Electronic Supplementary Information

Converting an amorphous covalent organic polymer to a crystalline covalent organic framework mediated by a repairing agent

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Section A Instruments and General Methods

Nuclear magnetic resonance spectroscopy (NMR)

^{1}H NMR and ^{13}C NMR data were recorded on a 500 MHz Agilent spectrometer with $CDCl_3$ as the solvent. ^{1}H chemical shifts were referenced to $CDCl_3$ at 7.26 ppm and ^{13}C chemical shifts were referenced to $CDCl_3$ at 77.16 ppm. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br).

Fourier transform infrared spectroscopy (FT-IR)

Fourier transform infrared spectroscopy (FT-IR) was obtained with a Nicolet iS10 spectrometer.

Solid-state nuclear magnetic resonance (NMR) spectroscopy

Solid-state ^{13}C cross-polarization/magic angle spinning (CP/MAS) spectra were collected on an Agilent DD2 600 Solid system equipped with a 3.2 mm HFXY MAS probe. The Hartmann-Hahn conditions of the CP experiment were acquired at a 15 kHz MAS spinning speed with a contact time of 2.0 ms. The cycle time is 5 s.

Scanning electron microscopy (SEM)

Scanning electron microscopy was carried out using an XL30 FEG scanning electron microscope. The samples were dispersed over a slice of conductive adhesive adhered to a flat copper platform sample holder and then coated with gold using a sputter 9 coater (ambient temperature, 85 torr pressure in a nitrogen atmosphere, sputtered for 80 s from a solid gold target at a current of 20 mA) before being submitted to SEM characterization.

Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis was performed on Waters TGA Q500 by heating the samples from 25 to 1000 ^oC under N_2 atmosphere at a heating rate of 10 ^oC /min.

Powder X-ray diffraction (PXRD)

Powder X-ray diffraction measurements were carried out with an X'Pert PROX system using monochromated Cu/Kα (λ = 0.1542 nm). Each sample was spread on the square recess of a XRD sample holder as a thin layer.

Nitrogen adsorption-desorption isotherm measurements

The measurements were carried out using a Quantachrome Autosorb-IQ instrument or a Micromeritics ASAP 2020 system. Before gas adsorption measurements, the as-prepared samples (~50 mg) were activated by being immersed in anhydrous THF for 12 h. The solvent was decanted and the samples were dried under dynamic vacuum at 160 ^{o}C for 6 h. The resulting samples were then used for gas adsorption measurements from 0 to 1 atm at 77 K. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas. By using the non-local density functional theory model, the pore size distributions were derived from the adsorption data.

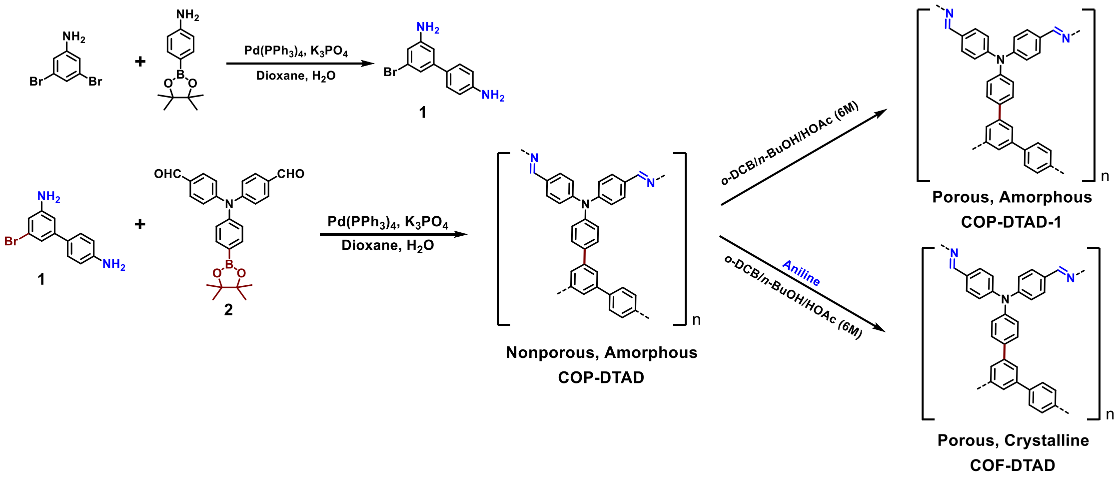
Structural simulations and powder X-ray diffraction analysis

Structural modeling was carried out using the Materials Studio 7.0. The predicted structures with eclipsed (AA) and staggered (AB) stacking models were firstly optimized in geometry optimizations by the Forcite molecular dynamics module method, after which the simulated PXRD patterns were determined by the Reflex module. The Pawley refinement of the experimental PXRD was conducted by the Reflex module.

Section B Synthesis

Materials: All the anhydrous solvents were purchased from Sigma-Aldrich or Alfa Chemicals Inc. All the chemicals and solvents were reagent grades and purchased from Aldrich, TCI, Macklin or other chemical companies and used without further purification.

Synthetic route:



5-bromo-[1,1'-biphenyl]-3,4'-diamine (compound 1): To a mixture of 3,5-dibromoaniline (5.0 g, 20.0 mmol), K_3PO_4 (8.6 g, 40.5 mmol), $Pd(PPh_3)_4$ (0.60 g, 0.52 mmol) and 4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)aniline (2.94 g, 13.4 mmol), a degassed mixture of 1,4-dioxane (180 mL) and H_2O (8 mL) was added. The mixture was heated at 90 °C for 24 h under the protection of nitrogen. After being cooled to room temperature, the solvent was removed under vacuum and the residue was purified by flash column chromatography to give a light gray solid (2.06 g, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 8.5 Hz, 2H), 7.06 (s, 1H), 6.74 (d, J = 1.3 Hz, 2H), 6.72 (d, J = 8.5 Hz, 2H), 3.74 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.95 (s), 146.40 (s), 144.10 (s), 130.29 (s), 128.04 (s), 123.41 (s), 119.85 (s), 115.82 (s), 115.36 (s), 111.83 (s).

HR-MS (EI) m/z calculated for $[M+H, C_{12}H_{12}BrN_2]^+$: 263.0181; found: 263.0178.

