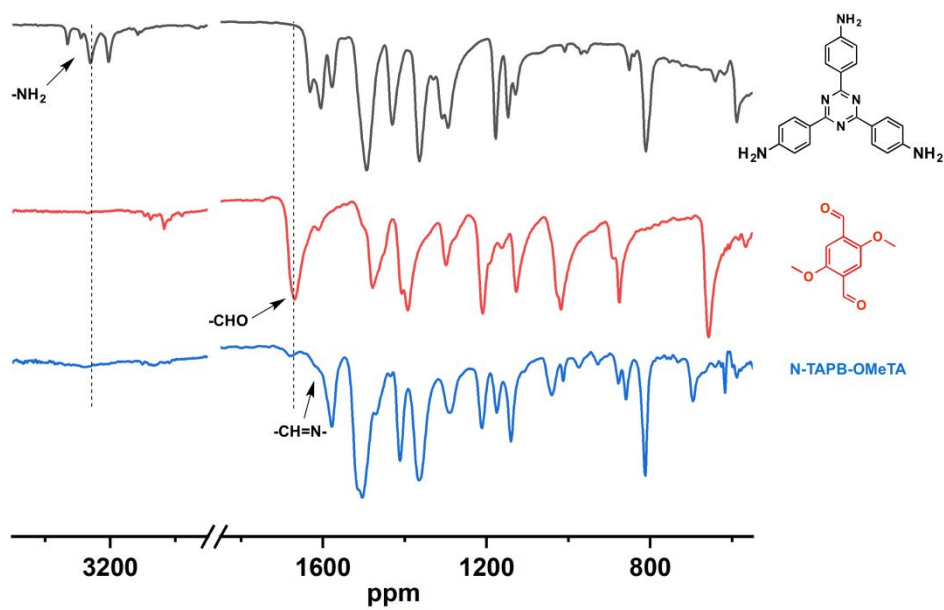


Figure S2. FTIR spectra of monomers and N-TAPB-OMeTA.

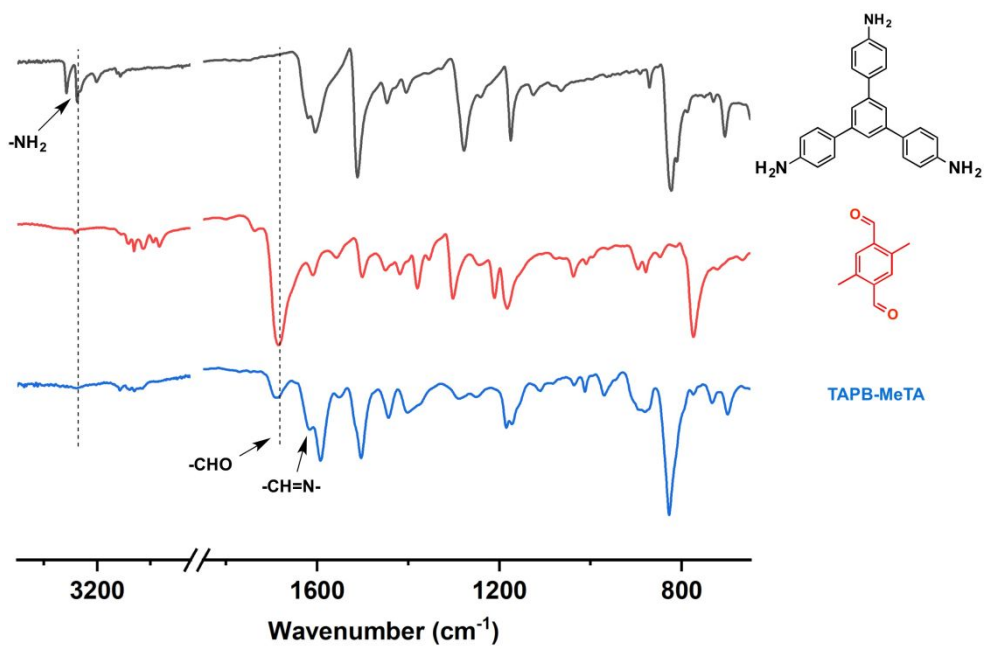


Figure S3. FTIR spectra of monomers and TAPB-MeTA.

