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Supporting Information for

Strategic Design of Triphenylamine- and Triphenyltriazine-Based Two-Dimensional Covalent Organic Frameworks for CO_2 Uptake and Energy Storage

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Contents

Section A. Characterization

Section B. Materials

Section C. Synthetic procedures

Section D. NMR spectral profiles

Section E. ESI

Section F. FT-IR spectral profiles

Section G. Elemental analysis

Section H. TGA profiles

Section I. PXRD patterns

Section J. SEM analysis

Section K. CO_2 isosteric heats of adsorption

Section L. Electrochemical analysis

Section A. Characterization

Proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were recorded using an INOVA 500 instrument with DMSO-d_6 and $CDCl_3$ as solvents and tetramethylsilane (TMS) as the external standard. Chemical shifts are provided in parts per million (ppm). Fourier transform mass spectra (electrospray ionization, ESI) of were recorded using a Bruker Solarix spectrometer. FTIR spectra were recorded using a Bruker Tensor 27 FTIR spectrophotometer and the conventional KBr plate method; 32 scans were collected at a resolution of 4 cm^{-1}. Solid state nuclear magnetic resonance (SSNMR) spectra were recorded using a Bruker Avance 400 NMR spectrometer and a Bruker magic angle spinning (MAS) probe, running 32,000 scans. Cross-polarization with MAS (CPMAS) was used to acquire ^{13}C NMR spectral data at 75.5 MHz. The CP contact time was 2 ms; ^{1}H decoupling was applied during data acquisition. The decoupling frequency corresponded to 32 kHz. The MAS sample spinning rate was 10 kHz. Elemental analysis (EA) was performed using an Elementar vario EL III apparatus. Powder X-ray diffraction (PXRD) was carried out with a Siemens D5000 using monochromated Cu/Kα ($\lambda = 0.1542$ nm). The sample was spread in a thin layer on the square recess of an XRD sample holder. Field emission scanning electron microscopy (FE-SEM) was conducted using a JEOL JSM-7610F scanning electron microscope. Samples were treated via Pt sputtering for 100 s prior to observation. BET surface area and porosimetry measurements of the prepared samples (ca. 20–100 mg) were performed using a Micromeritics ASAP 2020 Surface Area and Porosity analyzer. Nitrogen isotherms were generated through incremental exposure to ultrahigh-purity N_2 (up to ca. 1 atm) in a liquid nitrogen (77 K) bath. Carbon dioxide isotherms were generated using ultrahigh-purity CO_2 (to ca. 900 mmHg) in a water bath (295 K). Surface parameters were determined using BET adsorption models in the instrument's software. TGA was performed using a TA Q-50 analyzer under a flow of N_2 atmosphere. The samples were sealed in a Pt cell and heated from 40 to 800 °C at a heating rate of 20 °C min^{-1} under a flow of N_2 atmosphere at a flow rate of 50 mL min^{-1}. Molecular modeling was performed using Reflex, a software package for crystal determination from XRD patterns, implemented in MS modeling (v. 4.4, Accelrys). Unit cell dimensions were first manually determined from the observed XRD peak positions using the coordinates. The space group for the hexagonal crystal system was selected as *P*3.

For electrochemical measurement, the electrodes were prepared by coating slurries containing a COF powder (1 mg, 65 wt.%), a conducting agent (Super-P, 25 wt.%), and poly(vinylidene fluoride) binder (PVDF, 10 wt.%) dissolved in *N*-methyl-2-pyrrolidone (NMP)—on a carbon paper electrode. The electrodes were dried at 100 °C for 12 h in a vacuum oven. The electrochemical measurements were performed using an electrochemical workstation (CHI 660e, CH Instruments). For the three-electrode measurements, Ag/AgCl was used as the reference electrode and a Pt wire electrode as the counter electrode. All electrochemical measurements were performed using 0.5 M H_2SO_4 as the aqueous electrolyte. Gravimetric capacitances were calculated using the galvanostatic charge/discharge method and the following equation:

$$C_g = \frac{I \times \int V\,dt}{M \times \Delta V^2}$$

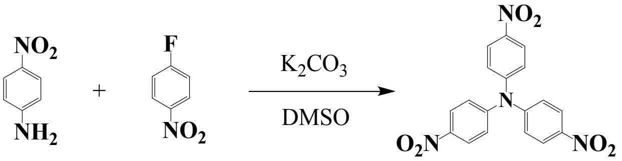
where C_g is the gravimetric capacitance (F g^{-1}), ΔV is the potential window, I is the current (A), t is the discharge time, and M is the total mass of active materials (in grams).

Section B. Materials

1-Fluoro-4-nitrobenzene (99%), trifluoromethanesulfonic acid (≥ 98%), 4-bromoacetophenone (≥ 98%), 4-bromobenzaldehyde (≥ 98%), and 4-bromobenzonitrile (≥ 98%) were purchased from Alfa Aesar. Palladium on activated carbon (10% Pd, unreduced), triphenylamine (99%), *N*-formylpiperidine (99%), and mesitylene (99%) were purchased from Acros. 4-Nitroaniline (99%) was purchased from Fluka. 4-Aminobenzonitrile (98%) was purchased from Matrix Scientific. *n*-Butyllithium (2.5 M in hexane) was purchased from Albemarle.

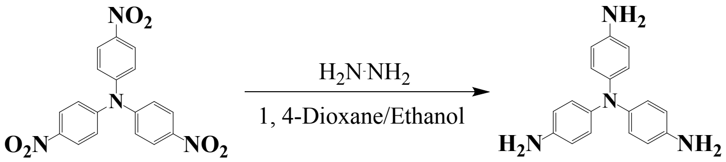
Section C. Synthetic procedures

Tris(4-nitrophenyl)amine (TPA-3NO$_2$)



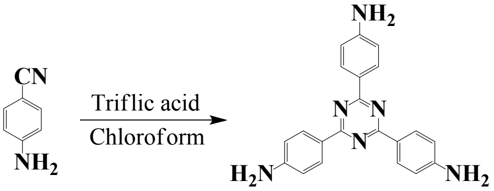
1-Fluoro-4-nitrobenzene (8 mL, 0.08 mmol) was added to a suspension of 4-nitroaniline (5.00 g, 36.2 mmol) and K_2CO_3 (30 g) in dry DMSO (40 mL) in a 100-mL two-neck bottle under a flow of N_2. The mixture was heated at 120 °C for 48 h and then the solvent was removed under vacuum. The formed solid was suspended in methanol and collected via vacuum filtration. The compound was washed with H_2O and methanol. The product was dried under vacuum overnight to yield a yellow solid of TPA-3NO$_2$. FT-IR (powder): 1582, 1508, 1338, 1314, 1270, 1180, 1110, 849, 749, 703, 692, 676, 506 cm^{-1}. ^{1}H NMR (DMSO-*d$_6$*, 25 °C, 600 MHz): δ = 8.26 (d, *J* = 12 Hz, 6H), 7.36 (d, *J* = 10.8 Hz, 6H). ^{13}C NMR (DMSO-*d$_6$*, 25 °C, 500 MHz): 150.83, 143.55, 125.77, 124.90.

Tris(4-aminophenyl)amine (TPA-3NH$_2$)



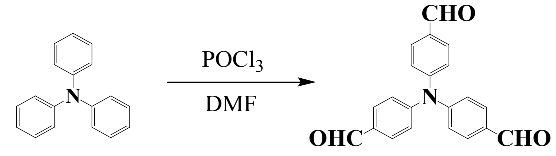
A suspension of tris(4-nitrophenyl)amine (10.0 g, 26.3 mmol) and palladium on activated carbon (0.658 g, 0.006 mmol) in dry 1,4-dioxane (46 mL) and EtOH (23 mL) was heated at 80 °C for 1 h in a 250-mL two-neck bottle under a flow of N_2 and then hydrazine monohydrate (26.3 mL, 0.84 mmol) was added. The mixture was heated at 80 °C for 48 h. Palladium on activated carbon was removed via vacuum filtration. The product was crystallized at low temperature. The precipitate was collected via vacuum filtration and dried under vacuum overnight to yield a gray solid of TPA-3NH$_2$. FT-IR (powder): 3406, 3334, 3207, 3034, 3003, 1620, 1504, 1328, 1259, 829, 568, 505 cm^{-1}. ^{1}H NMR (DMSO-*d$_6$*, 25 °C, 600 MHz): δ = 6.58 (s, 6H), 4.69 (s, 6H), 6.44 (d, *J* = 10.2 Hz, 6H). ^{13}C NMR (DMSO-*d$_6$*, 25 °C, 500 MHz): 143.17, 138.65, 124.08, 114.76.

2,4,6-Tris(4-aminophenyl)triazine (TPT-$3NH_2$)



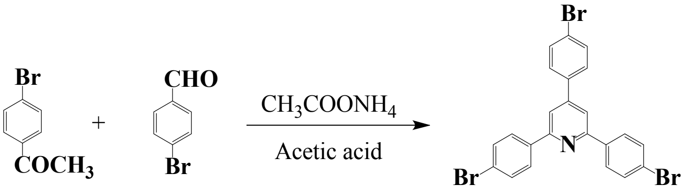
A suspension of 4-aminobenzonitrile (1.5 g, 12.70 mmol) in dry $CHCl_3$ (20 mL) in a 100-mL two-neck bottle was cooled in an ice bath under a flow of N_2 and then trifluoromethanesulfonic acid (4 mL, 0.045 mmol) was added. The mixture was stirred for 30 min in the ice bath and then warmed to room temperature. After stirring for an additional 24 h at room temperature, ice water was added. The aqueous suspension was neutralized by adding ammonium hydroxide. The precipitate was collected via vacuum filtration and dried under vacuum overnight to yield a white solid of TPT-$3NH_2$. FT-IR (powder): 3460, 3379, 3321, 3207, 1633, 1606, 1579, 1498, 1433, 1367, 1309, 1180, 1147, 813, 590, 513 cm^{-1}. ^1H NMR (DMSO-d_6, 25 °C, 600 MHz): δ = 5.89 (s, 6H), 8.36 (d, J = 10.2 Hz, 6H), 6.70 (d, J = 10.2 Hz, 6H). ^{13}C NMR (DMSO-d_6, 25 °C, 500 MHz): 170.45, 153.77, 130.82, 123.56, 113.69.

Tris(4-formylphenyl)amine (TPA-3CHO)



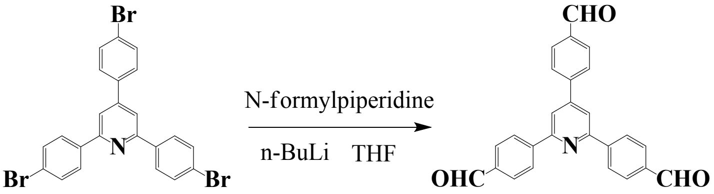
A suspension of triphenylamine (5.00 g, 20.4 mmol) in dry DMF (35 mL) in a 100-mL two-neck bottle was cooled in an ice bath under a flow of N_2 and then phosphoryl chloride (19 mL, 0.20 mmol) was added. The mixture was stirred for 30 min at room temperature and then heated at 110 °C for 12 h. The product was poured into ice water and then the aqueous suspension was neutralized through the addition of a NaOH solution. The aqueous phase was extracted with DCM; the combined organic extracts were dried (anhydrous $MgSO_4$) and filtered. The solvent was removed under rotary evaporation and after column chromatography [silica gel, ethyl acetate (EA): hexanes = 1:4] product was obtained as a yellow solid. FT-IR (powder): 2801, 2724, 1693, 1587, 1504, 1323, 1274, 1217, 1168, 819, 526 cm^{-1}. ^1H NMR (DMSO-d_6, 25 °C, 600 MHz): δ = 9.93 (s, 3H), 7.89 (d, J = 10.2 Hz, 6H), 7.26 (d, J = 10.2 Hz, 6H). ^{13}C NMR (DMSO-d_6, 25 °C, 500 MHz): 191.49, 150.73, 132.19, 131.44, 124.43.

2,4,6-Tris(4-bromophenyl)pyridine (TPP-3Br)



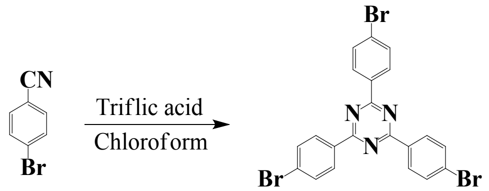
A 20-mL microwave vial equipped with a stirrer bar was charged with 4-bromoacetophenone (4.14 g, 20.8 mmol), 4-bromobenzaldehyde (1.94 g, 10.4 mmol), ammonium acetate (28.0 g, 363 mmol), and acetic acid (14.6 mL, 0.260 mmol). The contents were heated in a microwave oven under autogenous pressure at 500 W and 220 °C for 45 min. After cooling to room temperature, deionized water was added. The aqueous suspension was neutralized through the addition of a solution of $NaHCO_3$. The aqueous phase was extracted with DCM; the combined organic extracts were dried (anhydrous $MgSO_4$) and filtered. The solvent was evaporated under reduced pressure; the residue was recrystallized (acetone) and dried under vacuum overnight to yield a white solid of TPP-3Br. FT-IR (powder): 1593, 1573, 1541, 1500, 1420, 1376, 1177, 1067, 1007, 813, 489 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C, 600 MHz): 8.03 (d, J = 10.2 Hz, 2H), 7.57 (m, aromatic, 12H). ^{13}C NMR ($CDCl_3$, 25 °C, 500 MHz): 156.59, 149.38, 137.96, 137.50, 132.36, 131.91, 128.62, 123.80, 123.68, 116.75.

2,4,6-Tris(4-formylphenyl)pyridine (TPP-3CHO)



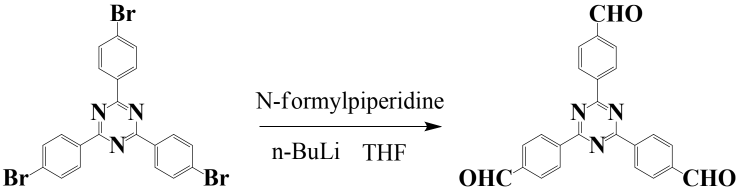
A suspension of 2,4,6-tris(4-bromophenyl)pyridine (1.00 g, 1.85 mmol) in dry THF (130 mL) in a 250-mL two-neck bottle was cooled to –78 °C under a flow of N_2 and then a solution of *n*-BuLi (7.40 mL, 18.8 mmol, 2.5 M in hexane) was added. The mixture was stirred at –70 °C for 3 h and then *N*-formylpiperidine (2.20 mL, 19.9 mmol) was added. The mixture was stirred for 1 h at –78 °C and then warmed to room temperature. After stirring for an additional 16 h at room temperature, 0.88 M HCl (40 mL) of was added. The aqueous phase was extracted with DCM; the combined organic extracts were dried (anhydrous $MgSO_4$) and filtered. The solvent was evaporated under reduced pressure. The residue was purified using the centrifugation method to yield a white solid of TPP-3CHO. FT-IR (powder): 2810, 2724, 1697, 1598, 1571, 1544, 1211, 856, 819, 792 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C, 600 MHz): 10.06 (d, J = 4.8 Hz, 3H), 8.31 (d, J = 9.6 Hz, 2H), 7.85 (m, aromatic, 12H). ^{13}C NMR ($CDCl_3$, 25 °C, 500 MHz): 192.90, 192.52, 157.49, 150.35, 145.02, 144.80, 137.54, 137.47, 131.24, 130.92, 128.63, 128.41, 119.33.