Procedure for the preparation of COP-DTAD

To a mixture of 5-bromo-[1,1'-biphenyl]-3,4'-diamine (1.82 g, 6.95 mmol), 4,4'-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)azanediyl)dibenzaldehyde (compound **2**, 3.00 g, 7.02 mmol),[1] K_3PO_4 (4.43 g, 20.87 mmol) and $Pd(PPh_3)_4$ (0.40 g, 0.35 mmol), a degassed mixture of 1,4-dioxane (150 mL) and H_2O (8 mL) was added. The mixture was heated at 90 ºC for 24 h under the protection of nitrogen. The reaction solution was filtered through celite, and a clear golden liquid was obtained. The solvent was quickly removed in a 50 ºC water bath under vacuum to afford COP-DTAD as a lumpy golden solid (3.04 g), which was insoluble in common organic solvents such as ethyl acetate, dichloromethane, tetrahydrofuran, 1,4-dioxane and dimethylacetamide, etc. Anal. Calcd. for chemical formula $C_{96}H_{63}N_9$: C, 85.88; H, 4.73; N, 9.39. Found: C, 80.09; H, 5.29; N, 8.15.

Procedure for the preparation of COP-DTAD-1

COP-DTAD (100 mg) was added to a mixture of *o*-dichlorobenzene (0.5 mL), *n*-butanol (0.5 mL), and acetic acid (6 M (aq.), 0.1 mL) in a glass ampoule. The ampoule was degassed through three freeze-pump-thaw cycles and then flame-sealed. After being heated at 120 ºC for three days in an oven, the ampoule was opened and the resulting precipitate was collected through filtration, and washed three times with anhydrous THF to afford a yellow powder, which was further immersed in anhydrous THF for 3 times and then dried under dynamic vacuum at 120 ºC for 2 h to give COP-DTAD-1 (76.2 mg, 76%). It is insoluble in common organic solvents such as ethyl acetate, dichloromethane, tetrahydrofuran, 1,4-dioxane and dimethylacetamide, etc. Anal. Calcd. for chemical formula $C_{96}H_{63}N_9$: C, 85.88; H, 4.73; N, 9.39. Found: C, 80.41; H, 4.97; N, 8.60.

Procedure for the preparation of COF-DTAD

COP-DTAD (100 mg) and aniline (27.2 μL) were added to a mixture of *o*-dichlorobenzene (0.5 mL), *n*-butanol (0.5 mL), and acetic acid (6 M (aq.), 0.1 mL) in a glass ampoule. The ampoule was degassed through three freeze-pump-thaw cycles, flame-sealed, and heated at 120 ºC for three days in an oven. After being cooled to room temperature, the resulting precipitate was collected through filtration, washed three times with anhydrous THF, and the as-obtained powder was immersed in anhydrous THF for 3 times and then dried under dynamic vacuum at 120 ºC for 2 h to afford COF-DTAD as a yellow powder (70.6 mg, 71%). COF-DTAD is insoluble in common organic solvents such as ethyl acetate, dichloromethane, tetrahydrofuran, 1,4-dioxane and dimethylacetamide, etc. Anal. Calcd. for chemical formula $C_{96}H_{63}N_9$: C, 85.88; H, 4.73; N, 9.39. Found: C, 83.24; H, 4.74; N, 9.10.

For the studies using different equivalents of aniline or different time, the above procedure was followed.

Reference for the synthesis:

1 Z.-J. Yin, S.-Q. Xu, T.-G. Zhan, Q.-Y. Qi, Z.-Q. Wu and X. Zhao, *Chem. Commun.*, 2017, **53**, 7266-7269.

Section C Characterization of COP-DTAD, COP-DTAD-1, and COF-DTAD

Fig. S1 Photographs of (a) COP-DTAD, (b) COP-DTAD-1, and (c) COF-DTAD.

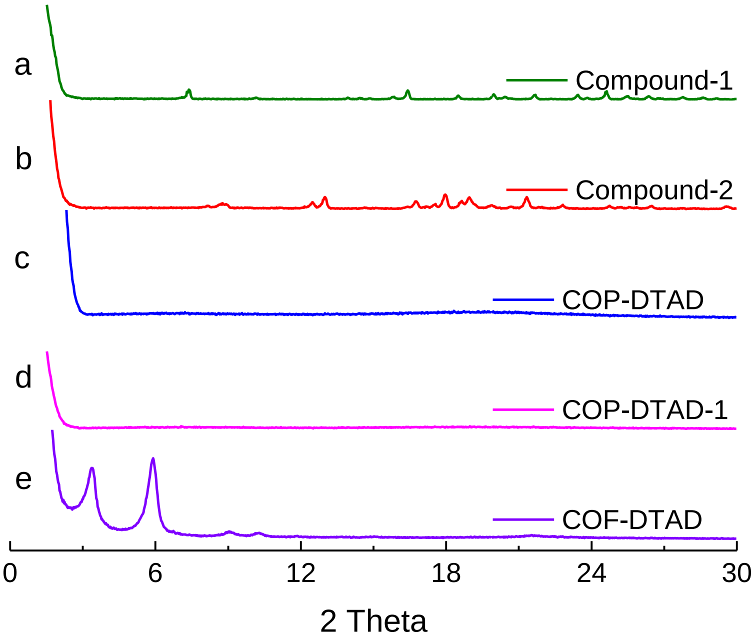


Fig. S2 PXRD patterns of (a) compound **1**, (b) compound **2**, (c) COP-DTAD**,** (d) COP-DTAD-1, and (e) COF-DTAD.

Table S1. Attempts to converting COP-DTAD to COF-DTAD in different solvents without aniline additive.

Entry	Solvent (1 mL)	Catalyst (0.1 mL)	Temperature	Time
1	Mes/*n*-BuOH= 1/1	6.0 mol/L HOAc	120 °C	72 h
2	Mes			
3	*n*-BuOH			
4	*o*-DCB/ EtOH = 1/1			
5	Mes/ Dio= 1/1			
6	*o*-DCB/ *n*-BuOH = 1/1			
7	Dio			
8	DMSO/ Mes = 1/1			
9	DMSO/ *o*-DCB = 1/1			
10	*o*-DCB/ *t*-BuOH = 1/1			
11	*o*-DCB/ *i*-PrOH = 1/1			
12	*o*-DCB/ *glycol* = 1/1			