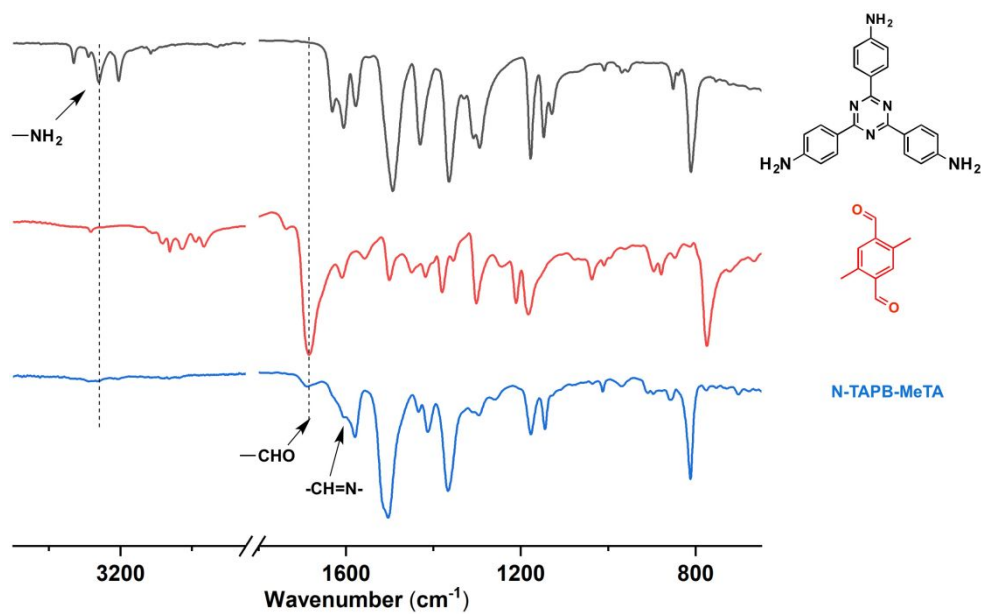


Figure S4. FTIR spectra of monomers and N-TAPB-MeTA.

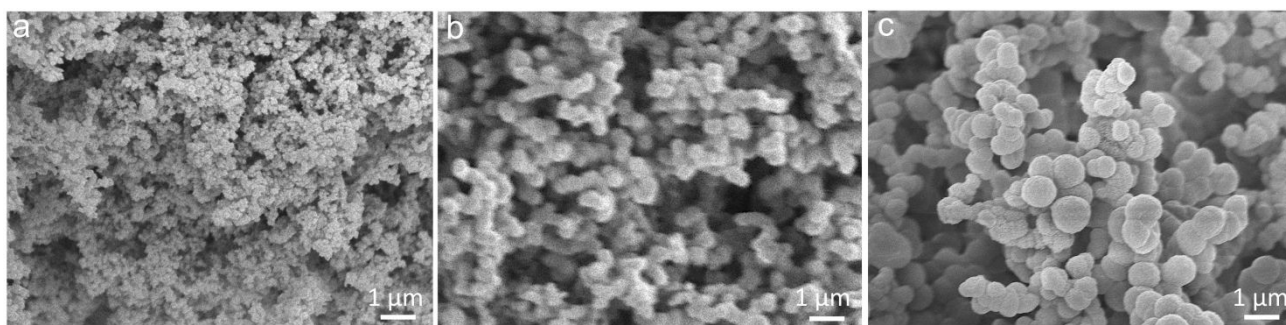


Figure S5. SEM images of TAPB-OMeTA with different crystallinities: (a) TAPB-OMeTA-A; (b) TAPB-OMeTA-M; (c) H-TAPB-OMeTA-H.

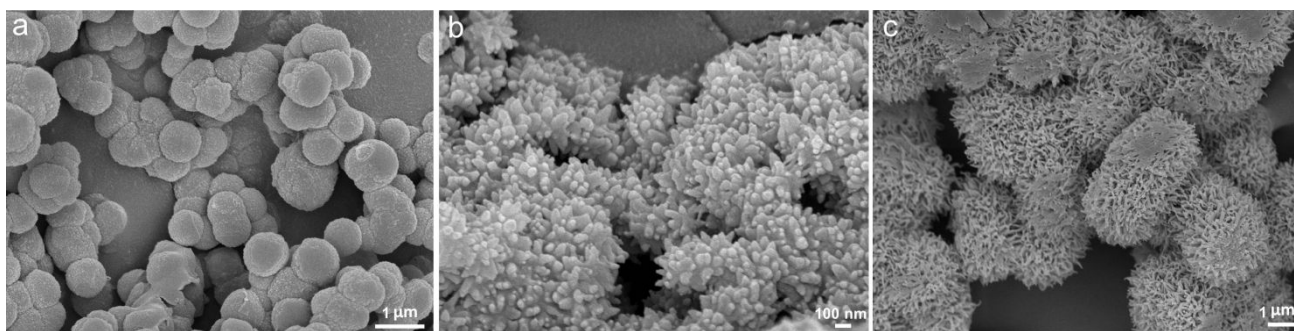


Figure S6. SEM images of (a) N-TAPB-OMeTA, (b) TAPB-MeTA, and (c) N-TAPB-MeTA.