2,4,6-Tris(4-bromophenyl)-1,3,5-triazine (TPT-3Br)



A suspension of 4-bromobenzonitrile (1.50 g, 8.24 mmol) in dry $CHCl_3$ (20 mL) in a 100-mL two-neck bottle was cooled in an ice bath under a flow of N_2 and then trifluoromethanesulfonic acid (4 mL, 0.045 mmol) was added. The mixture was stirred for 30 min in the ice bath and then warmed to room temperature. *After* stirring for an additional 20 h at room temperature, ice water was added. The aqueous suspension was neutralized through the addition of ammonium hydroxide. The precipitate was collected via vacuum filtration and dried under vacuum overnight to yield a white solid of TPT-3Br. FT-IR (powder): 1578, 1518, 1400, 1372, 1173, 1069, 1011, 843, 806, 498 cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C, 600 MHz): 8.60 (d, J = 12 Hz, 6H), 7.71 (d, J = 12Hz, 6H). ^{13}C NMR ($CDCl_3$, 25 °C, 500 MHz): 171.10, 134.77, 132.01, 130.48, 127.84.

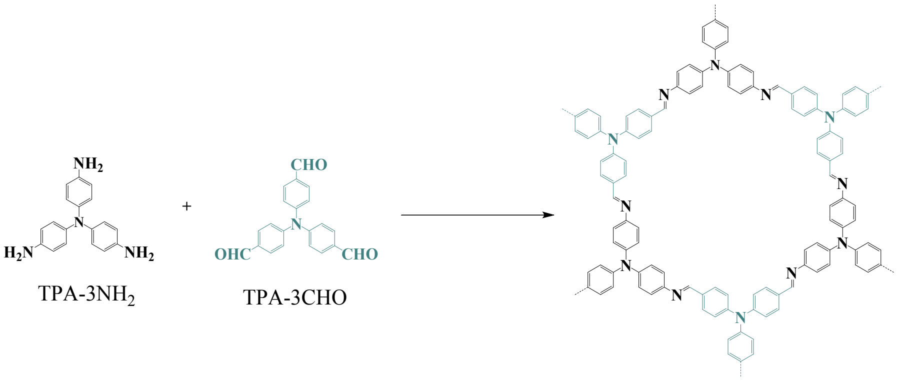
2,4,6-Tris(4-formylphenyl)triazine (TPT-3CHO)



A suspension of 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (1.00 g, 1.83 mmol) in dry THF (130 mL) in a 250-mL two-neck bottle was cooled to –78 °C under a flow of N_2 and then a solution of *n*-BuLi (7.30 mL, 18.6 mmol, 2.5 M in hexane) was added. The mixture was stirred at –70 °C for 3 h and then *N*-formylpiperidine (2.2 mL, 19.9 mmol) was added. The mixture was stirred for 30 min at –78 °C and then warmed to room temperature. After stirring for an additional 16 h at room temperature, 2.88 M HCl (50 mL) was added. The aqueous phase was extracted with $CHCl_3$; the combined organic extracts were dried (anhydrous $MgSO_4$) and filtered. The solvent was evaporated under reduced pressure. The residue was purified using the centrifugation method to yield a white solid of TPT-3CHO. FT-IR (powder): 2821, 2729, 1706, 1583, 1517, 1419, 1357, 1298, 1201, 1105, 1012, 806, 499 cm^{-1}. ^1H NMR ($CDCl_3$ and

DMSO-d_6, 25 °C, 600 MHz): 10.12 (s, 3H), 8.89 (d, J = 9.6 Hz, 6H), 8.06 (d, J = 9.6Hz, 6H). ^{13}C NMR (CDCl$_3$, 25 °C, 500 MHz): 192.48, 171.47, 140.77, 139.46, 130.03, 129.80.

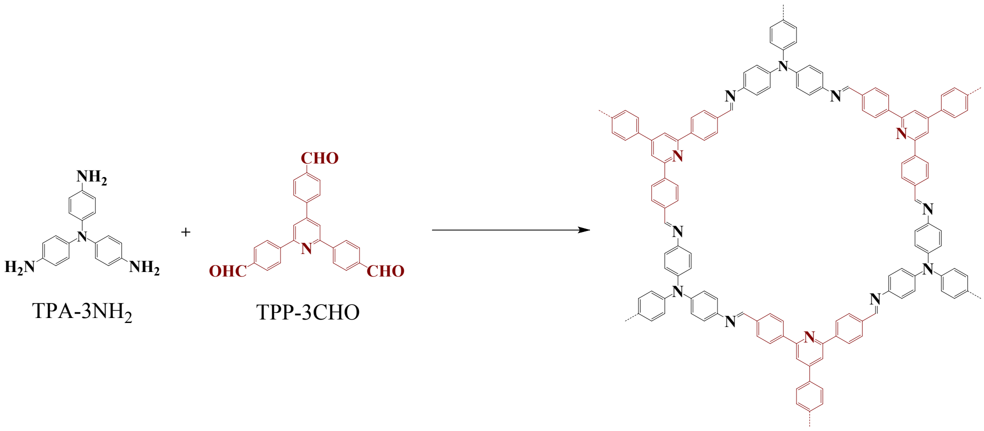
TPA-TPA-COF (TPA-COF-1)



TPA-TPA-COF (TPA-COF-1)

A mixture of TPA-3NH$_2$ (70.0 mg, 0.240 mmol), TPA-3CHO (79.4 mg, 0.240 mmol), acetic acid (6 M, 1.2 mL) in 1,4-dioxane/mesitylene (5 mL/5 mL) in a Pyrex tube (25 mL) was degassed using three freeze/pump/thaw cycles. The tube was sealed off under a flame and then heated at 120 °C for 96h. After cooling to room temperature, the yellow precipitate was washed several times with THF, MeOH, and acetone, respectively, and then dried under vacuum at 120 °C overnight to yield a yellow solid (87%).

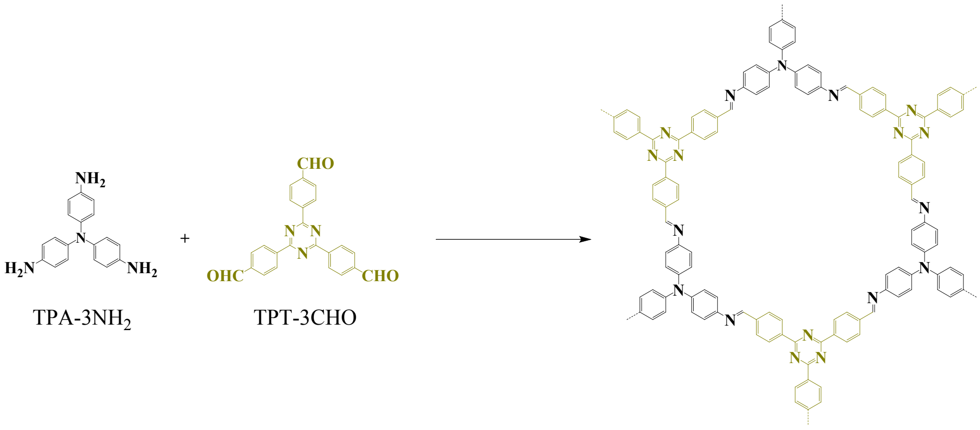
TPA-TPP COF (TPA-COF-2)



TPA-TPP COF (TPA-COF-2)

A mixture of TPA-3NH$_2$ (70.0 mg, 0.240 mmol), TPP-3CHO (94.4 mg, 0.240 mmol), and acetic acid (6 M, 1.2 mL) in 1,4-dioxane/mesitylene (5 mL/5 mL) in a Pyrex tube (25 mL) was degassed using three freeze/pump/thaw cycles. The tube was sealed off under a flame and then heated at 120 °C for 96 h. After cooling to room temperature, the yellow precipitate was washed several times with THF, MeOH, and acetone, respectively, and then dried under vacuum at 120 °C overnight to yield a yellow solid (85%).

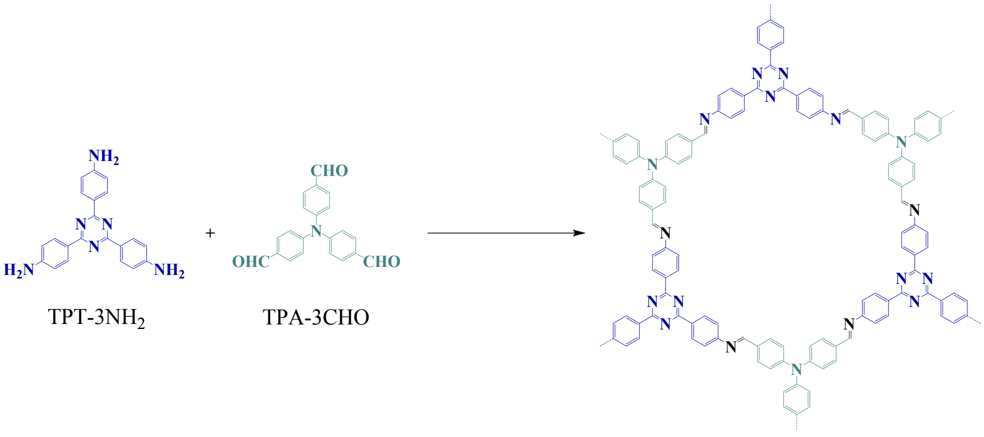
TPA-TPT COF (TPA-COF-3)



TPA-TPT COF (TPA-COF-3)

A mixture of TPA-3NH$_2$ (70.0 mg, 0.240 mmol), TPT-3CHO (94.8 mg, 0.240 mmol), and acetic acid (6 M, 1.2 mL) in 1,4-dioxane/mesitylene (5 mL/5 mL) in a Pyrex tube (25 mL) was degassed using three freeze/pump/thaw cycles. The tube was sealed off under a flame and then heated at 120 °C for 96 h. After cooling to room temperature, the red precipitate was washed several times with THF, MeOH, and acetone, respectively, and then dried under vacuum at 120 °C overnight to yield a red solid (88%).

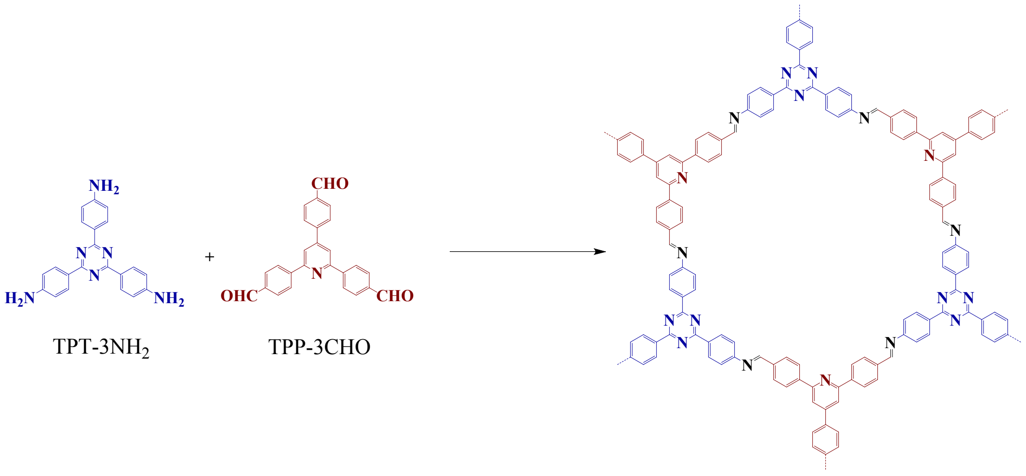
TPT-TPA COF (TPT-COF-4)



TPT-TPA COF (TPT-COF-4)

A mixture of TPT-3NH$_2$ (70.0 mg, 0.200 mmol), TPA-3CHO (77.5 mg, 0.200 mmol), and acetic acid (6 M, 1.2 mL) in 1,4-dioxane/mesitylene (5 mL/5 mL) in a Pyrex tube (25 mL) was degassed using three freeze/pump/thaw cycles. The tube was sealed off under a flame and then heated at 120 °C for 96 h. After cooling to room temperature, the yellow precipitate was washed several times with THF, MeOH, and acetone, respectively, and then dried under vacuum at 120 °C overnight to yield a yellow solid (82%).

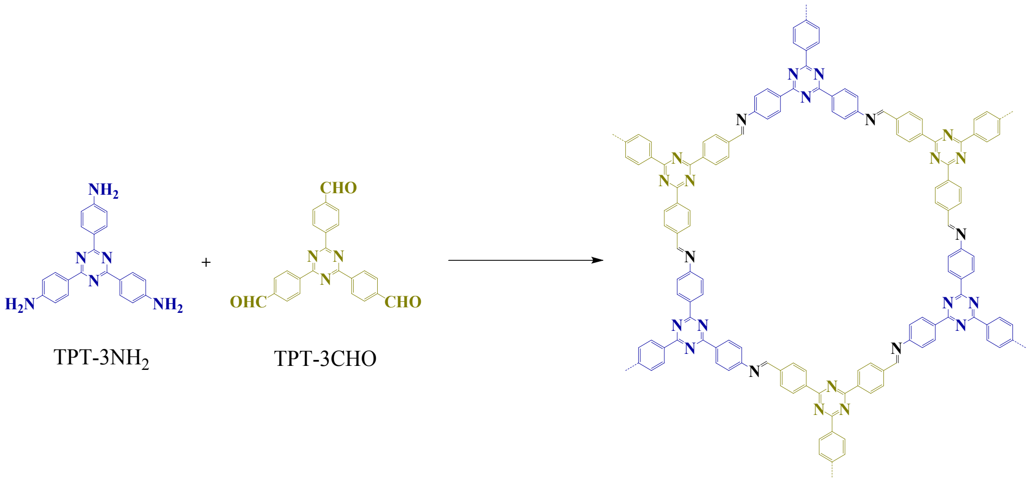
TPT-TPP COF (TPT-COF-5)



TPT-TPP COF (TPT-COF-5)

A mixture of TPT-3NH$_2$ (70.0 mg, 0.200 mmol), TPP-3CHO (77.3 mg, 0.200 mmol), and acetic acid (6 M, 1.2 mL) in 1,4-dioxane/mesitylene (5 mL/5 mL) in a Pyrex tube (25 mL) was degassed using three freeze/pump/thaw cycles. The tube was sealed off under a flame and then heated at 120 °C for 96 h. After cooling to room temperature, the yellow precipitate was washed several times with THF, MeOH, and acetone, respectively, and then dried under vacuum at 120 °C overnight to yield a yellow solid (86%).