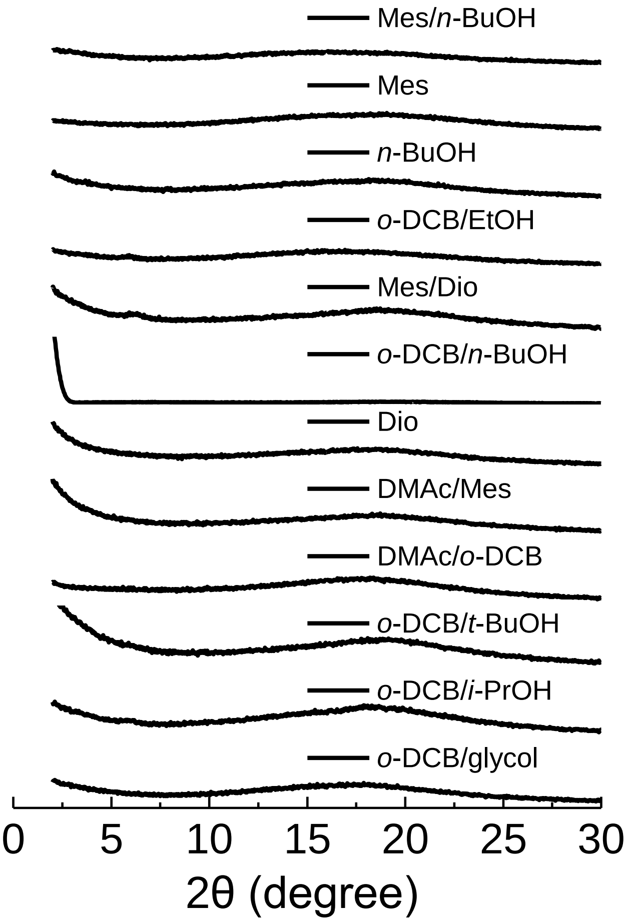


Fig. S3 PXRD patterns of the polymers obtained by heating COP-DTAD in different solvents.

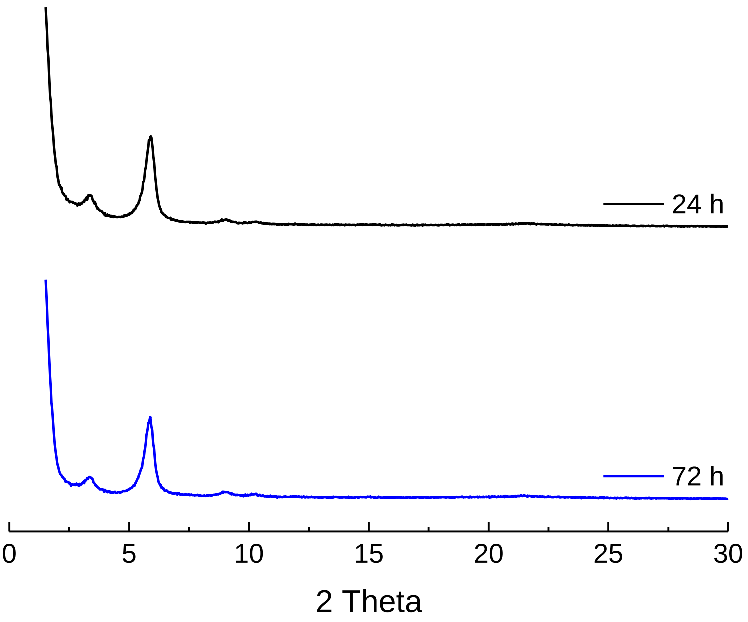
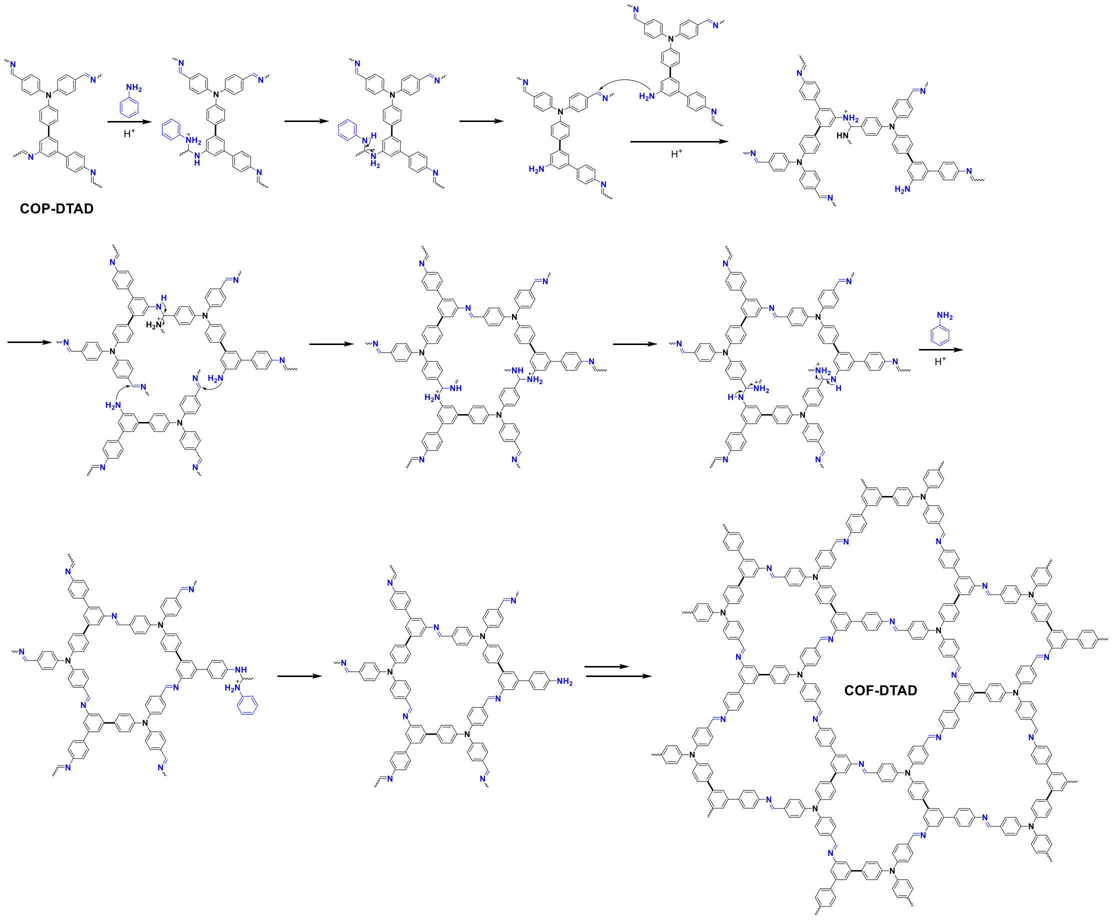


Fig. S4 PXRD patterns of COF-DTAD prepared by heating mixtures of COP-DTAD and 4 equivalents of aniline for 24 h and 72 h, respectively.