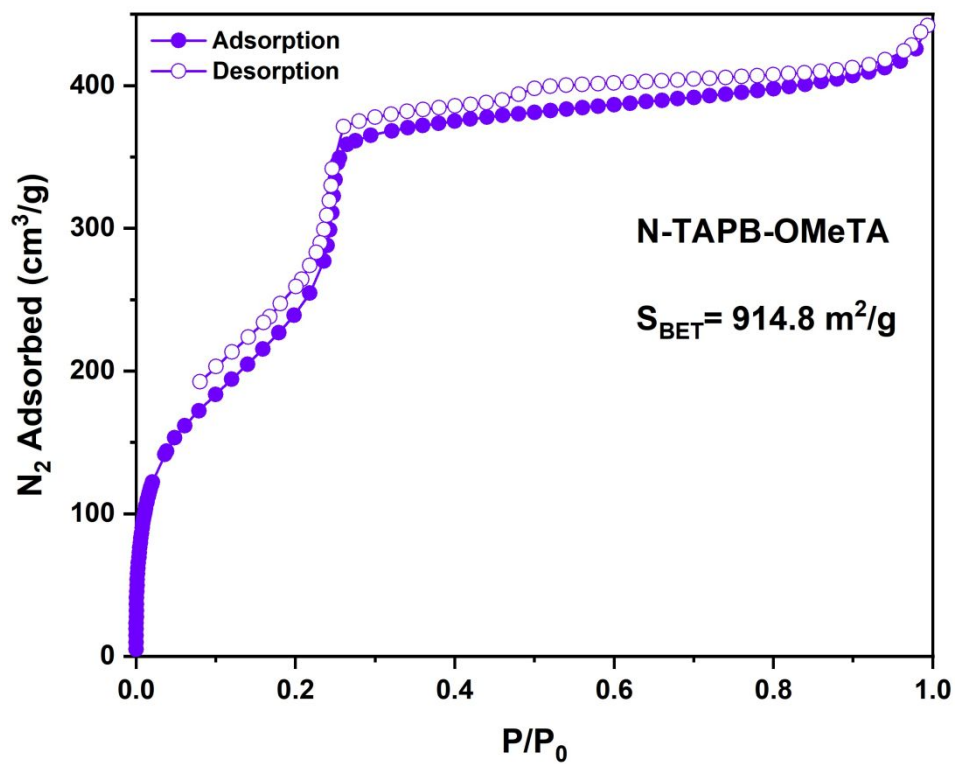


Figure S7. N₂ sorption isotherm of N-TAPB-OMeTA at 77 K (closed, adsorption; open, desorption).

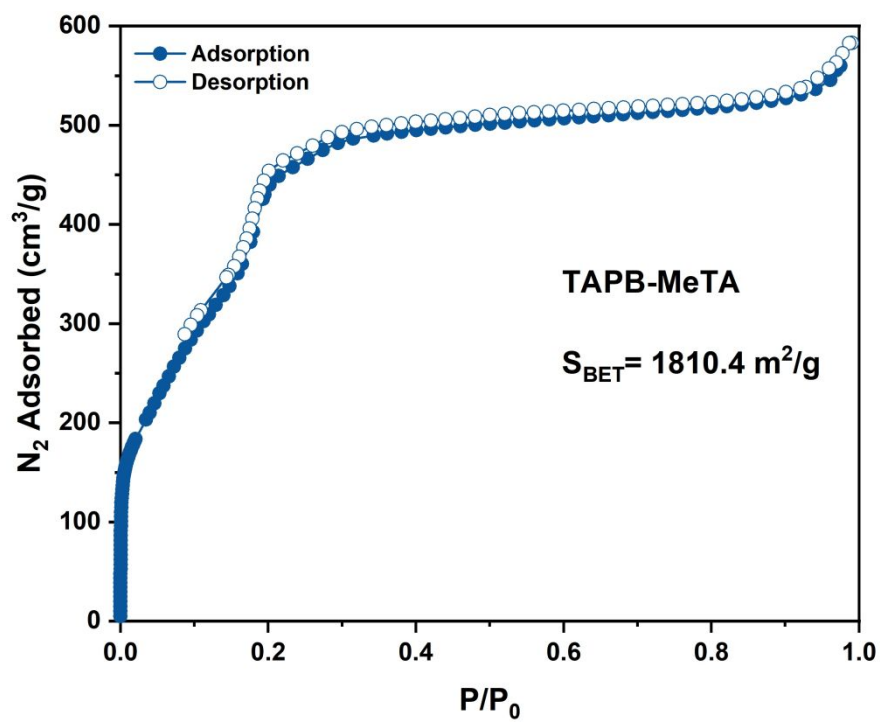


Figure S8. N₂ sorption isotherm of TAPB-MeTA at 77 K (closed, adsorption; open, desorption).