TPT-TPT COF (TPT-COF-6)



TPT-3NH$_2$

TPT-3CHO

TPT-TPT COF (TPT-COF-6)

A mixture of TPT-3NH$_2$ (70.0 mg, 0.200 mmol), TPT-3CHO (77.7 mg, 0.200 mmol), and acetic acid (6 M, 1.2 mL) in 1,4-dioxane/mesitylene (5 mL/5 mL) in a Pyrex tube (25 mL) was degassed using three freeze/pump/thaw cycles. The tube was sealed off under a flame and then heated at 120 °C for 96 h. After cooling to room temperature, the yellow precipitate was washed several times with THF, MeOH, and acetone, respectively, and then dried under vacuum at 120 °C overnight to yield a yellow solid (89%).

Section D. NMR spectral profiles

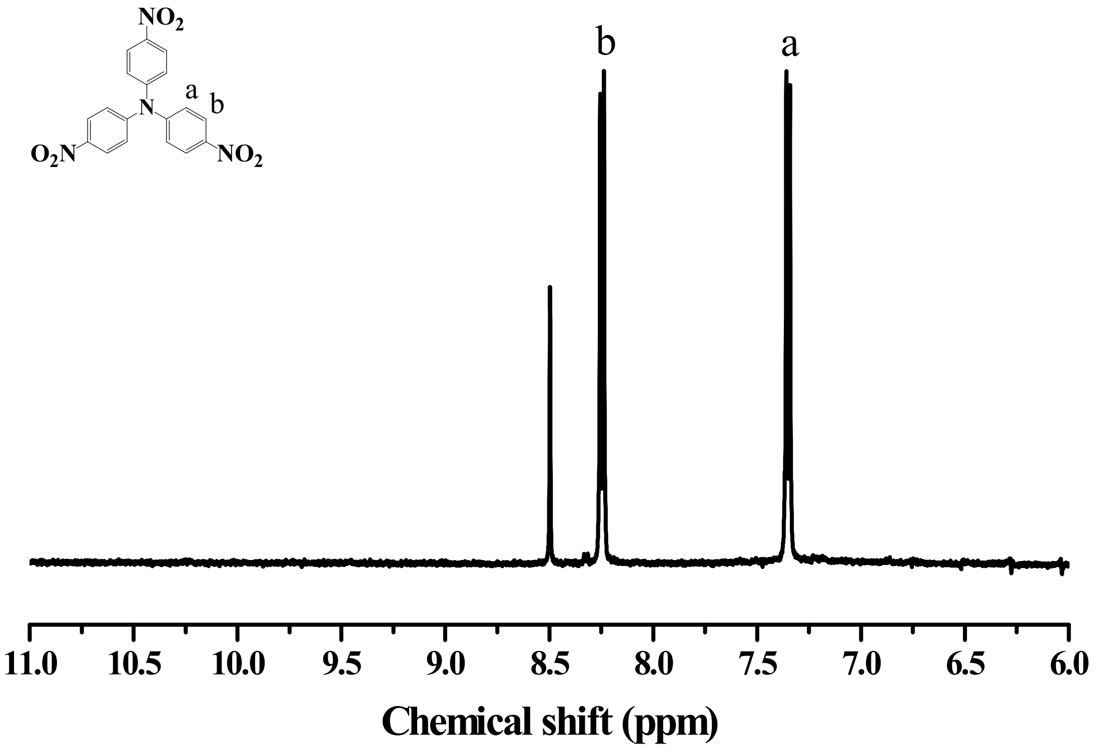


Figure S1. ^{1}H NMR spectrum of tris(4-nitrophenyl)amine (TPA-$3NO_2$).

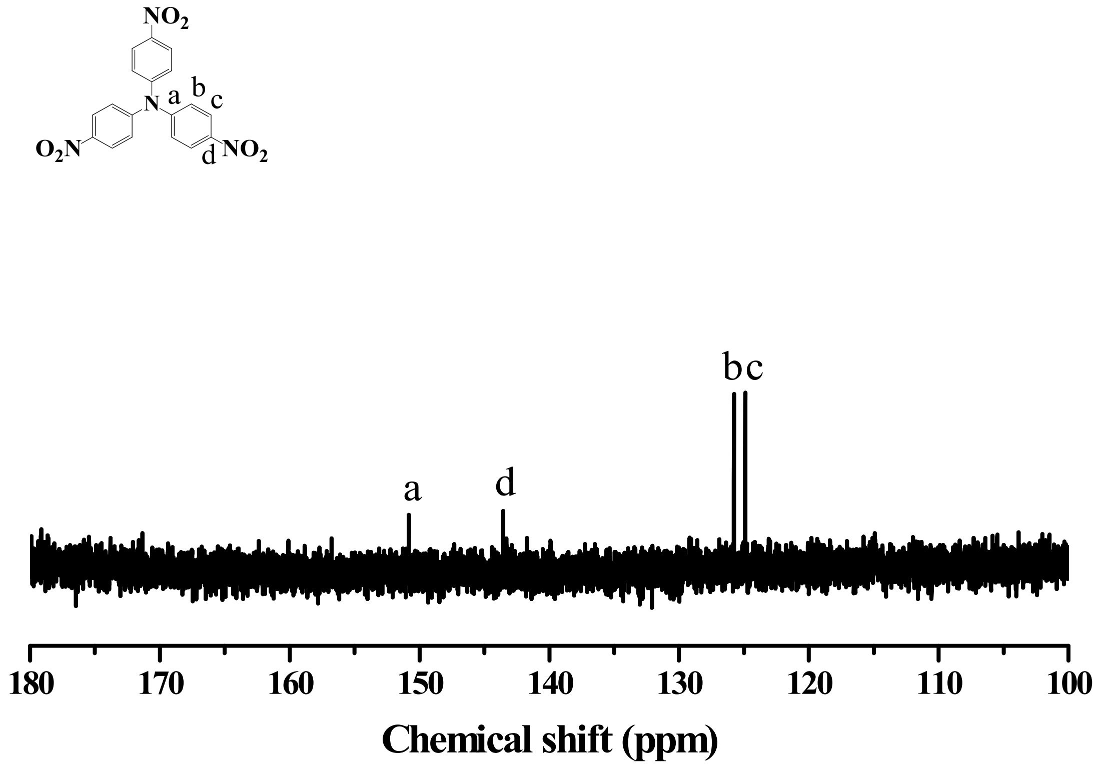


Figure S2. ^{13}C NMR spectrum of tris(4-nitrophenyl)amine (TPA-$3NO_2$).

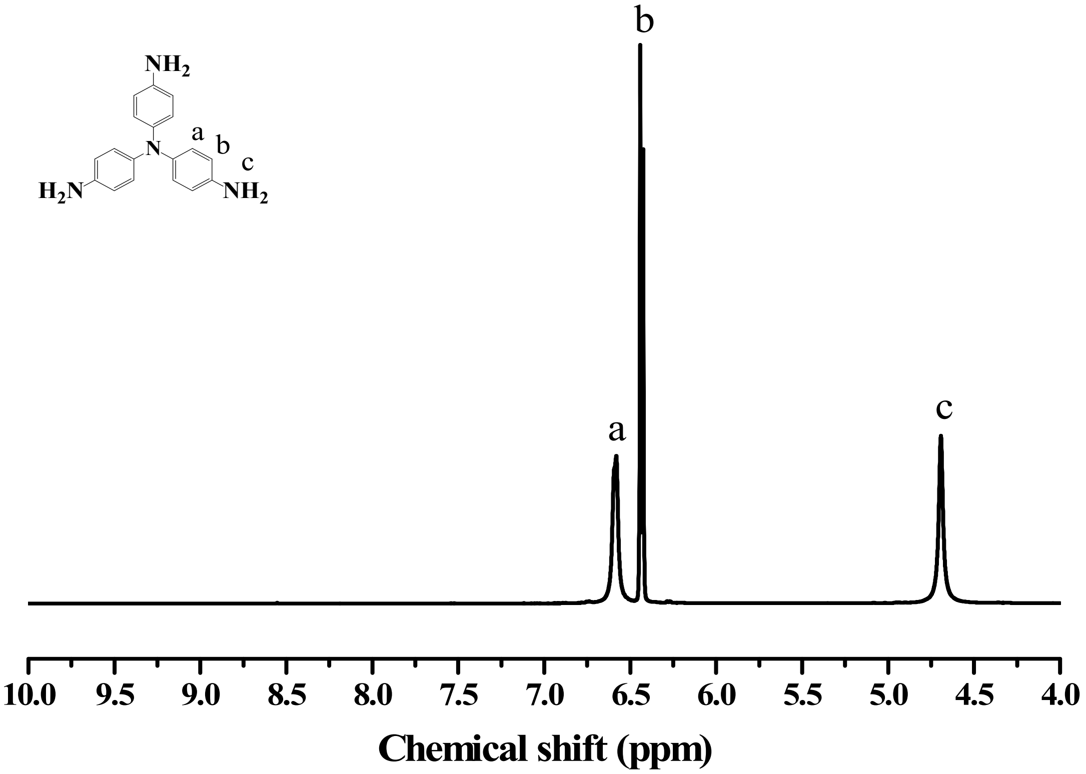


Figure S3. ^{1}H NMR spectrum of tris(4-aminophenyl)amine(TPA-$3NH_2$).

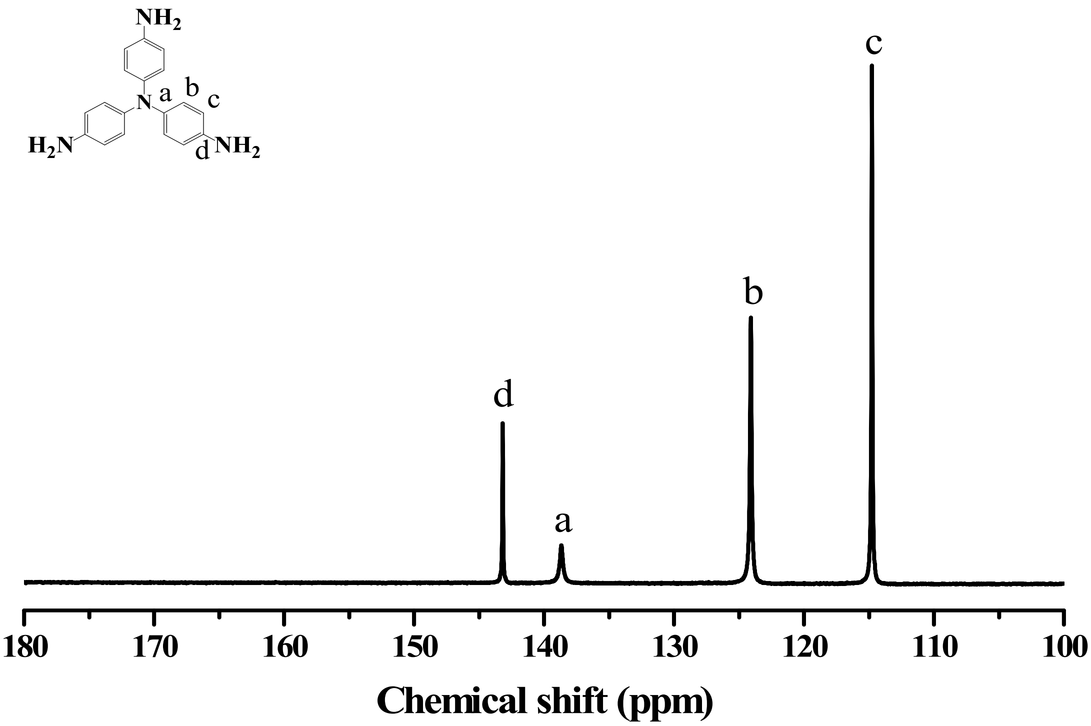


Figure S4. ^{13}C NMR spectrum of tris(4-aminophenyl)amine(TPA-$3NH_2$).

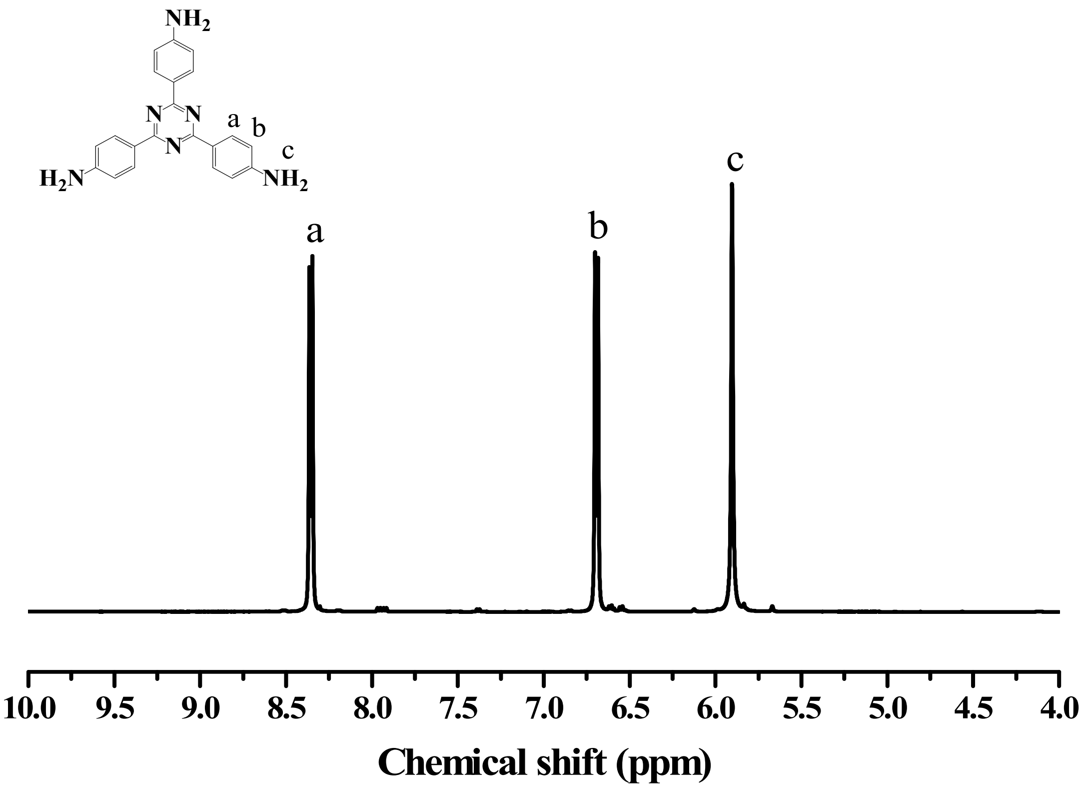


Figure S5. ^{1}H NMR spectrum of 2,4,6-tris(4-aminophenyl)triazine (TPT-3NH$_2$).