Scheme S1 The proposed mechanism for the conversion from COP-DTAD to COF-DTAD.

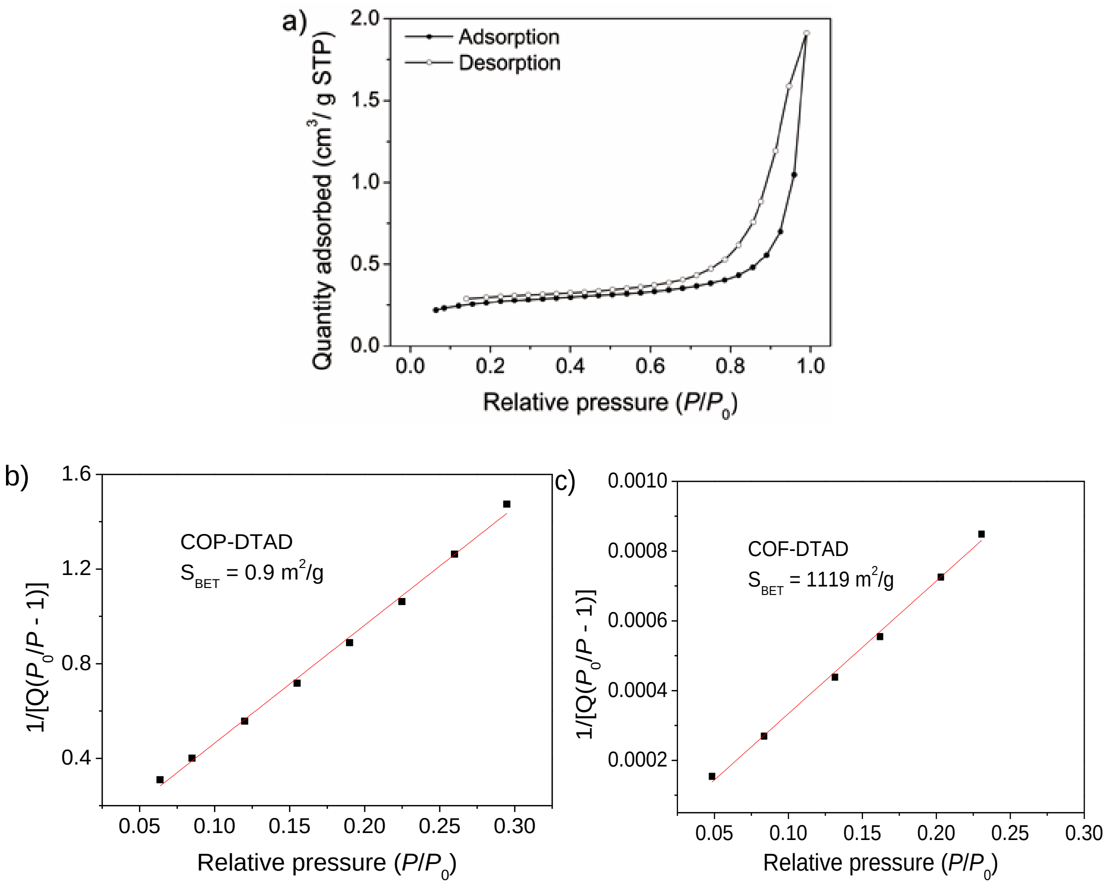


Fig. S5 (a) N_2 adsorption−desorption isotherm (77 K) of COP-DTAD, and BET surface area plots for (b) COP-DTAD and (c) COF-DTAD calculated from their adsorption data.

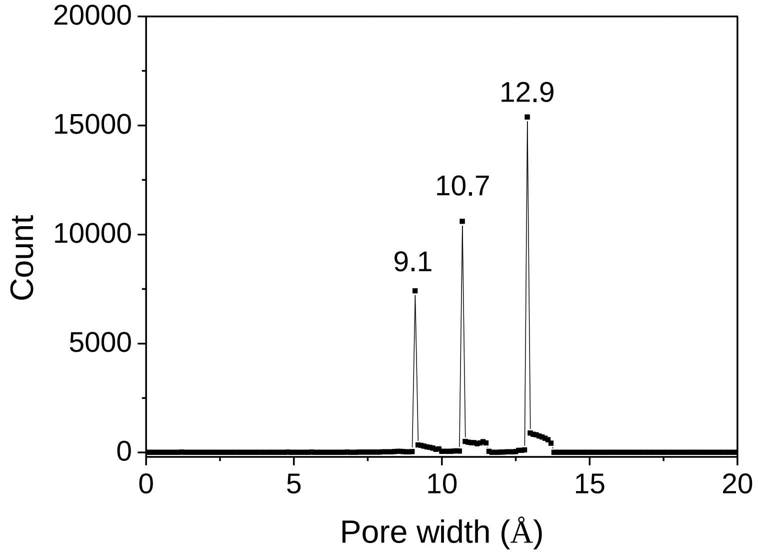


Fig. S6 Illustration of the theoretical pore size distribution for COF-DTAD with eclipsed AA stacking based on Zeo++ calculations.