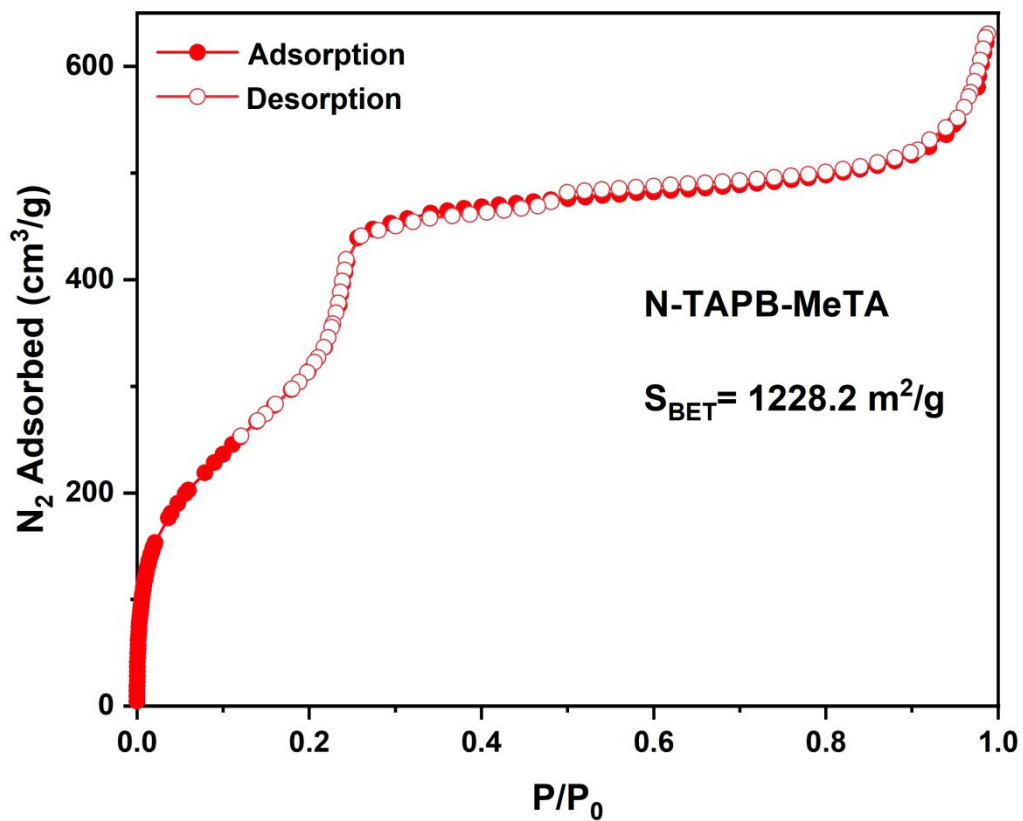


Figure S9. N₂ sorption isotherm of N-TAPB-MeTA at 77 K (closed, adsorption; open, desorption).

Table S1. Detailed atom information of the simulated AA stacking N-TAPB-OMeTA.

a = 37.34 Å, b = 37.34 Å, c = 3.61 Å; $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$; Space group P3(C3-1)			
	x	y	z
C	0.55779	0.47003	0.47058
C	0.64746	0.29123	0.58691
N	0.68938	0.31427	0.58673
C	0.6189	0.37342	0.58239
C	0.63827	0.41679	0.59267
C	0.61485	0.43651	0.58343
C	0.57144	0.41313	0.5606
C	0.55213	0.36997	0.55734
C	0.5755	0.35021	0.56664
N	0.5458	0.43172	0.54991
C	0.52809	0.48537	0.47349
C	0.48635	0.45878	0.56476
C	0.45776	0.47309	0.57295
O	0.41596	0.44784	0.67908
C	0.60306	0.59378	0.47159
C	0.44161	0.52978	0.46334
C	0.35261	0.70877	0.31355
N	0.31068	0.68579	0.31382
C	0.38096	0.62644	0.32106
C	0.36151	0.58305	0.31483
C	0.38485	0.56327	0.33026
C	0.42824	0.58659	0.3553
C	0.44764	0.62976	0.35313
C	0.42436	0.64958	0.3377
N	0.45376	0.56792	0.37513
C	0.47124	0.51434	0.471
C	0.51294	0.54077	0.37832
C	0.54171	0.52703	0.39131
O	0.58357	0.5537	0.30344
C	0.40274	0.40745	0.82209
H	0.5895	0.49105	0.39277
H	0.6716	0.43562	0.60923
H	0.63095	0.46985	0.59979
H	0.51874	0.35155	0.54419
H	0.5595	0.31676	0.56004
H	0.4764	0.4269	0.62863
H	0.61324	0.61794	0.25517
H	0.63081	0.59838	0.62436
H	0.58274	0.59806	0.66971
H	0.40985	0.50908	0.54163
H	0.32818	0.56426	0.29755
H	0.3687	0.5299	0.31757
H	0.48103	0.64813	0.36772
H	0.44042	0.68304	0.34109
H	0.52329	0.57227	0.29345

H	0.42386	0.40869	1.04208
H	0.40121	0.38611	0.60229
H	0.37131	0.3948	0.94083

Table S2. Detailed atom information of the simulated AA stacking TAPB-MeTA.

a = 37.63 Å, b = 37.63 Å, c = 3.72 Å; $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$; Space group P6(C6-1)			
	x	y	z
C	0.55828	0.47083	0.52485
C	0.64692	0.28998	0.48
C	0.68998	0.31383	0.47997
C	0.61817	0.37394	0.48038
C	0.63242	0.41185	0.6469
C	0.60931	0.43158	0.64468
C	0.57112	0.41361	0.47806
C	0.55641	0.37555	0.31914
C	0.57979	0.35612	0.31585
N	0.54582	0.43222	0.47381
C	0.5288	0.48619	0.51873
C	0.4864	0.45808	0.5164
C	0.45753	0.47131	0.51645
H	0.5905	0.49225	0.56337
H	0.66093	0.42588	0.78823
H	0.62091	0.46006	0.78348
H	0.52704	0.3613	0.1902
H	0.56804	0.32758	0.17707
H	0.4756	0.42545	0.51763
C	0.41253	0.43957	0.51203
H	0.70801	0.29876	0.48015
H	0.4073	0.4079	0.48728
H	0.39707	0.44531	0.29787
H	0.39769	0.44132	0.74836

Table S3. Detailed atom information of the simulated AA stacking N-TAPB-MeTA.

a = 37.41 Å, b = 37.41 Å, c = 3.66 Å; $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$; Space group P6(C6-1)			
	x	y	z
C	0.55852	0.47073	0.44833
C	0.64735	0.29129	0.50258
N	0.68922	0.31417	0.50259
C	0.61924	0.37364	0.50396
C	0.63871	0.41692	0.52272
C	0.61543	0.43672	0.52566
C	0.57206	0.41354	0.50661
C	0.55267	0.37047	0.49235
C	0.5759	0.35062	0.48958
N	0.54656	0.43222	0.51416
C	0.52895	0.48613	0.47162
C	0.48632	0.45784	0.4788
C	0.45731	0.47115	0.48601
H	0.58992	0.49172	0.3656
H	0.672	0.43559	0.53833
H	0.6316	0.46995	0.54982
H	0.51932	0.35218	0.48178
H	0.55983	0.31725	0.47629
H	0.4754	0.425	0.47729
C	0.41225	0.43909	0.51986
H	0.40829	0.41051	0.65037
H	0.39752	0.43072	0.24926
H	0.39547	0.45061	0.68779