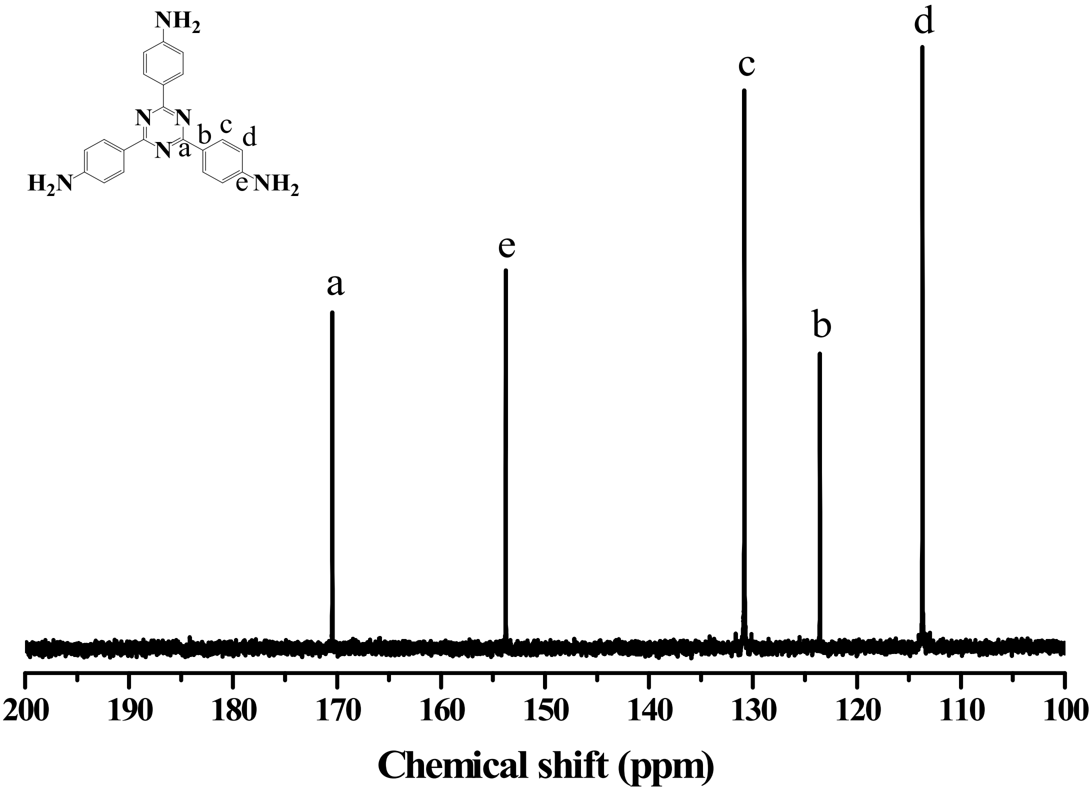


Figure S6. ^{13}C NMR spectrum of 2,4,6-tris(4-aminophenyl)triazine (TPT-3NH$_2$).

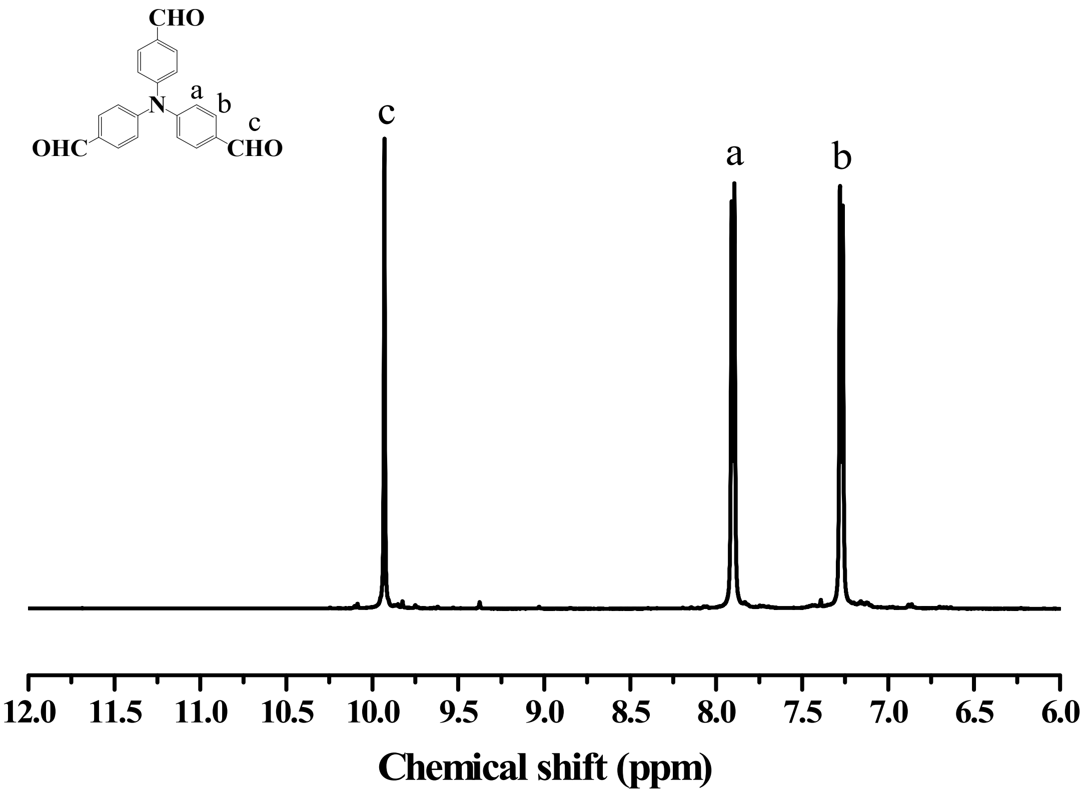


Figure S7. ^{1}H NMR spectrum of tris(4-formylphenyl)amine (TPA-3CHO).

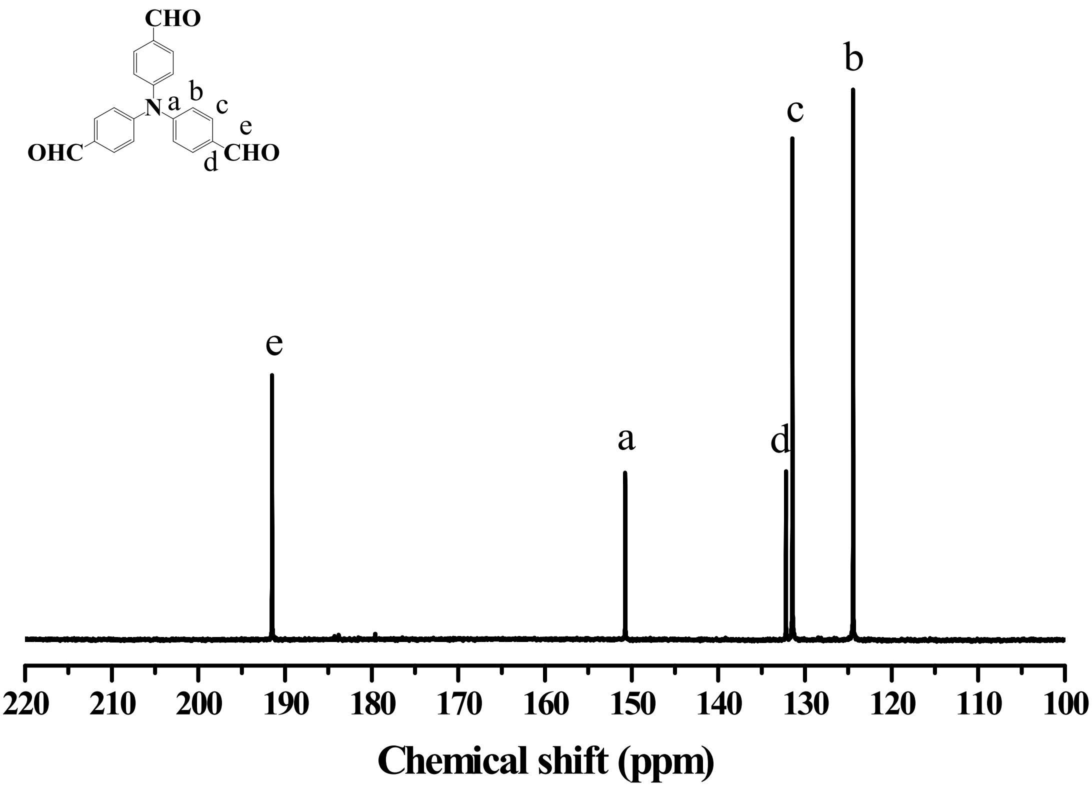


Figure S8. ^{13}C NMR spectrum of tris(4-formylphenyl)amine (TPA-3CHO).

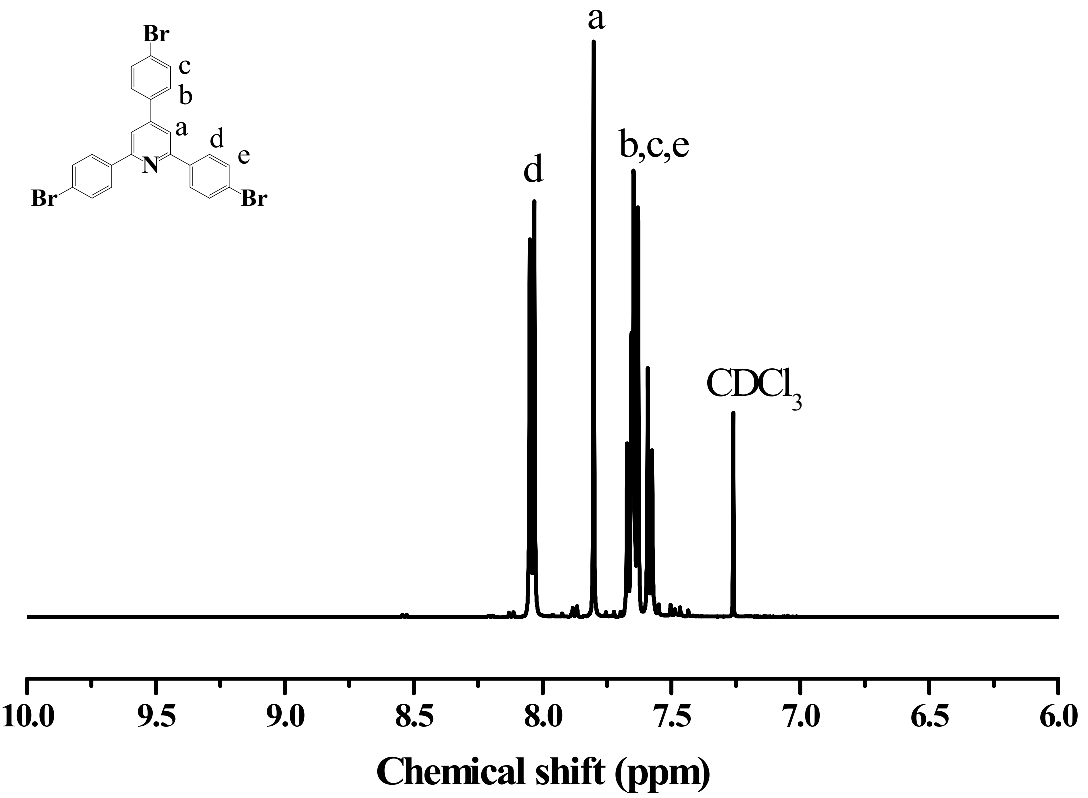


Figure S9. ^{1}H NMR spectrum of tris(4-bromophenyl)pyridine (TPP-3Br).

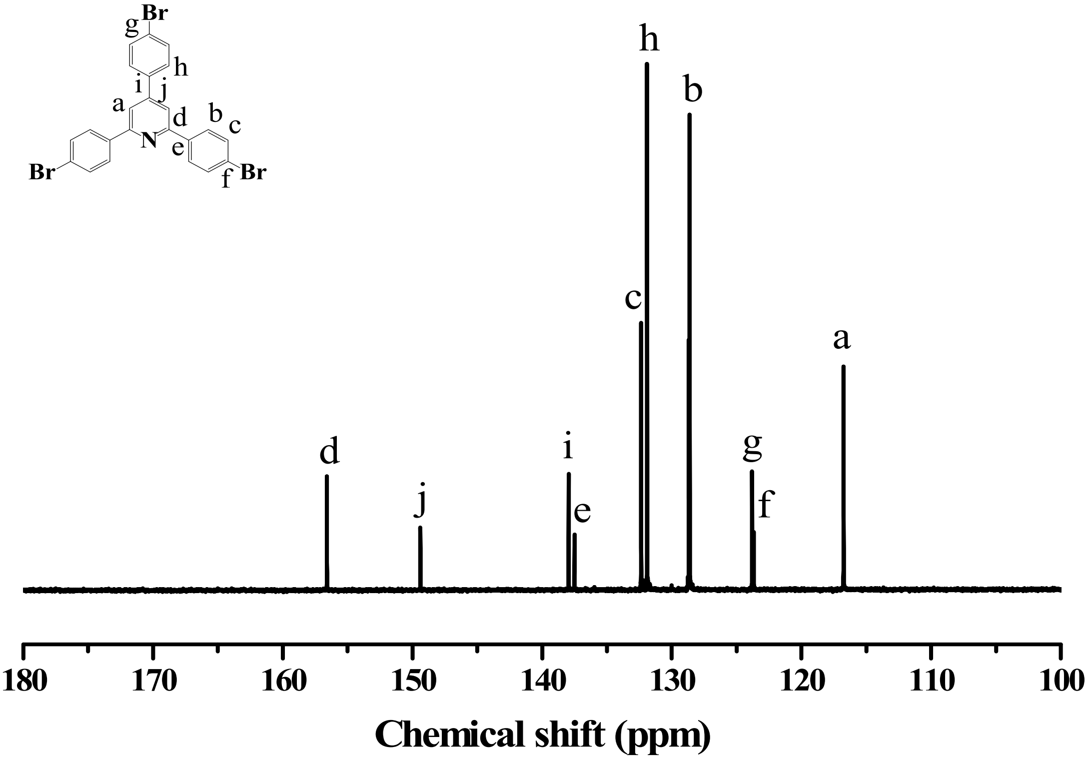


Figure S10. ^{13}C NMR spectrum of tris(4-bromophenyl)pyridine (TPP-3Br).