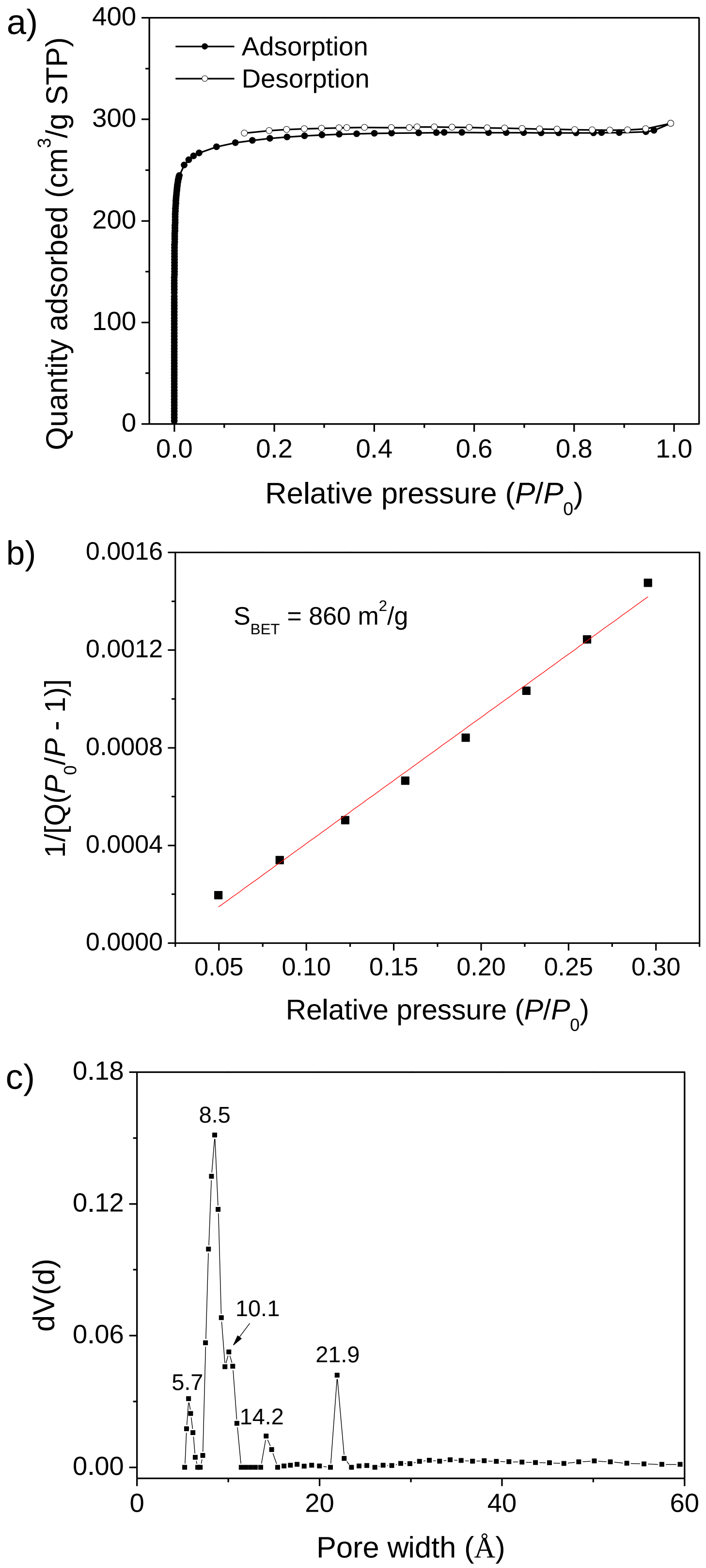


Fig. S7 (a) N_2 adsorption−desorption isotherm (77 K), (b) BET surface area plot, and (c) pore size distribution profile of COP-DTAD-1 calculated from the adsorption data.

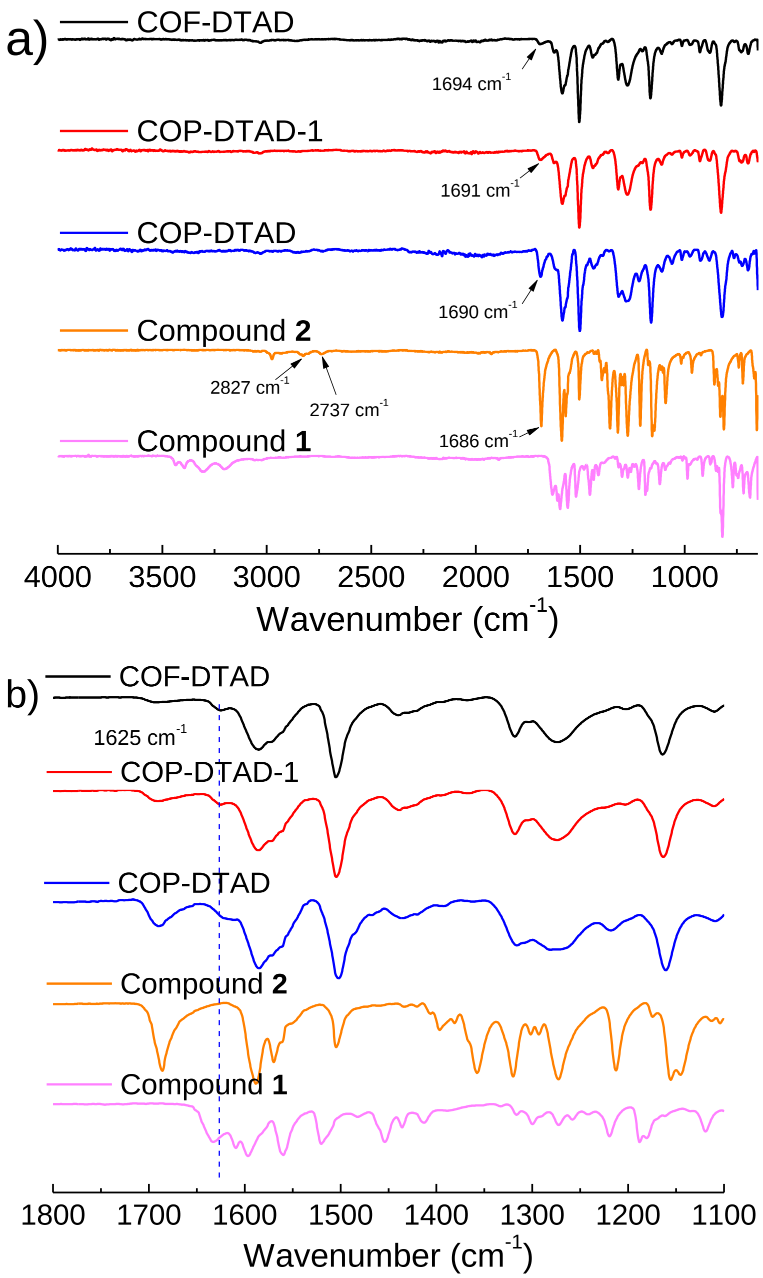


Fig. S8 FT-IR spectra of compound **1**, compound **2**, COP-DTAD, COP-DTAD-1, and COF-DTAD at the wavenumber of (a) 4000–650 cm^{-1} and (b) 1800–1100 cm^{-1}.