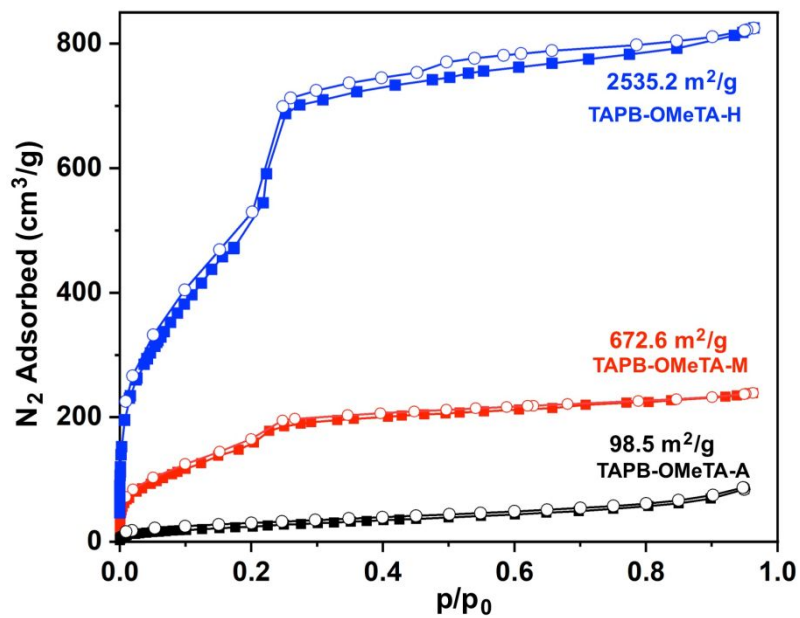


Figure S10. N₂ sorption isotherms of TAPB-OMeTA-H (blue), TAPB-OMeTA-M (red), and TAPB-OMeTA-A (black) at 77 K (closed, adsorption; open, desorption).

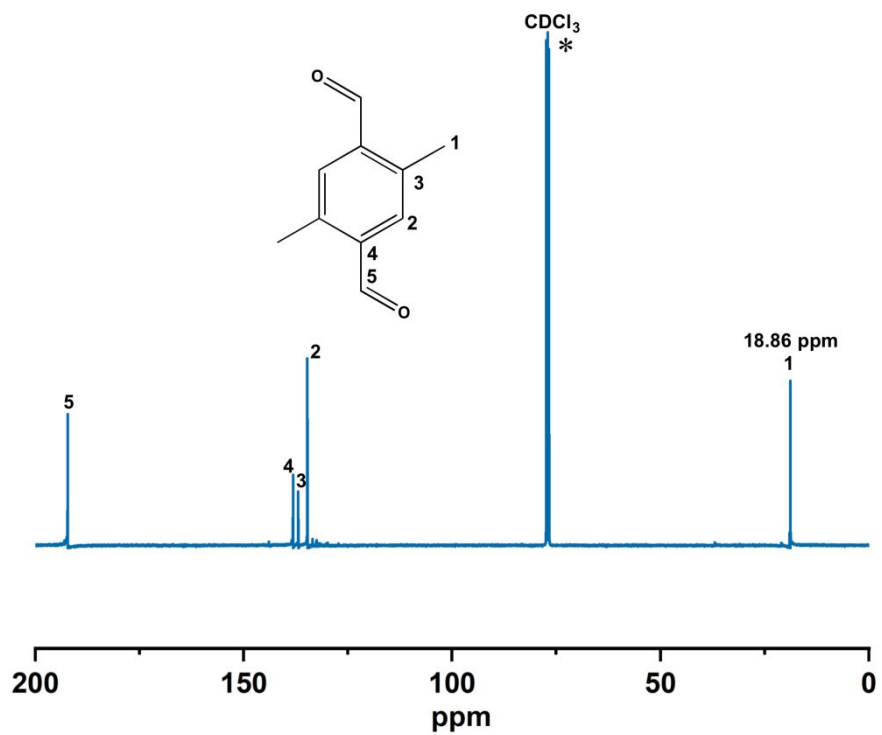


Figure S11. ¹³C NMR spectrum of MeTA monomer in CDCl₃.