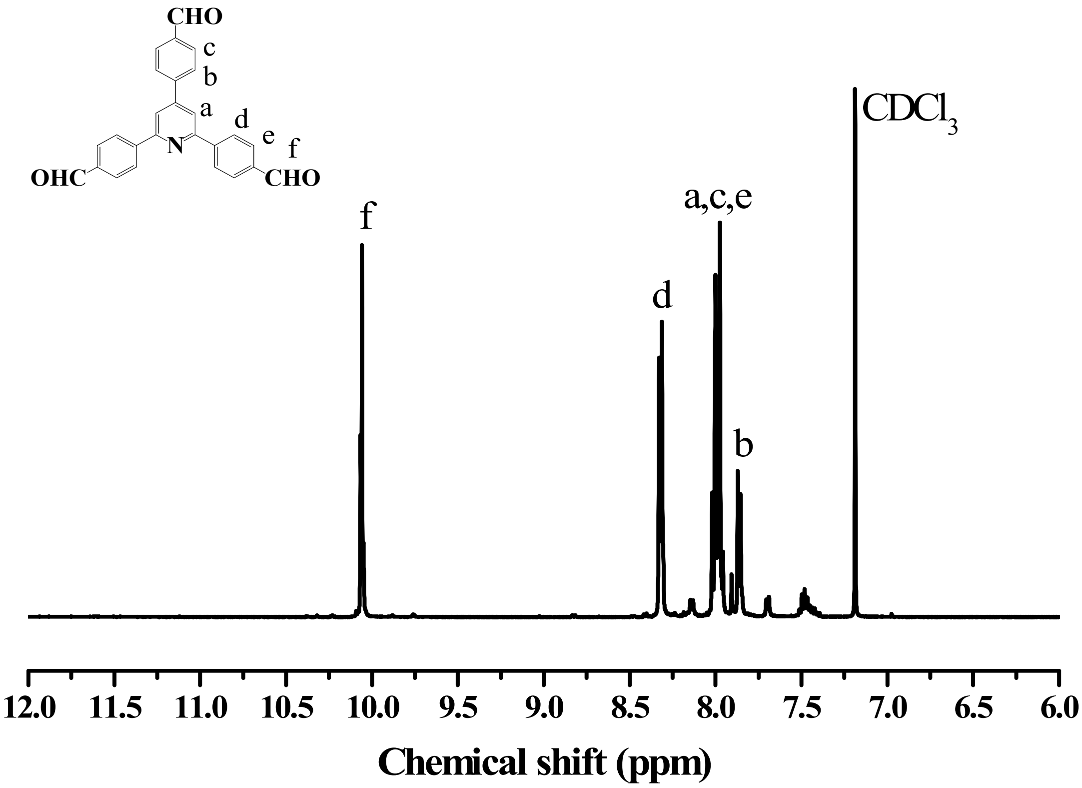


Figure S11. ^{1}H NMR spectrum of 2,4,6-tris(4-formylphenyl)pyridine (TPP-3CHO).

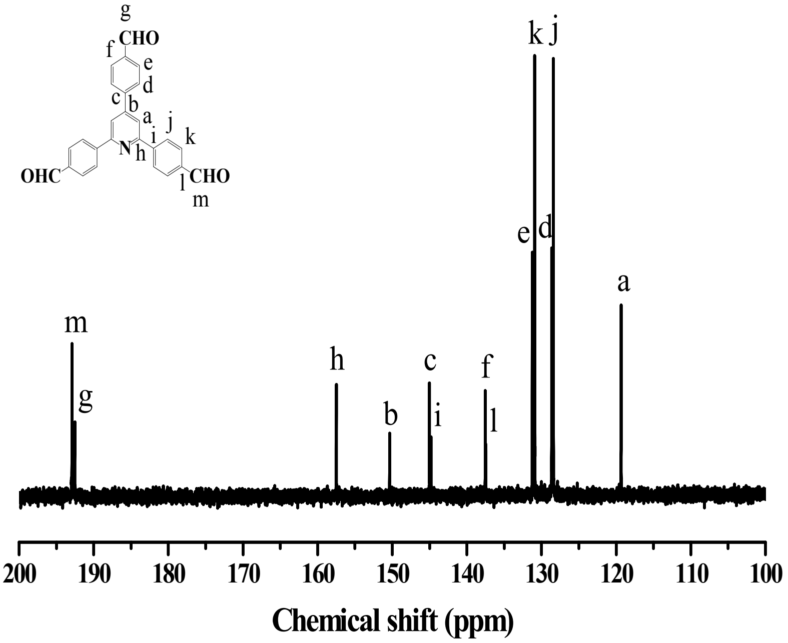


Figure S12. ^{13}C NMR spectrum of 2,4,6-tris(4-formylphenyl)pyridine (TPP-3CHO).

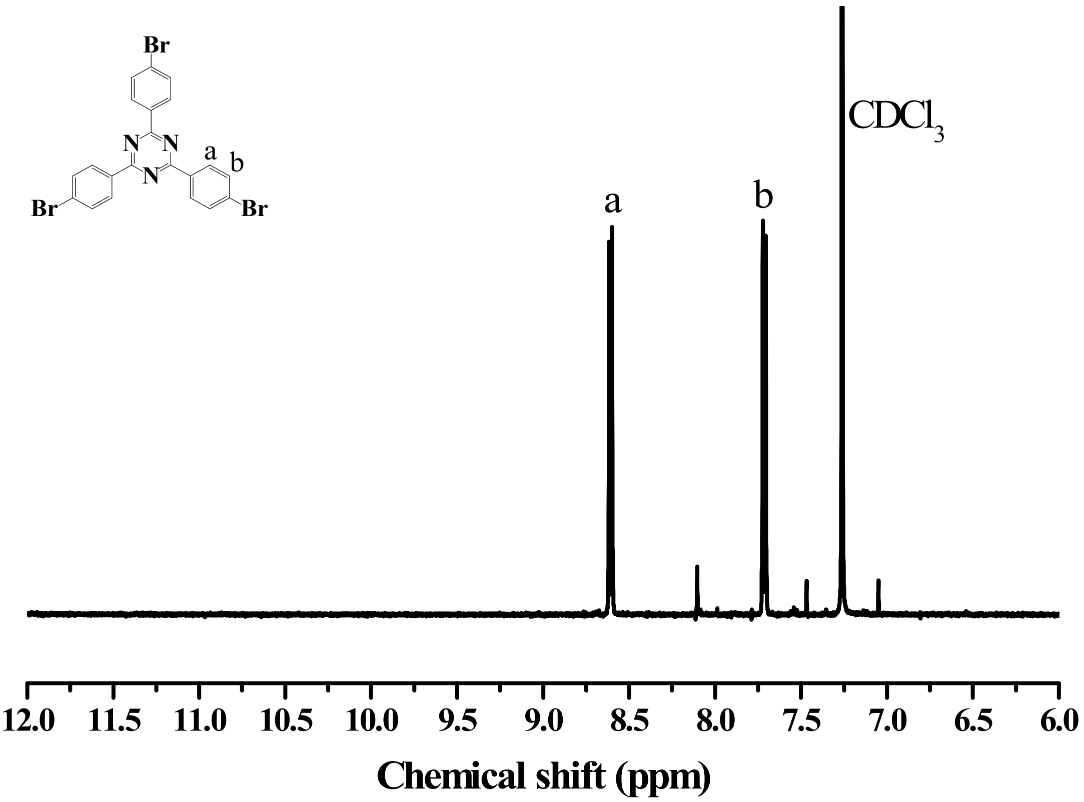


Figure S13. ^{1}H NMR spectrum of 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (TPT-3Br).

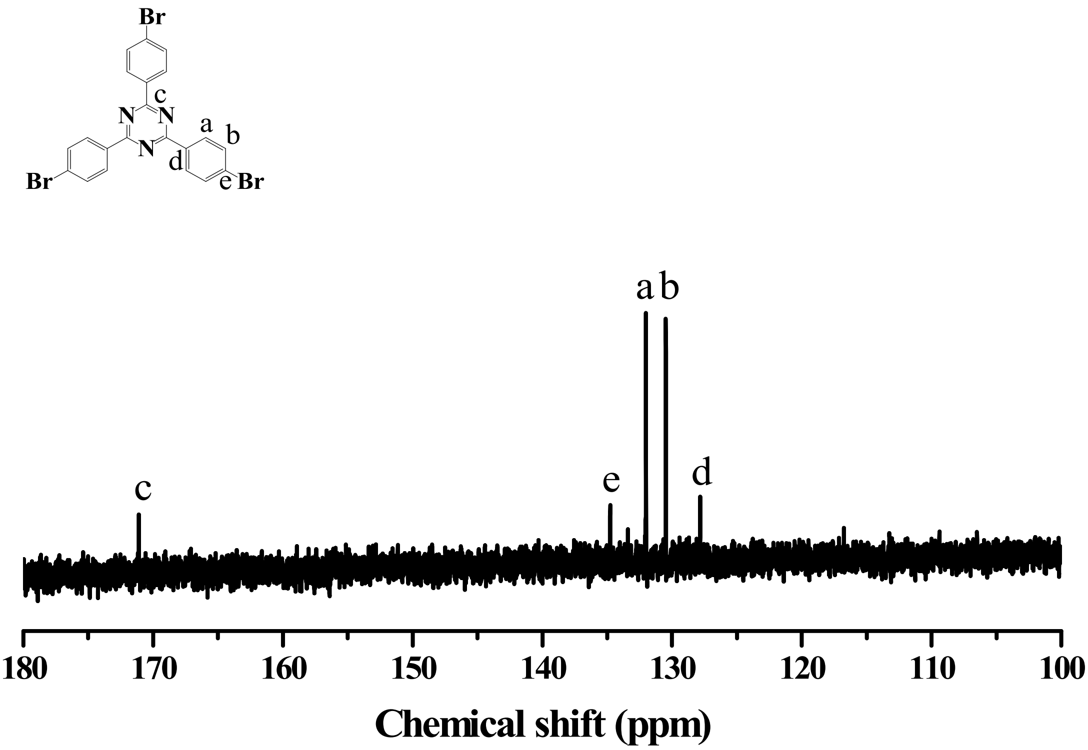


Figure S14. ^{13}C NMR spectrum of 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (TPT-3Br).

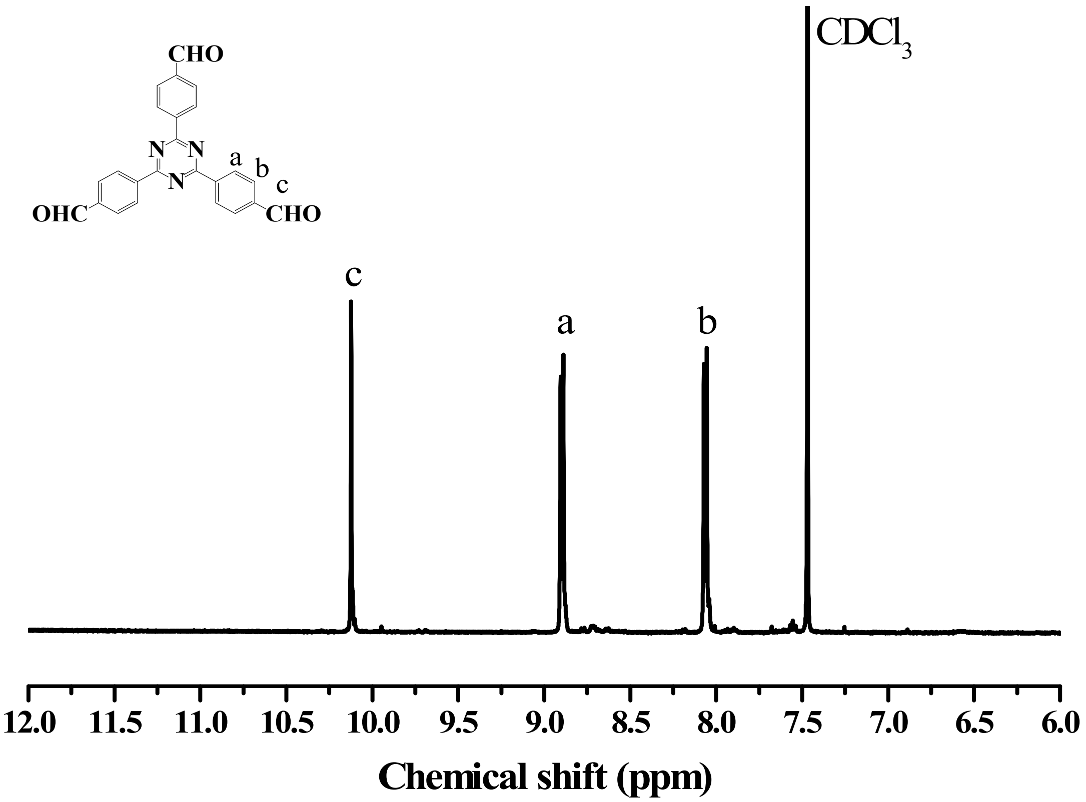


Figure S15. ^{1}H NMR spectrum of 2,4,6-tris(4-formylphenyl)triazine (TPT-3CHO).

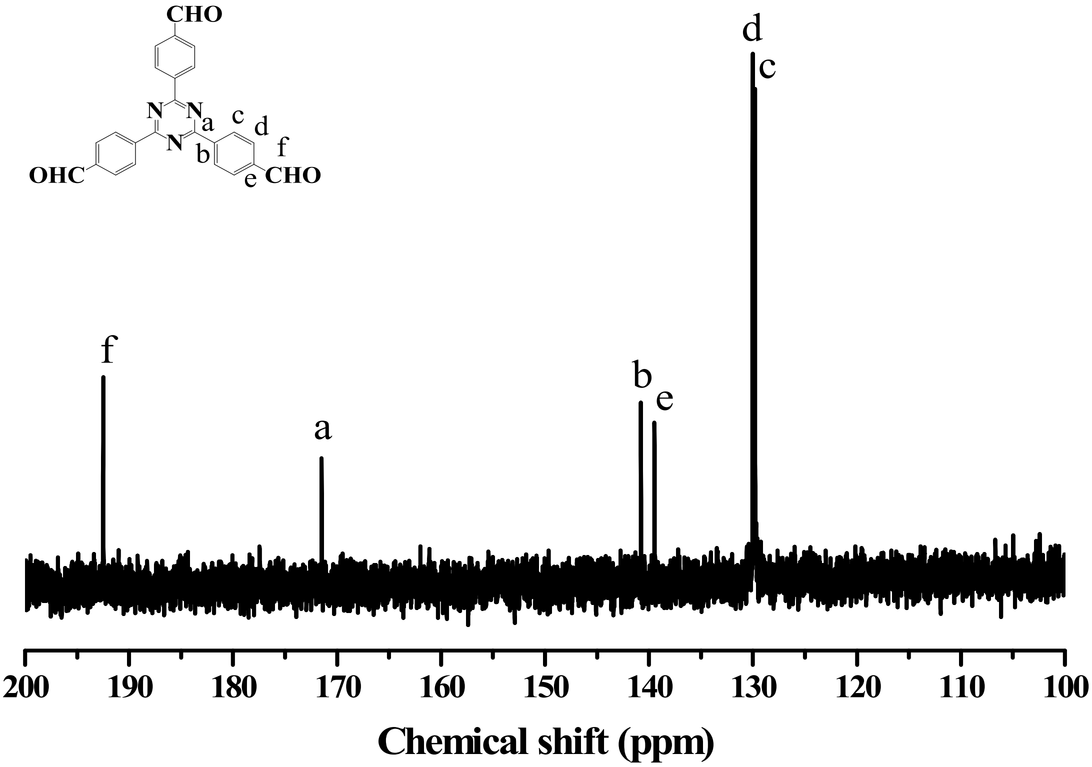


Figure S16. ^{13}C NMR spectrum of 2,4,6-tris(4-formylphenyl)triazine (TPT-3CHO).