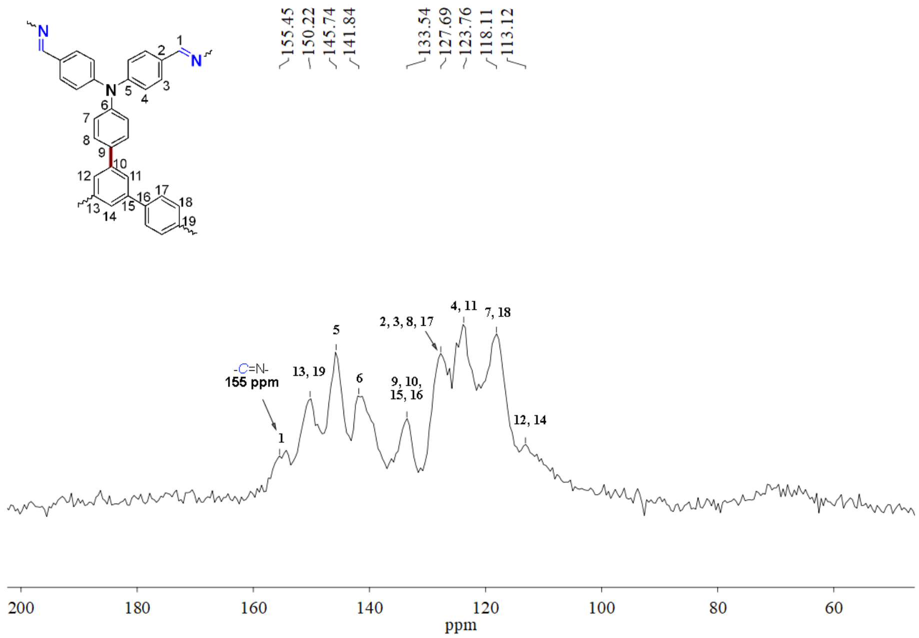


Fig. S9 Solid-state ^{13}C CP/MAS NMR spectrum of COF-DTAD.

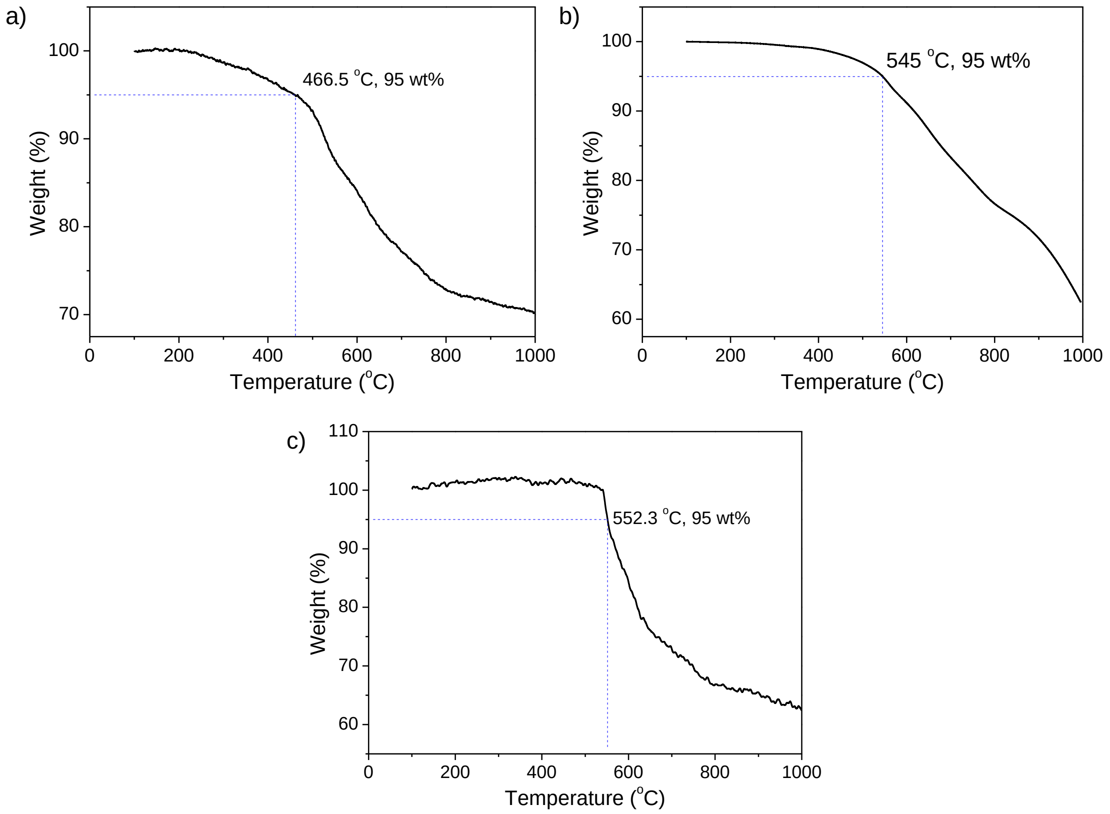


Fig. S10 TGA profiles of (a) COP-DTAD, (b) COP-DTAD-1, and (c) COF-DTAD.

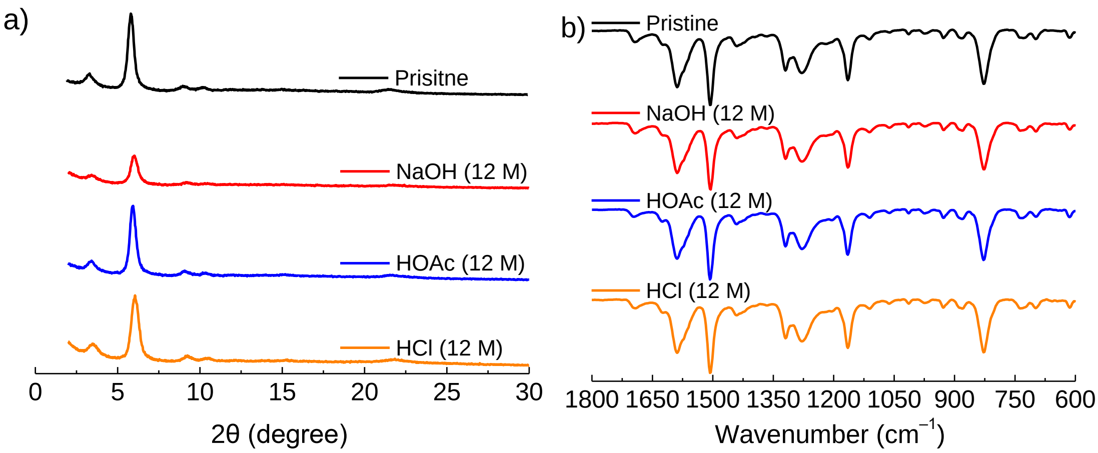


Fig. S11 (a) PXRD patterns and (b) FT-IR spectra of COF-DTAD upon treatment in aqueous solutions of HOAc (12 M), HCl (12 M), and NaOH (12 M) at 25 °C for 3 days, respectively.