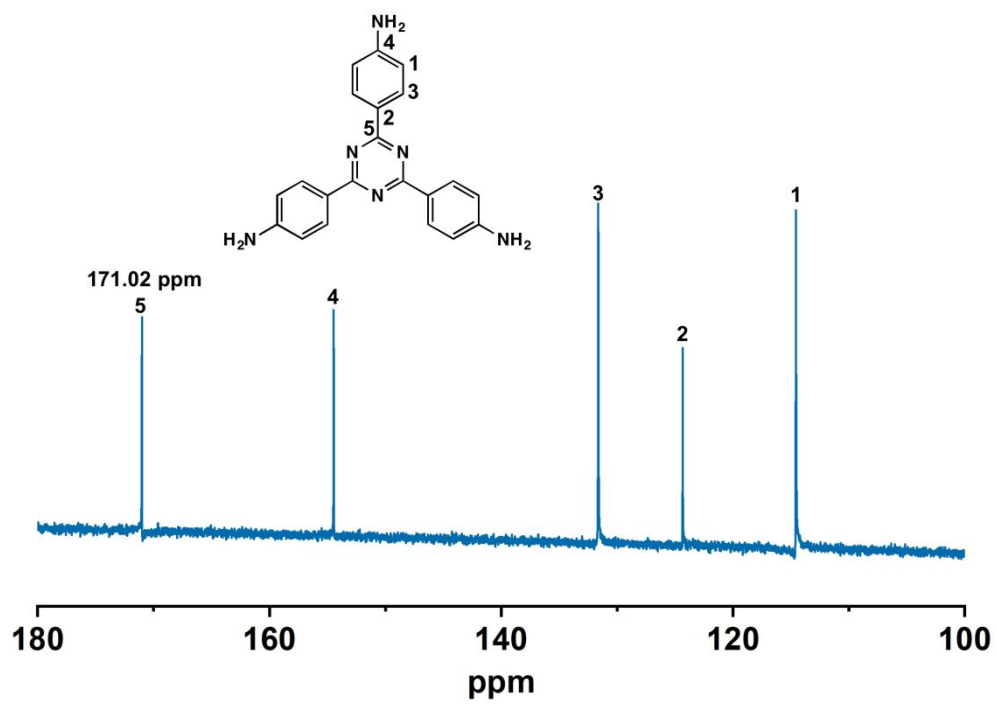


Figure S12. ^{13}C NMR spectrum of N-TAPB monomer in $\text{DMSO-}d_6$.

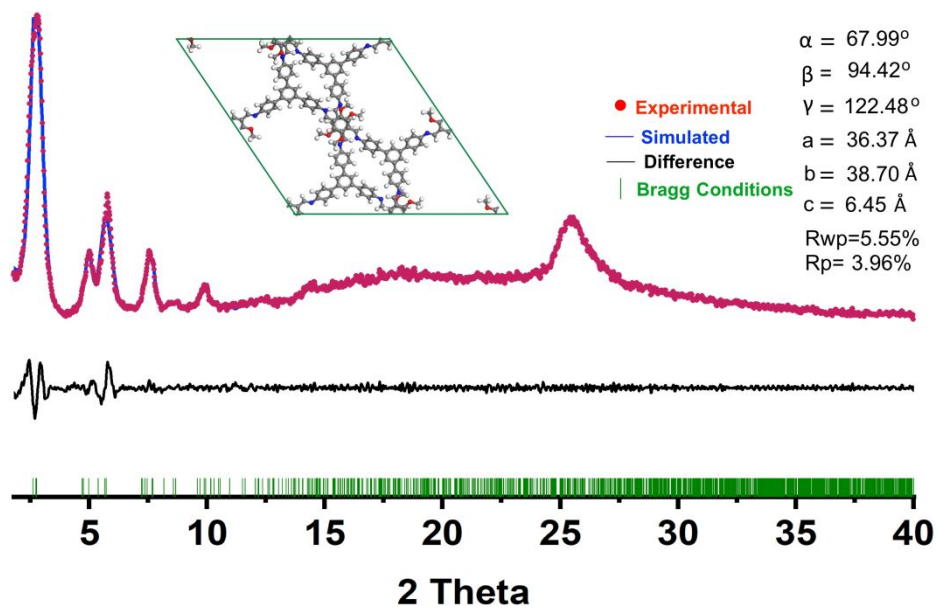


Figure S13. Pawley refinement of CDCl_3 -solvated TAPB-OMeTA-H structure.

Table S4. Detailed atom information of the simulated quasi-AB stacking TAPB-OMeTA-H in CDCl_3 .

a = 36.37, b = 38.70, c = 6.45; $\alpha = 67.99^\circ$, $\beta = 94.42^\circ$, $\gamma = 122.48^\circ$; P1 space group			
	x	y	z
C	0.53476	-0.03493	0.3537
C	0.62353	-0.20908	0.2095
C	0.66832	-0.18442	0.20879
C	0.68738	-0.14313	0.22389
C	0.66131	-0.1264	0.24207
C	0.61638	-0.15048	0.24853
C	0.59766	-0.19191	0.23104
C	0.58959	-0.13178	0.27204
C	0.6043	-0.25268	0.18796
C	0.73469	-0.11712	0.21896
C	0.60053	-0.1011	0.40283
C	0.57739	-0.08163	0.41677
C	0.54307	-0.09194	0.2991
C	0.53072	-0.12377	0.17698
C	0.55396	-0.14346	0.16245
C	0.76329	-0.12134	0.08004
C	0.80795	-0.09582	0.07412
C	0.82526	-0.06575	0.2096
C	0.79761	-0.06062	0.34916
C	0.753	-0.08519	0.35825
C	0.62629	-0.26544	0.05542
C	0.60997	-0.3064	0.04386
C	0.57089	-0.3353	0.15946
C	0.54819	-0.32283	0.2895
C	0.56482	-0.28178	0.30396
N	0.51966	-0.07128	0.30417
N	0.55688	-0.37697	0.15153
N	0.87093	-0.03881	0.20639
H	0.6885	-0.19745	0.20013
H	0.67626	-0.09422	0.24687
H	0.5631	-0.21071	0.2339
H	0.62674	-0.09251	0.49539
H	0.58639	-0.05869	0.52126
H	0.50375	-0.13262	0.089
H	0.54483	-0.16679	0.05986
H	0.75103	-0.14373	-0.02789
H	0.82853	-0.09968	-0.03972
H	0.81067	-0.03741	0.45244
H	0.73216	-0.081	0.46952
H	0.6564	-0.24388	-0.03889
H	0.62813	-0.31545	-0.05486
H	0.51845	-0.34447	0.38503
H	0.54739	-0.27298	0.4105
C	0.50892	-0.01534	0.35737
C	0.46369	-0.03732	0.36221
C	0.4417	-0.01607	0.36506
C	0.46401	0.02601	0.36199
C	0.50918	0.04779	0.36191
C	0.53103	0.02651	0.35953
C	0.43869	0.04586	0.34741
N	0.45509	0.08392	0.36635
H	0.56792	-0.01717	0.38433
H	0.40708	-0.03195	0.36651
H	0.56552	0.04219	0.3593
H	0.40537	0.02763	0.3189
C	0.4325	0.10487	0.33607
C	0.40291	0.09441	0.19098
C	0.38101	0.11484	0.1665
C	0.38822	0.14627	0.28642