Section E. ESI

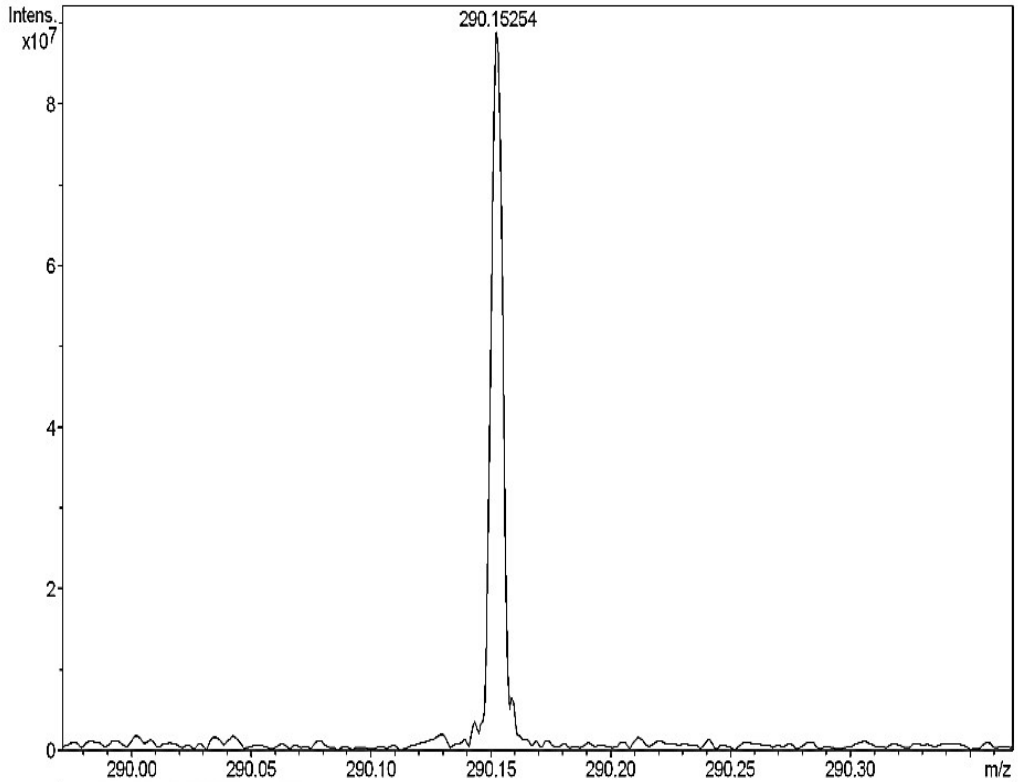


Figure S17. High-resolution FT mass spectrum of TPA-3NH_2.

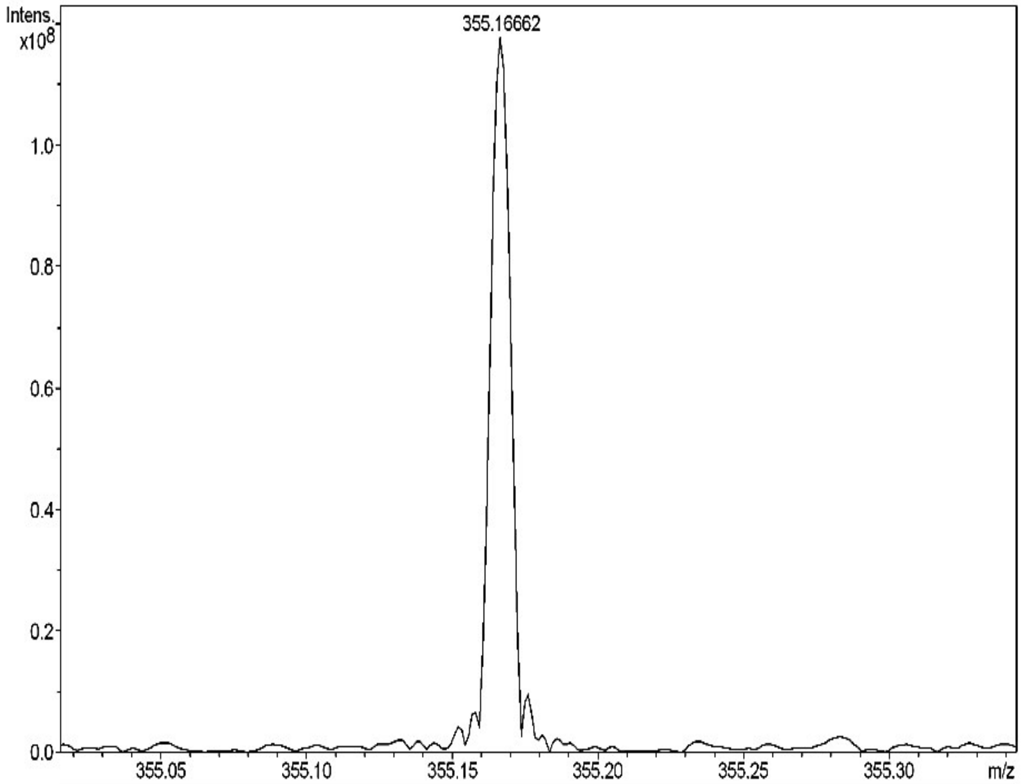


Figure S18. High-resolution FT mass spectrum of TPT-3NH_2.

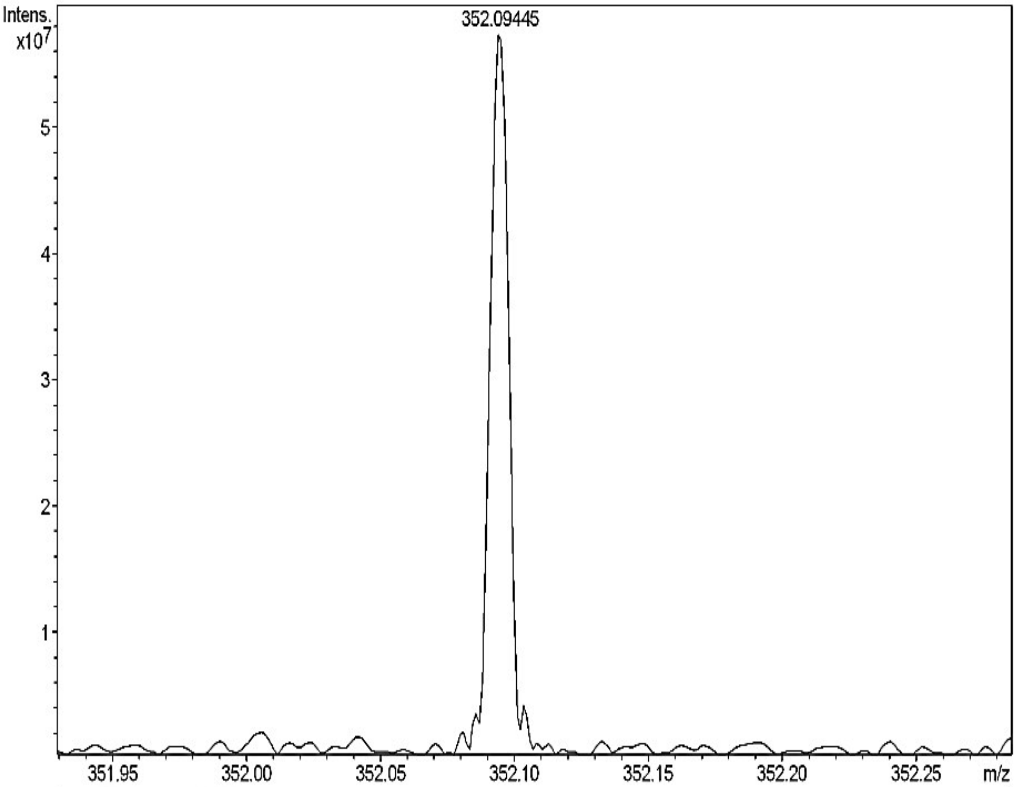


Figure S19. High-resolution FT mass spectrum of TPA-3CHO.

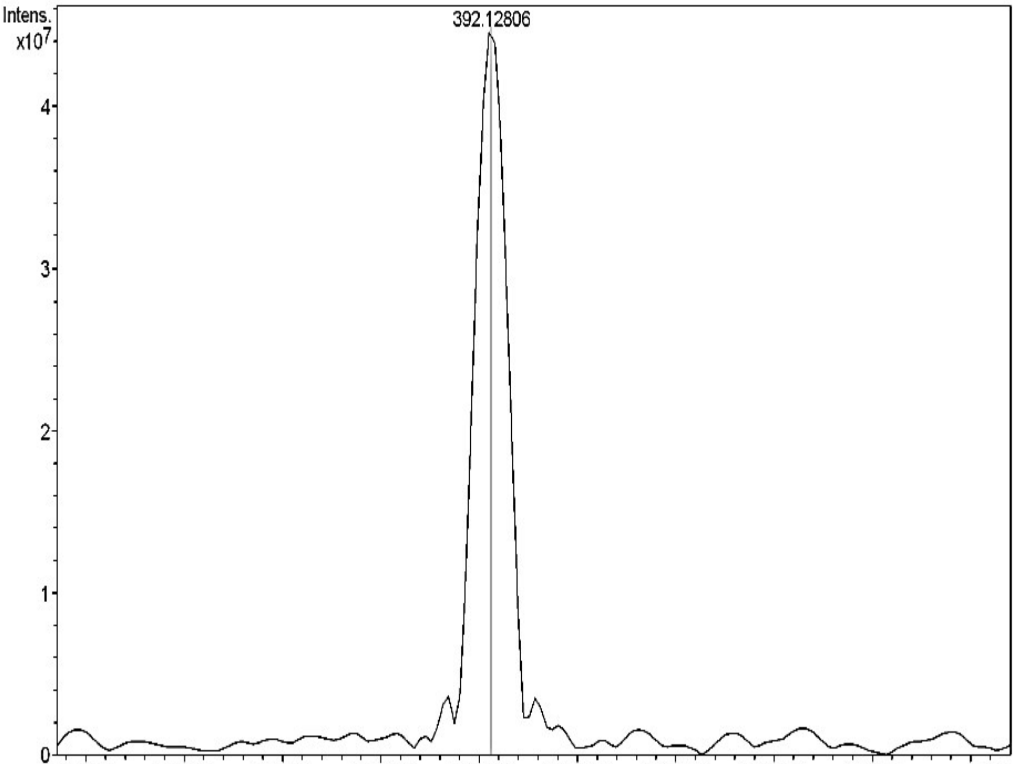


Figure S20. High-resolution FT mass spectrum of TPP-3CHO.

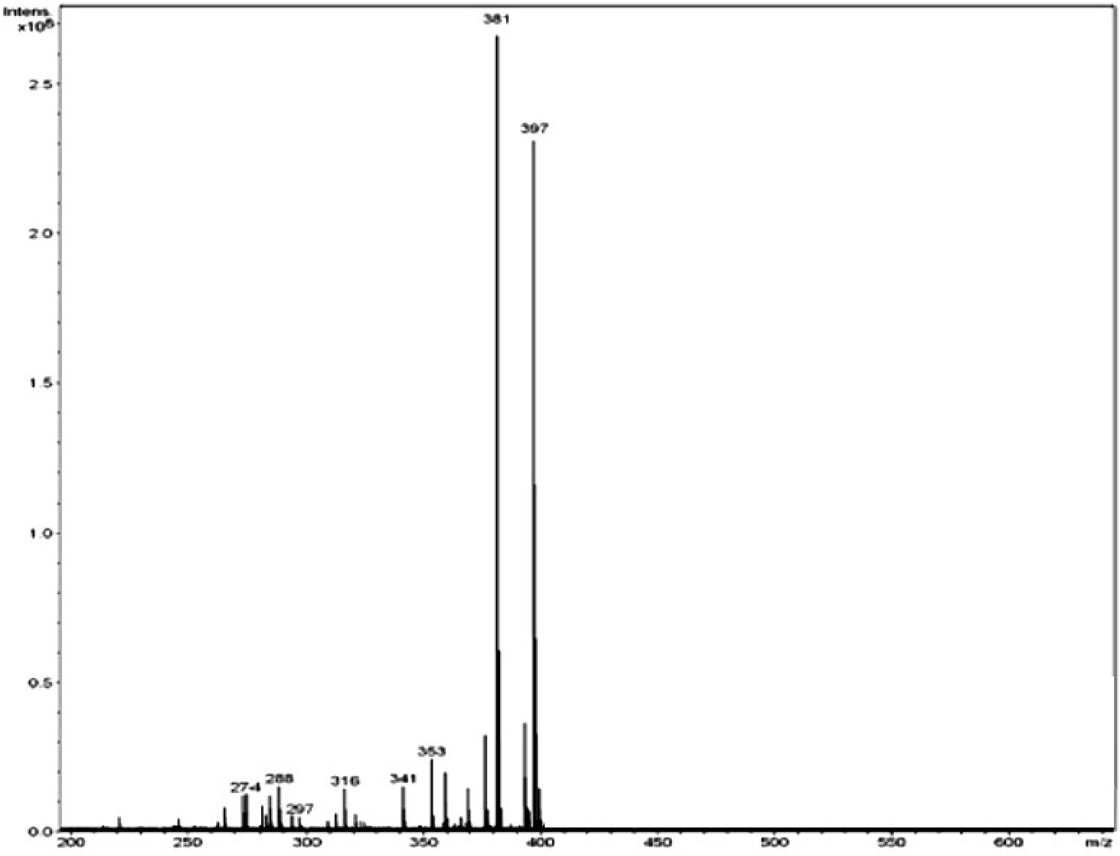


Figure S21. FT-MS of TPT-3CHO.

Section F. FT-IR spectral profiles

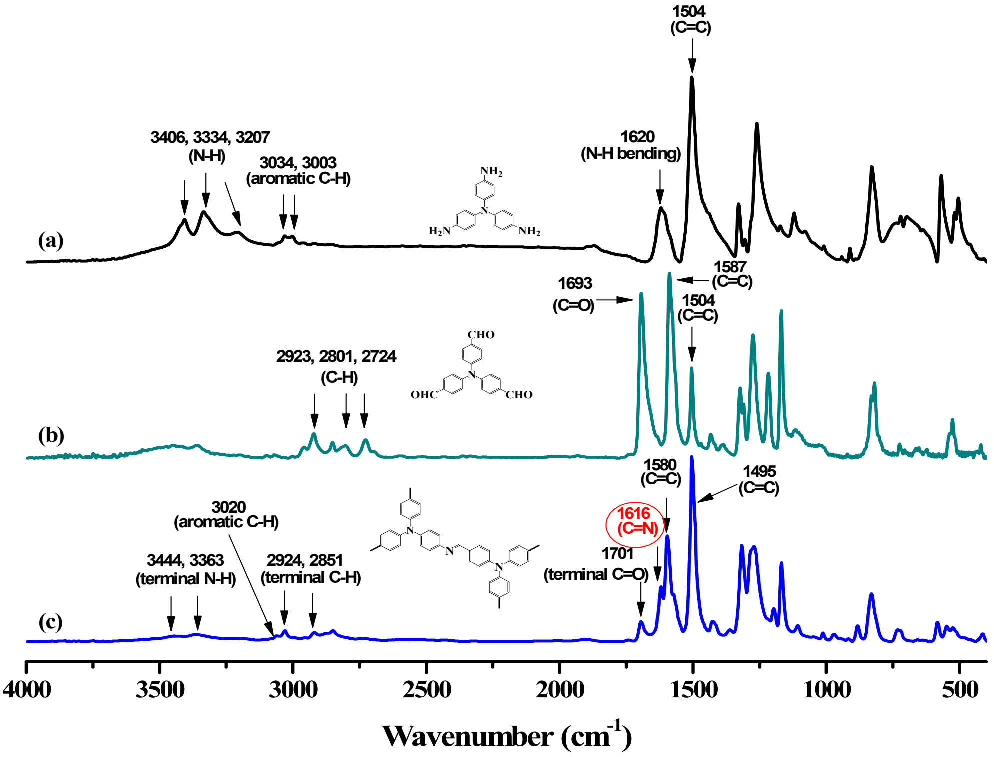


Figure S22. FTIR spectra of (a) TPA-3NH$_2$, (b) TPA-3CHO, and (c) TPA-TPA-COF (TPA-COF-1).