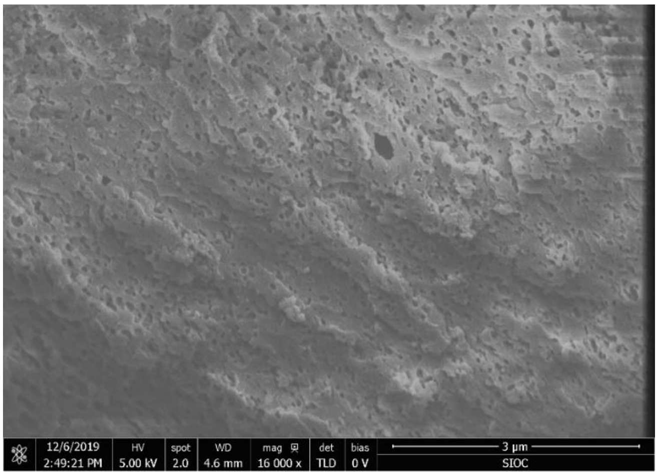


Fig. S12 Field-emission SEM image of COP-DTAD.

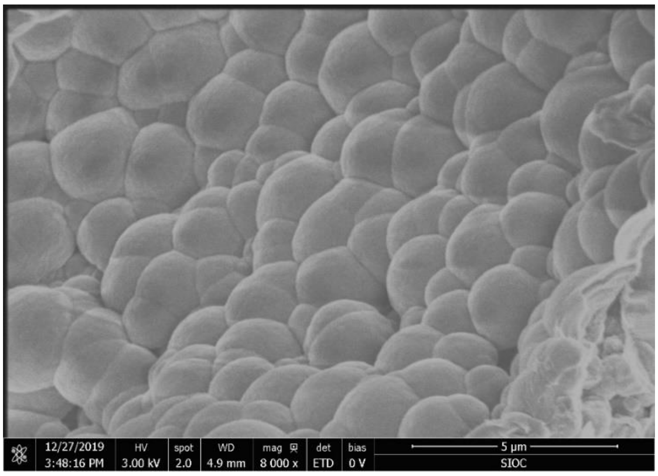


Fig. S13 Field-emission SEM image of COF-DTAD.

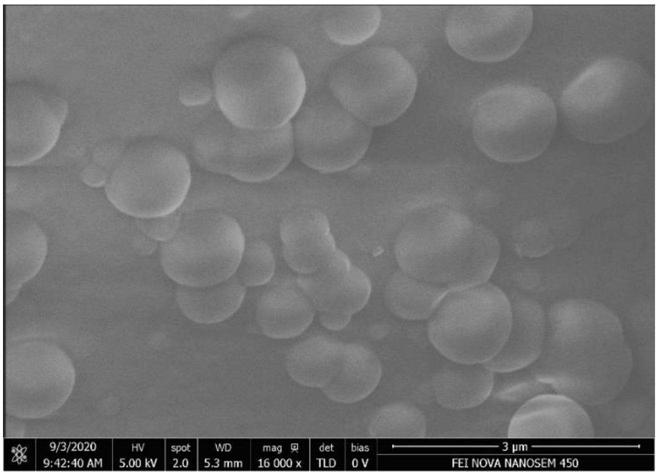


Fig. S14 Field-emission SEM image of COP-DTAD-1.

Section D Fractional atomic coordinates

Table S2 The space groups and cell parameters of the predicted structures of COF-DTAD with AA and AB stacking.

Structure	Space Group	Cell Parameters
AA	P3	a = b = 29.98 Å, c = 4.13 Å, α = β = 90° and γ = 120°
AB	P3(C3-1)	a = b = 29.98 Å, c = 8.26 Å, α = β = 90° and γ = 120°

Table S3 Fractional atomic coordinates for the unit cell of COF-DTAD with AA stacking.

P3									
a = b = 29.98 Å, c = 4.13 Å, α = β = 90° and γ = 120° (residuals R_p = 3.81 %, R_{wp} = 5.52 %)									
Element	Number	x	y	z	Element	Number	x	y	z
1	C	1.58523	-0.16168	0.18302	29	C	0.97536	-0.3386	-0.0828
2	C	1.58058	-0.21012	0.15577	30	C	1.35254	-0.58262	0.06558
3	C	1.65436	-0.17457	-0.20123	31	C	1.45077	-0.49355	0.08281
4	C	1.65842	-0.12641	-0.17604	32	C	1.39269	-0.5814	0.24783
5	C	1.62446	-0.11891	0.01938	33	C	1.44143	-0.53765	0.25362
6	N	1.62911	-0.06846	0.04674	34	C	1.41062	-0.49363	-0.0915
7	C	1.60631	-0.36369	-0.08437	35	C	1.36226	-0.53774	-0.10114
8	C	1.65456	-0.31877	-0.0724	36	H	1.55808	-0.15778	0.3329
9	C	1.65701	-0.27094	-0.05164	37	H	1.55064	-0.24187	0.29167
10	C	1.61201	-0.26765	-0.05478	38	H	1.68112	-0.17884	-0.35624
11	C	1.56404	-0.31297	-0.06833	39	H	1.68843	-0.09486	-0.3079
12	C	1.56108	-0.36086	-0.07137	40	H	1.60382	-0.40081	-0.10767
13	N	1.51153	-0.40619	-0.05927	41	H	1.69401	-0.23619	-0.02482
14	C	1.70237	-0.3216	-0.07334	42	H	1.52877	-0.31131	-0.07
15	C	1.61544	-0.21691	-0.03464	43	H	1.67149	-0.39097	0.21946
16	C	1.70457	-0.36162	0.08992	44	H	1.75168	-0.39374	0.22748
17	C	1.75027	-0.36311	0.09748	45	H	1.82593	-0.25517	-0.34474
18	C	1.7946	-0.32403	-0.04915	46	H	1.74561	-0.25333	-0.36975
19	C	1.79243	-0.28463	-0.2189	47	H	1.53287	-0.45013	0.21692
20	C	1.74656	-0.28362	-0.23252	48	H	1.89011	-0.24714	0.03141
21	N	1.84127	-0.32556	-0.02677	49	H	1.05714	-0.22105	0.24165
22	C	1.50255	-0.44827	0.0853	50	H	0.98008	-0.21425	0.22276
23	C	1.88629	-0.28486	0.00317	51	H	0.89612	-0.36639	-0.19029
24	C	1.02203	-0.29829	0.04001	52	H	0.97224	-0.37394	-0.1674
25	C	1.02249	-0.25357	0.15127	53	H	1.38677	-0.61482	0.37872
26	C	0.97836	-0.24924	0.1375	54	H	1.47182	-0.53827	0.3919
27	C	0.93243	-0.28978	0.01645	55	H	1.41667	-0.46002	-0.22591
28	C	0.93117	-0.33455	-0.09328	56	H	1.33262	-0.53661	-0.24101