C	0.41889	0.15751	0.42671
C	0.44113	0.1372	0.44974
C	0.36316	0.16646	0.26541
C	0.31908	0.14349	0.24374
C	0.29481	0.16186	0.21717
C	0.3151	0.20379	0.2161
C	0.35886	0.22725	0.24278
C	0.38284	0.20845	0.26565
C	0.24827	0.13709	0.19323
C	0.37917	0.27133	0.25025
C	0.23322	0.10462	0.07295
C	0.18933	0.08097	0.05331
C	0.15963	0.08942	0.1518
C	0.17448	0.12175	0.27314
C	0.2183	0.14534	0.29326
C	0.35598	0.2865	0.35427
C	0.3741	0.32793	0.35623
C	0.41587	0.35496	0.25908
C	0.43959	0.34013	0.15624
C	0.42127	0.29854	0.15188
N	0.43164	0.39718	0.25666
N	0.1147	0.06336	0.13155
H	0.39702	0.07072	0.09431
H	0.35845	0.1061	0.05359
H	0.425	0.1813	0.52267
H	0.46431	0.14586	0.56014
H	0.30322	0.11104	0.25212
H	0.29685	0.21827	0.19023
H	0.41666	0.22633	0.28469
H	0.25546	0.09766	-0.00774
H	0.17845	0.0562	-0.0406
H	0.15232	0.12825	0.35739
H	0.22876	0.16967	0.39025
H	0.32373	0.2665	0.43372
H	0.35548	0.33908	0.43417
H	0.4714	0.36036	0.07323
H	0.4396	0.28773	0.06753
C	0.08473	0.07195	0.16536
H	0.09288	0.1014	0.20722
C	0.90148	-0.04373	0.12525
H	0.89375	-0.071	0.0571
C	0.50686	-0.44937	0.19569
C	0.51755	-0.40696	0.19419
H	0.49144	-0.4014	0.22863
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O	0.44225	-0.07958	0.36891
C	0.39635	-0.10225	0.37241
C	0.4648	0.5216	0.21225
C	0.45103	0.48015	0.22204
C	0.48251	0.469	0.21579
C	0.52614	0.4991	0.19773
C	0.53899	-0.45986	0.18744
C	0.47142	0.4265	0.22308
C	0.94773	-0.01333	0.13307
C	0.97836	-0.0232	0.06562
C	0.02538	0.00507	0.07015
C	0.0388	0.04215	0.14894
C	0.0082	0.05228	0.21333
C	0.96135	0.02438	0.20544
O	0.58275	-0.4286	0.17087
C	0.61551	-0.43863	0.1643

O	0.40709	0.44964	0.23581
C	0.37503	0.46046	0.23674
O	0.05696	-0.00377	-0.00237
C	0.04291	-0.04163	-0.08045
O	0.93013	0.03452	0.26379
C	0.94416	0.07273	0.33658
H	0.58965	0.10776	0.18807
H	0.58968	0.10466	0.46795
H	0.588	0.14527	0.33064
H	0.38502	-0.13479	0.38568
H	0.38695	-0.09461	0.22708
H	0.38029	-0.09723	0.50962
H	0.44119	-0.4694	0.21822
H	0.54983	0.49019	0.19182
H	0.49727	0.42031	0.20159
H	0.96725	-0.05214	0.00994
H	0.01938	0.08102	0.27254
H	0.61567	-0.45379	0.0241
H	0.61147	0.54242	0.3085
H	0.64726	-0.41034	0.15434
H	0.34277	0.4325	0.24813
H	0.37997	0.47917	0.08977
H	0.37547	0.4764	0.37355
H	0.07164	-0.04357	-0.13025
H	0.02591	-0.04395	-0.21827
H	0.02204	-0.06674	0.04315
H	0.96667	0.09742	0.21401
H	0.95924	0.07499	0.48112
H	0.91554	0.07549	0.37394
C	0.54955	0.47174	0.7214
C	0.63253	0.29203	0.8084
C	0.67718	0.31665	0.81571
C	0.69724	0.35874	0.79978
C	0.67191	0.37619	0.78252
C	0.62699	0.35225	0.78318
C	0.60757	0.31008	0.7941
C	0.60101	0.37178	0.77293
C	0.61266	0.24755	0.81307
C	0.74455	0.38452	0.80139
C	0.61111	0.40515	0.88193
C	0.58868	0.42531	0.86502
C	0.5554	0.4124	0.73861
C	0.54376	0.37799	0.63738
C	0.56654	0.35795	0.65274
C	0.77328	0.37488	0.70205
C	0.81781	0.39995	0.70056
C	0.83513	0.43553	0.7982
C	0.80751	0.44638	0.89667
C	0.76294	0.42203	0.9032
C	0.63533	0.23194	0.70836
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N	0.53267	0.43329	0.71284
N	0.56108	0.12144	0.82586
N	0.88066	0.46205	0.7973
H	0.6963	0.30295	0.83583
H	0.68748	0.40875	0.76329
H	0.57306	0.2914	0.79224
H	0.6365	0.41577	0.98085
H	0.59697	0.45059	0.95263