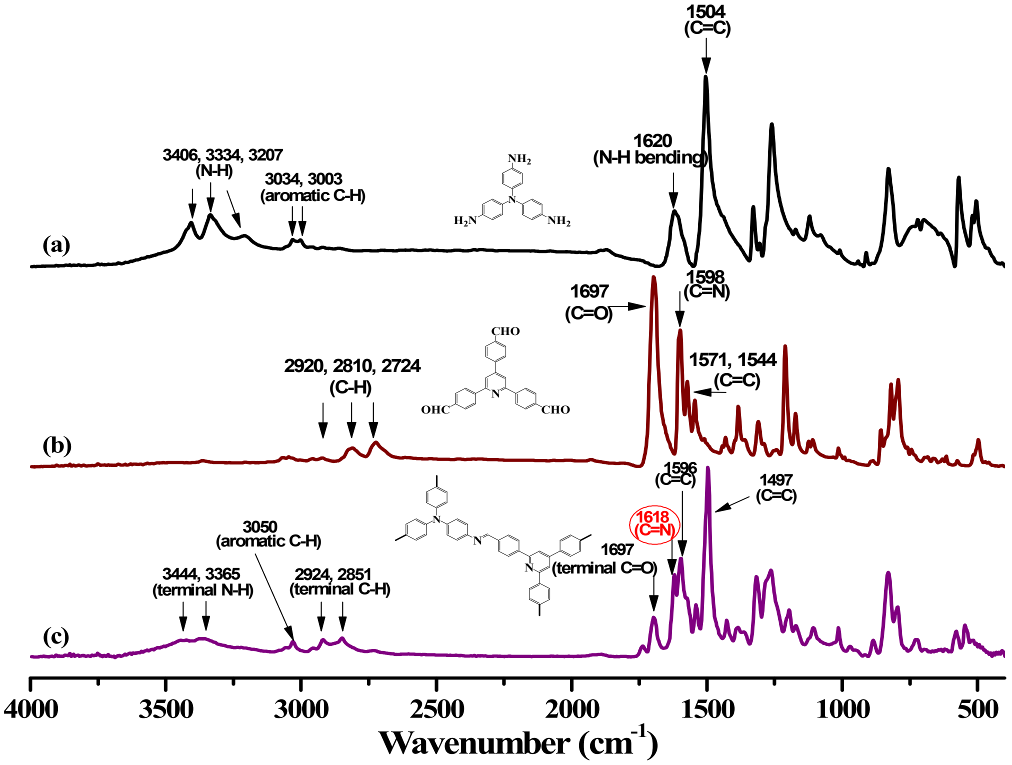


Figure S23. FTIR spectra of (a) TPA-3NH$_2$, (b) TPP-3CHO, and (c) TPA-TPP-COF (TPA-COF-2).

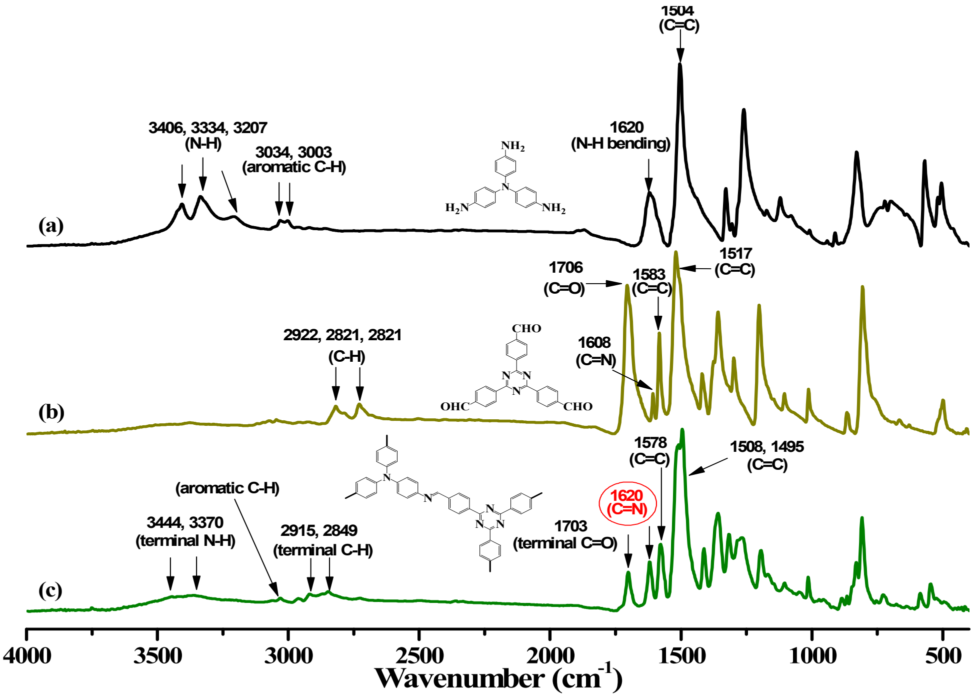


Figure S24. FTIR spectra of (a) TPA-3NH$_2$, (b) TPT-3CHO, and (c) TPA-TPT-COF (TPA-COF-3).

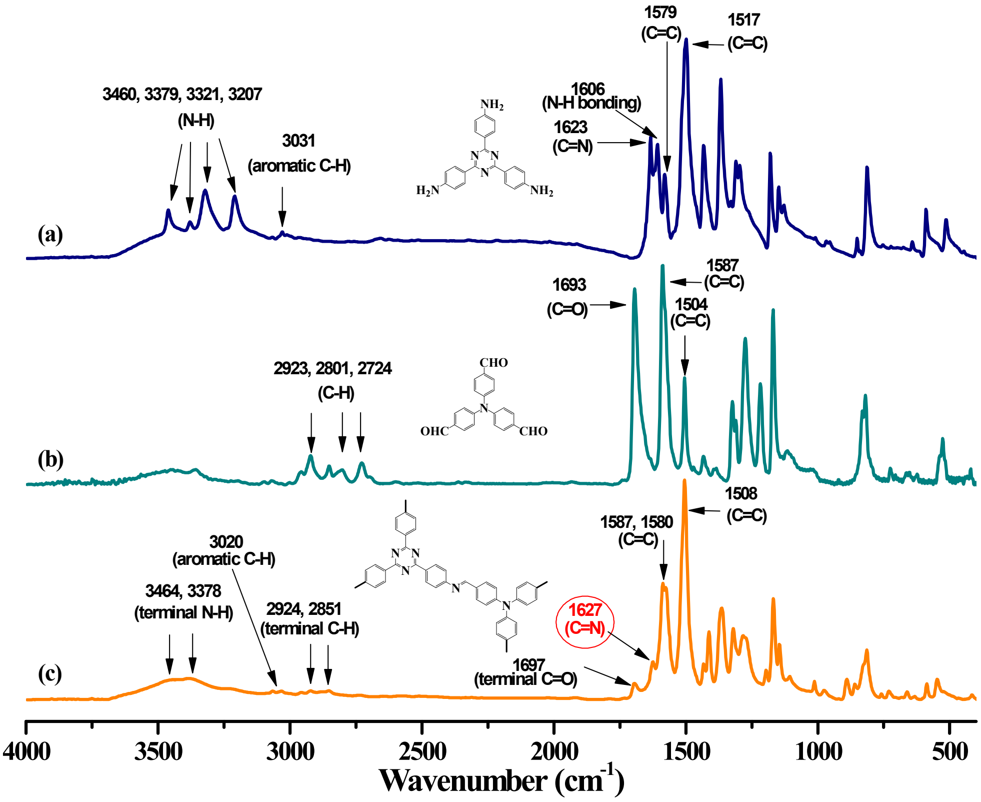


Figure S25. FTIR spectra of (a) TPT-3NH$_2$, (b) TPA-3CHO, and (c) TPT-TPA-COF (TPT-COF-4).

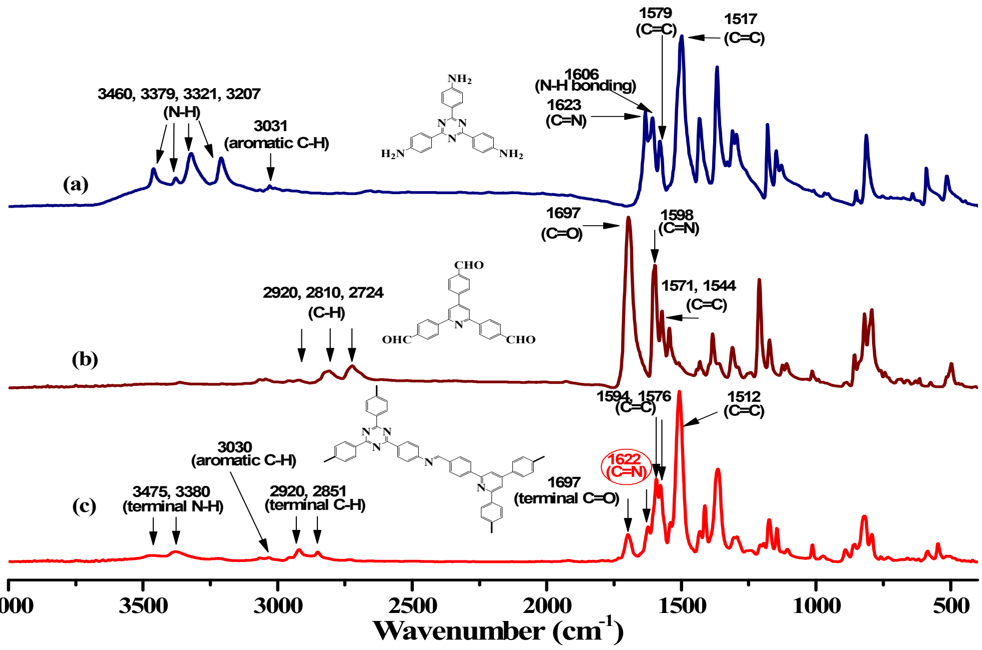


Figure S26. FTIR spectra of (a) TPT-3NH$_2$, (b) TPP-3CHO, and (c) TPT-TPP-COF (TPT-COF-5).

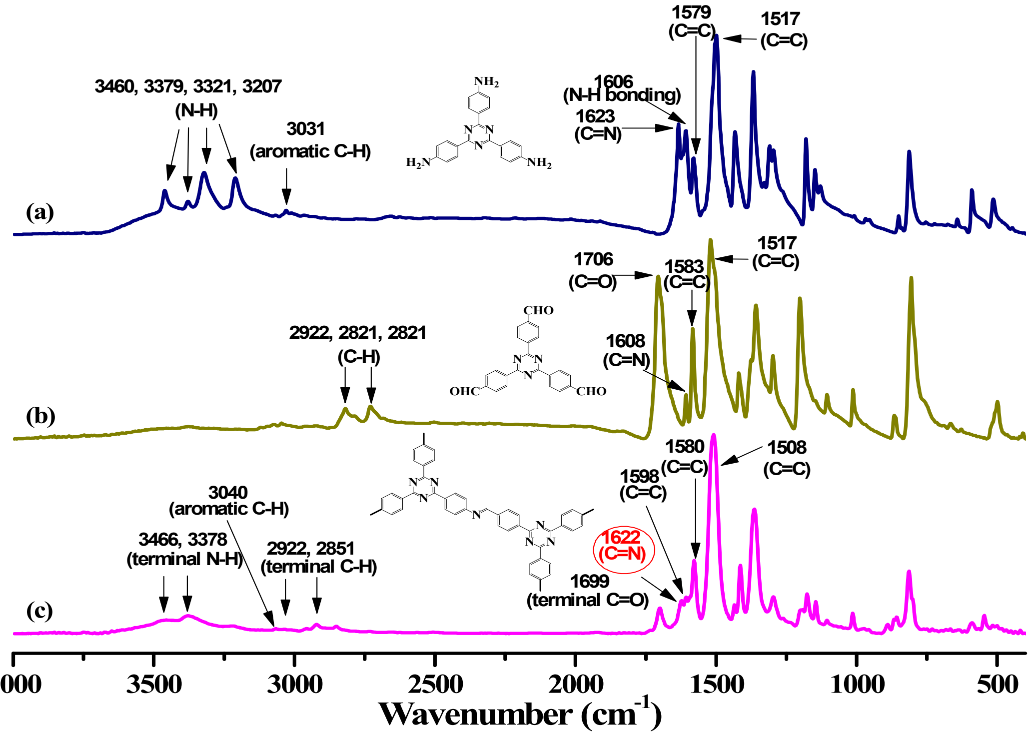


Figure S27. FTIR spectra of (a) TPT-3NH$_2$, (b) TPT-3CHO, and (c) TPT-TPT-COF (TPT-COF-6).

Section G. Elemental analysis

Table S1. Elemental analyses of TPA-TPA-COF (TPA-COF-1), TPA-TPP-COF (TPA-COF-2), TPA-TPT-COF (TPA-COF-3), TPT-TPA-COF (TPT-COF-4), TPT-TPP-COF (TPT-COF-5), and TPT-TPT-COF (TPT-COF-6).