Section E ^{1}H NMR and ^{13}C NMR spectra of compound 1

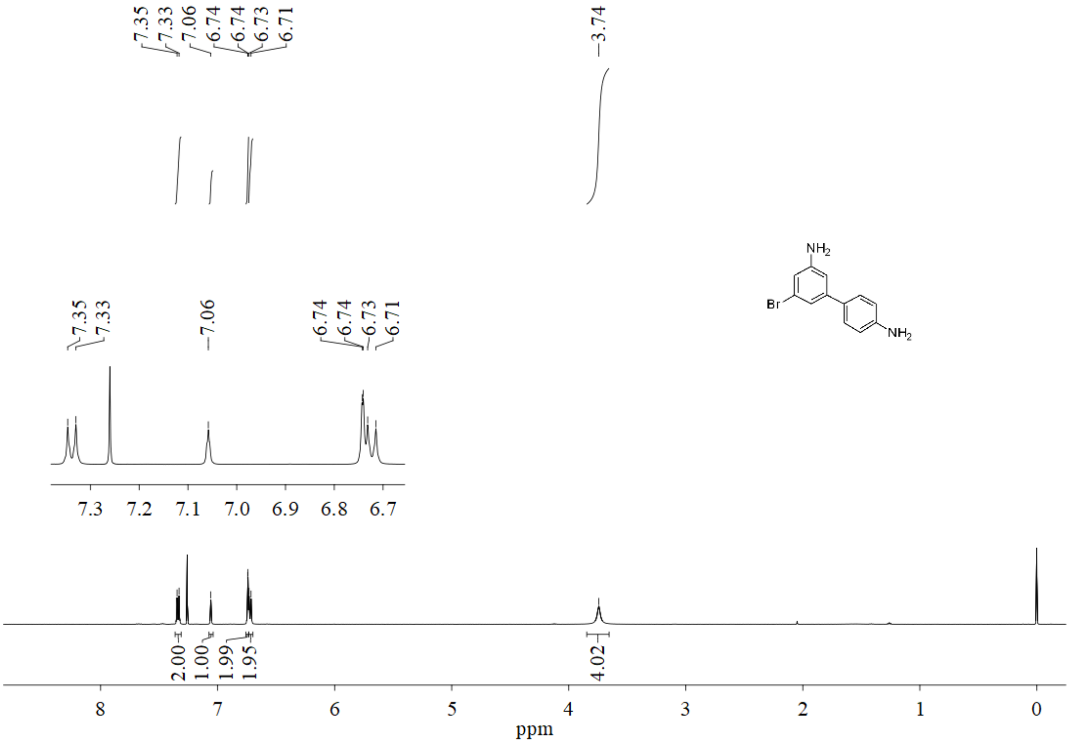


Fig. S15 ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 25 °C) of compound **1**.

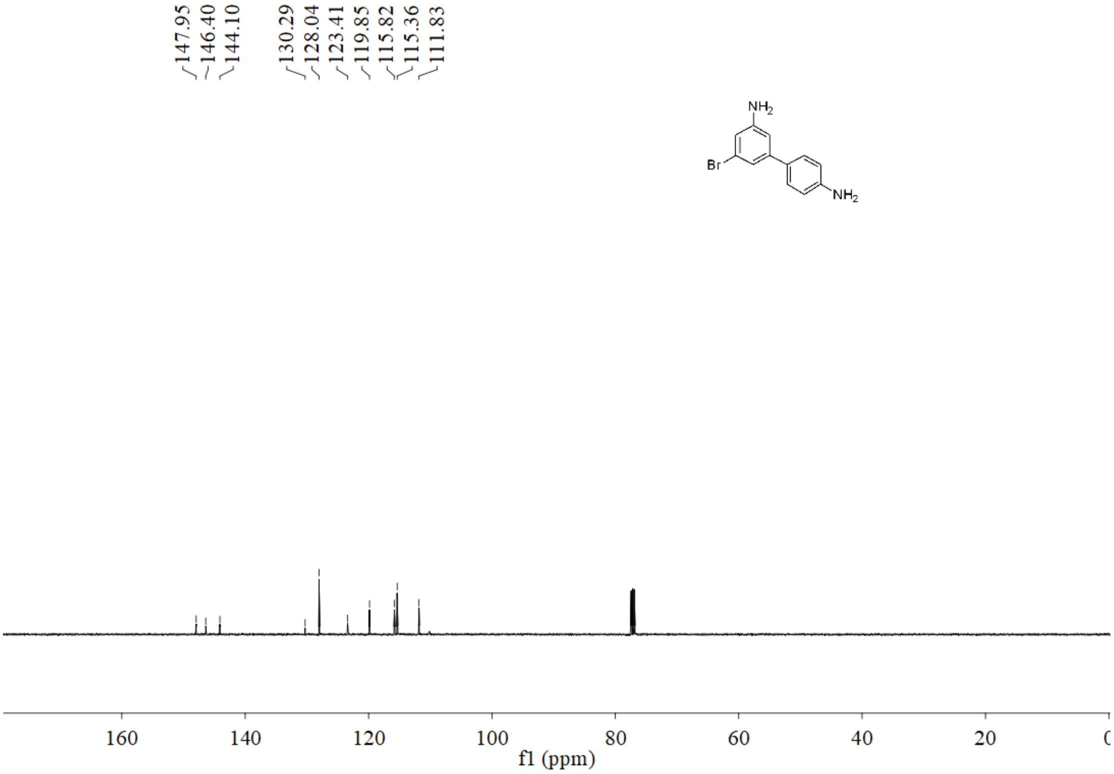


Fig. S16 ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) spectrum of compound **1**.