H	0.51772	0.36732	0.54194
H	0.55787	0.33236	0.56628
H	0.7614	0.34827	0.62146
H	0.8387	0.39156	0.61921
H	0.82079	0.47381	0.97113
H	0.74223	0.43046	0.98593
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H	0.63589	0.17916	0.63469
H	0.52241	0.15858	1.01774
H	0.5535	0.23141	1.00779
C	0.52415	0.49165	0.70631
C	0.4787	0.46969	0.71902
C	0.45689	0.49107	0.71671
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C	0.4538	0.55299	0.69752
N	0.47006	0.59052	0.72973
H	0.58331	0.49033	0.73985
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H	0.58141	0.54989	0.68051
H	0.42035	0.5352	0.6723
C	0.4473	0.61153	0.72095
C	0.41549	0.60201	0.58868
C	0.39269	0.62197	0.58911
C	0.40133	0.65207	0.72044
C	0.43469	0.66285	0.84551
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N	0.12183	0.56132	0.71735
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H	0.36833	0.61384	0.48526
H	0.44212	0.68577	0.94955
H	0.48284	0.65114	0.94303
H	0.31537	0.6152	0.71272
H	0.30292	0.71855	0.74812
H	0.427	0.73052	0.76498
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C	0.0915	0.5676	0.78588
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C	0.51045	0.04975	0.86411
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O	0.45683	0.42709	0.73608
C	0.41076	0.40455	0.75628
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C	0.4535	0.97922	0.86201
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C	0.98605	0.47019	0.74728
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C	0.01587	0.55043	0.80205
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H	0.97719	0.59787	0.7214
H	0.97089	0.58412	1.00192
H	0.92666	0.58021	0.87935

References

- (1) Harris, R. K.; Becker, E. D.; Cabral De Menezes, S. M.; Goodfellow, R.; Granger, P. NMR Nomenclature: Nuclear Spin Properties and Conventions for Chemical Shifts (IUPAC Recommendations 2001). *Int. Union Pure Appl. Chem.* **2002**, *1* (1), 43–64.
- (2) Harris, R. K.; Becker, E. D.; Cabral de Menezes, S. M.; Granger, P.; Hoffman, R. E.; Zilm, K. W. Further Conventions for NMR Shielding and Chemical Shifts (IUPAC Recommendations 2008). *Pure Appl. Chem.* **2008**, *80* (1), 59–84.
- (3) Kang, C.; Zhang, Z.; Wee, V.; Usadi, A. K.; Calabro, D. C.; Baugh, L. S.; Wang, S.; Wang, Y.; Zhao, D. Interlayer Shifting in Two-Dimensional Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2020**, *142* (30), 12995–13002.
- (4) Xu, H.; Gao, J.; Jiang, D. Stable, Crystalline, Porous, Covalent Organic Frameworks as a Platform for Chiral Organocatalysts. *Nat. Chem.* **2015**, *7* (11), 905–912.
- (5) Gomes, R.; Bhanja, P.; Bhaumik, A. A Triazine-Based Covalent Organic Polymer for Efficient CO₂ Adsorption. *Chem. Commun.* **2015**, *51* (49), 10050–10053.
- (6) Sun, Q.; Fu, C.-W.; Aguila, B.; Perman, J.; Wang, S.; Huang, H.-Y.; Xiao, F.-S.; Ma, S. Pore Environment Control and Enhanced Performance of Enzymes Infiltrated in Covalent Organic Frameworks. *J. Am. Chem. Soc.* **2018**, *140* (3), 984–992.
- (7) Krishnaraj, C.; Sekhar Jena, H.; Bourda, L.; Laemont, A.; Pachfule, P.; Roeser, J.; Chandran, C. V.; Borgmans, S.; Rogge, S. M. J.; Leus, K.; Stevens, C. V.; Martens, J. A.; Van Speybroeck, V.; Breynaert, E.; Thomas, A.; Van Der Voort, P. Strongly Reducing (Diarylamino)Benzene-Based Covalent Organic Framework for Metal-Free Visible Light Photocatalytic H₂O₂ Generation. *J. Am. Chem. Soc.* **2020**, *142* (47), 20107–20116.
- (8) Feriante, C. H.; Jhulki, S.; Evans, A. M.; Dasari, R. R.; Slicker, K.; Dichtel, W. R.; Marder, S. R. Rapid Synthesis of High Surface Area Imine-Linked 2D Covalent Organic Frameworks by Avoiding Pore Collapse During Isolation. *Adv. Mater.* **2020**, *32* (2), 1905776.