COFs		C%	H%	N%
TPA-COF-1	Calcd.	84.44	5.19	10.37
	Found	77.69	5.17	11.70
TPA-COF-2	Calcd.	85.71	4.98	9.30
	Found	78.34	5.08	10.38
TPA-COF-3	Calcd.	81.45	4.64	13.61
	Found	73.93	4.75	14.02
TPT-COF-4	Calcd.	81.45	4.64	13.61
	Found	76.28	4.66	14.73
TPT-COF-5	Calcd.	85.46	4.71	9.83
	Found	80.02	4.30	13.74
TPT-COF-6	Calcd.	81.60	4.40	14.00
	Found	74.70	4.02	17.47

Section H. TGA profiles

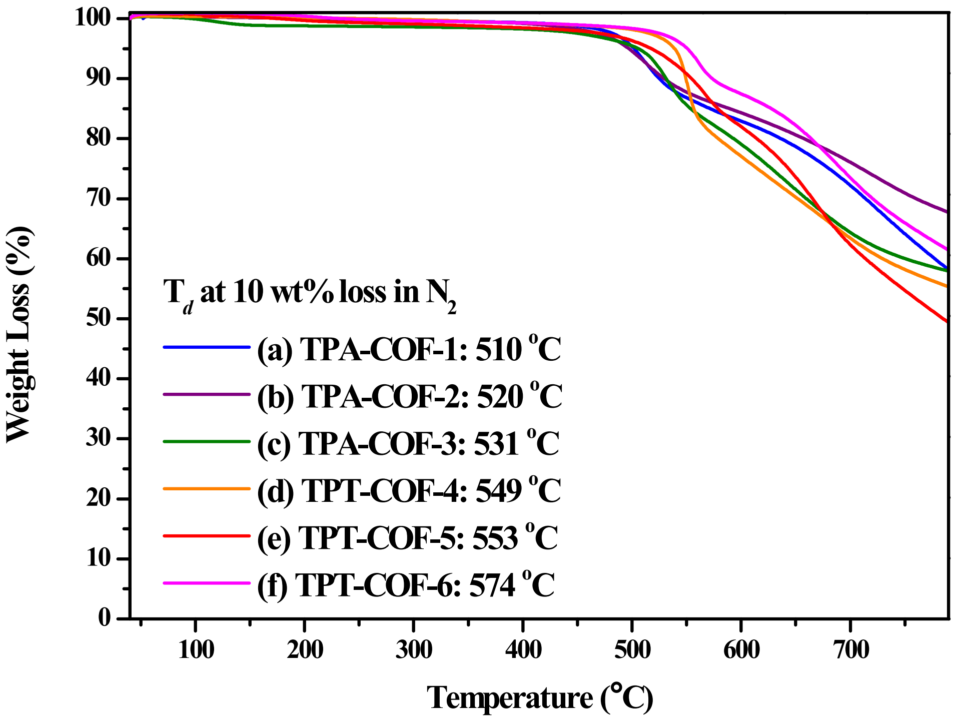


Figure S28. TGA curves of TPA-COF-1 (blue), TPA-COF-2 (purple), TPA-COF-3 (olive), TPT-COF-4 (orange), TPT-COF-5 (red), and TPT-COF-6 (magenta).

Table S2. Values of $T_{\mathrm{d}10\%}$, $\mathrm{T}_{\mathrm{onset}}$ and char yields

	TPA-COF-1	TPA-COF-2	TPA-COF-3	TPT-COF-4	TPT-COF-5	TPT-COF-6
$\mathrm{T}_{d10\%}$ (°C)	510	520	531	549	553	574
$\mathrm{T}_{\mathrm{onset}}$(°C)	475	485	503	539	541	554
Char yield (%)	58	67	58	55	49	61

Section I. PXRD patterns

Table S3. Fractional atomic coordinates for the unit cell of TPA-COF-1 with AA-stacking

Space group: P3 (No. 143)							
a = b = 20.22971 Å, c = 4.68099 Å, $\alpha = \beta = 90^{o}$, $\gamma = 120^{o}$							
R_{wp} = 8.61%, R_p = 6.80%							
N1	0.15606	0.84400	0.46788	C14	0.30196	0.71399	0.62933
N2	0.33333	0.66667	0.62719	C15	0.33380	0.77853	0.79678
N3	0.00000	0.00000	0.41036	C16	0.30280	0.82355	0.80415
C4	0.04176	0.96258	0.41828	H17	-0.03063	0.87501	0.13003
C5	0.01829	0.89725	0.26175	H18	0.03854	0.80949	0.15564
C6	0.05726	0.85980	0.27772	H19	0.19331	0.97562	0.73955
C7	0.11977	0.88613	0.45335	H20	0.12531	1.04035	0.70812
C8	0.14448	0.95236	0.60635	H21	0.22813	0.89626	0.81446
C9	0.10574	0.98999	0.58799	H22	0.15994	0.72683	0.33726
C10	0.20791	0.85370	0.64918	H23	0.21297	0.64655	0.33757
C11	0.23999	0.80564	0.63848	H24	0.38252	0.79372	0.92266
C12	0.20840	0.74164	0.46747	H25	0.32791	0.87243	0.93906
C13	0.23876	0.69603	0.46579				

Table S4. Fractional atomic coordinates for the unit cell of TPA-COF-2 with AA-stacking

<table>
<tr><td colspan="8">Space group: P1 (No. 1)</td></tr>
<tr><td colspan="8">a = 21.37104 Å, b = 22.96124 Å, c = 3.76045 Å, $\alpha = \beta = 90^o$, $\gamma = 120^o$</td></tr>
<tr><td colspan="8">R_{wp} = 9.14%, R_p = 6.76%</td></tr>
<tr><td>N1</td><td>0.14587</td><td>0.86438</td><td>0.57900</td><td>C40</td><td>0.04065</td><td>0.17149</td><td>0.39727</td></tr>
<tr><td>N2</td><td>0.37085</td><td>0.72916</td><td>0.39912</td><td>C41</td><td>0.00840</td><td>0.10371</td><td>0.41046</td></tr>
<tr><td>N3</td><td>0.71974</td><td>0.85984</td><td>0.51793</td><td>C42</td><td>0.03506</td><td>0.07114</td><td>0.58174</td></tr>
<tr><td>N4</td><td>0.13777</td><td>0.27860</td><td>0.54500</td><td>C43</td><td>0.09539</td><td>0.10917</td><td>0.74164</td></tr>
<tr><td>N5</td><td>-0.99844</td><td>1.00040</td><td>0.59067</td><td>C44</td><td>0.12805</td><td>0.17702</td><td>0.72754</td></tr>
<tr><td>C6</td><td>0.03995</td><td>0.96750</td><td>0.59357</td><td>C45</td><td>0.82783</td><td>0.86731</td><td>0.40286</td></tr>
<tr><td>C7</td><td>0.01682</td><td>0.90768</td><td>0.75216</td><td>C46</td><td>0.89652</td><td>0.90214</td><td>0.42477</td></tr>
<tr><td>C8</td><td>0.05268</td><td>0.87518</td><td>0.74750</td><td>C47</td><td>0.92976</td><td>0.96273</td><td>0.58156</td></tr>
<tr><td>C9</td><td>0.11261</td><td>0.90132</td><td>0.58378</td><td>C48</td><td>0.89125</td><td>0.98625</td><td>0.72403</td></tr>
<tr><td>C10</td><td>0.13713</td><td>0.96176</td><td>0.42942</td><td>C49</td><td>0.82256</td><td>0.95149</td><td>0.70320</td></tr>
<tr><td>C11</td><td>0.10107</td><td>0.99410</td><td>0.43458</td><td>H50</td><td>-0.02983</td><td>0.88515</td><td>0.87317</td></tr>
<tr><td>C12</td><td>0.19861</td><td>0.87745</td><td>0.41692</td><td>H51</td><td>0.03358</td><td>0.82896</td><td>0.86969</td></tr>
<tr><td>C13</td><td>0.22604</td><td>0.83352</td><td>0.43097</td><td>H52</td><td>0.18359</td><td>0.98442</td><td>0.30319</td></tr>
<tr><td>C14</td><td>0.19362</td><td>0.77431</td><td>0.59933</td><td>H53</td><td>0.12126</td><td>1.04010</td><td>0.31407</td></tr>
<tr><td>C15</td><td>0.21911</td><td>0.73227</td><td>0.60033</td><td>H54</td><td>0.22277</td><td>0.91967</td><td>0.26261</td></tr>
<tr><td>C16</td><td>0.27763</td><td>0.74868</td><td>0.43287</td><td>H55</td><td>0.14856</td><td>0.76070</td><td>0.73037</td></tr>
<tr><td>C17</td><td>0.31075</td><td>0.80866</td><td>0.27149</td><td>H56</td><td>0.19358</td><td>0.68757</td><td>0.73704</td></tr>
<tr><td>C18</td><td>0.28502</td><td>0.85049</td><td>0.26907</td><td>H57</td><td>0.35575</td><td>0.82227</td><td>0.13963</td></tr>
<tr><td>C19</td><td>0.30462</td><td>0.70403</td><td>0.42230</td><td>H58</td><td>0.31073</td><td>0.89576</td><td>0.13659</td></tr>
<tr><td>C20</td><td>0.26323</td><td>0.63637</td><td>0.42383</td><td>H59</td><td>0.21044</td><td>0.61552</td><td>0.43790</td></tr>
<tr><td>C21</td><td>0.29029</td><td>0.59557</td><td>0.40360</td><td>H60</td><td>0.38049</td><td>0.59284</td><td>0.36713</td></tr>
</table>

C22	0.35881	0.62359	0.38136	H61	0.47305	0.64932	0.04975
C23	0.39907	0.69132	0.37806	H62	0.59291	0.70023	0.03790
C24	0.47174	0.72243	0.35935	H63	0.60965	0.85578	0.64074
C25	0.24722	0.52388	0.40186	H64	0.48919	0.80458	0.65529
C26	0.50211	0.69373	0.18478	H65	0.17303	0.52384	0.08909
C27	0.57066	0.72307	0.17533	H66	0.10289	0.40562	0.08034
C28	0.61018	0.78145	0.34054	H67	0.24076	0.38698	0.69741
C29	0.58005	0.81074	0.51099	H68	0.31033	0.50530	0.71342
C30	0.51148	0.78170	0.51834	H69	0.70322	0.79069	0.16710
C31	0.18778	0.49459	0.22770	H70	0.08268	0.29653	0.20972
C32	0.14793	0.42705	0.22055	H71	0.01751	0.19365	0.26380
C33	0.16662	0.38746	0.38748	H72	-0.03784	0.07674	0.28800
C34	0.22572	0.41657	0.56374	H73	0.11781	0.08648	0.87400
C35	0.26564	0.48411	0.57074	H74	0.17446	0.20528	0.85232
C36	0.68242	0.81085	0.33242	H75	0.80495	0.82090	0.28180
C37	0.12436	0.31622	0.37196	H76	0.92346	0.88115	0.32082
C38	0.79028	0.89248	0.53805	H77	0.91412	1.03239	0.84436
C39	0.10146	0.20884	0.55383	H78	0.79405	0.97080	0.81291

Table S5. Fractional atomic coordinates for the unit cell of TPA-COF-3 with AA-stacking

Space group: P3 (No. 143)							
a = b = 22.01013 Å, c = 3.75035 Å, $\alpha = \beta = 90^{o}$, $\gamma = 120^{o}$							
R_{wp} = 10.66%, R_p = 7.68%							
N1	0.14306	0.86208	1.06915	C14	0.27918	0.75038	0.94236
N2	0.26765	0.64087	0.94638	C15	0.31381	0.81284	0.79848
N3	-1.00000	1.00000	1.10282	C16	0.28655	0.85358	0.78808
C4	0.03785	0.96632	1.09885	C17	0.30741	0.70676	0.94655
C5	0.01447	0.90514	1.25260	H18	-0.03195	0.88194	1.37529
C6	0.04994	0.87216	1.24176	H19	0.03081	0.82505	1.36129
C7	0.10979	0.89914	1.07711	H20	0.18078	0.98399	0.79923
C8	0.13448	0.96073	0.92690	H21	0.11934	1.04047	0.82218
C9	0.09878	0.99348	0.93799	H22	0.22189	0.92064	0.76447
C10	0.19673	0.87673	0.91163	H23	0.14287	0.75447	1.18467
C11	0.22475	0.83310	0.92652	H24	0.18998	0.68206	1.19511
C12	0.19042	0.77098	1.07428	H25	0.36136	0.82935	0.68767
C13	0.21715	0.72975	1.07955	H26	0.31361	0.90104	0.67055

Table S6. Fractional atomic coordinates for the unit cell of TPT-COF-4 with AA-stacking

Space group: P3 (No. 143)							
a = b = 22.95627 Å, c = 3.95771 Å, $\alpha = \beta = 90^{o}$, $\gamma = 120^{o}$							
R_{wp} = 11.87%, R_p = 9.82%							
N1	0.16968	0.82226	-0.05888	C14	0.30492	0.70941	0.10553
N2	-2.03289	0.93380	0.87295	C15	0.33647	0.77075	0.26428
N3	0.33333	0.66667	0.10499	C16	0.30923	0.81156	0.26727
C4	0.06995	0.93081	-0.11732	C17	-2.06659	-0.03350	-0.12742
C5	0.04030	0.86538	-0.22406	H18	-0.00900	0.84122	-0.32332
C6	0.07433	0.83098	-0.20635	H19	0.05129	0.78075	-0.29091
C7	0.13776	0.86053	-0.07680	H20	0.21767	0.95150	0.11716
C8	0.16811	0.92642	0.02458	H21	0.15832	1.01157	0.08778
C9	0.13446	0.96119	0.00386	H22	0.24416	0.87860	0.27278
C10	0.22139	0.83589	0.11492	H23	0.17146	0.71565	-0.17733
C11	0.24956	0.79231	0.10869	H24	0.21834	0.64414	-0.17153
C12	0.21762	0.73154	-0.05210	H25	0.38277	0.78775	0.38295
C13	0.24490	0.69076	-0.05213	H26	0.33482	0.85821	0.39417

Table S7. Fractional atomic coordinates for the unit cell of TPT-COF-5 with AA-stacking

Space group: P1 (No. 1)							
a = 24.75939 Å, b = 26.10230 Å, c = 3.53306 Å, $\alpha = \beta = 90^{o}$, $\gamma = 120^{o}$							
R_{wp} = 10.80%, R_p = 8.73%							
N1	0.18730	0.80969	0.52417	C43	0.06250	0.12427	0.46889
N2	0.39348	0.68721	0.49933	C44	0.09493	0.09425	0.48053
N3	0.18847	0.28049	0.51826	C45	0.15802	0.12682	0.51229
N4	0.71339	0.81577	0.32136	C46	0.18782	0.18797	0.52630
N5	-0.99725	1.91119	1.41244	C47	0.81059	0.81581	0.29792
N6	-0.90675	1.99979	1.47633	C48	0.87348	0.84659	0.31687
N7	-0.99793	1.99927	1.41790	C49	0.90515	0.90777	0.35700
C8	0.09660	0.90782	0.47492	C50	0.87244	0.93753	0.36693
C9	0.06585	0.84681	0.42465	C51	0.80952	0.90659	0.34812
C10	0.09671	0.81577	0.44332	C52	-1.02826	0.94024	0.39409
C11	0.15855	0.84445	0.51484	C53	-0.93654	1.94055	1.45380
C12	0.18982	0.90554	0.56388	C54	-0.93728	2.02943	1.45839
C13	0.15902	0.93686	0.54442	H55	0.01793	0.82315	0.36796
C14	0.24205	0.82588	0.62923	H56	0.07254	0.76892	0.40103
C15	0.26443	0.78405	0.61364	H57	0.23775	0.92943	0.61340
C16	0.22685	0.72616	0.49401	H58	0.18390	0.98380	0.58420
C17	0.24855	0.68715	0.47284	H59	0.27189	0.86962	0.73202
C18	0.30841	0.70491	0.57477	H60	0.18087	0.71147	0.40927
C19	0.34593	0.76298	0.69437	H61	0.21876	0.64382	0.36351
C20	0.32415	0.80211	0.71417	H62	0.39214	0.77789	0.77494
C21	0.33299	0.66457	0.53966	H63	0.35392	0.84648	0.80850

C22	0.29528	0.60350	0.54546	H64	0.24793	0.58458	0.60770
C23	0.31930	0.56678	0.48083	H65	0.40042	0.56514	0.35112
C24	0.38149	0.59237	0.42288	H66	0.20217	0.50234	0.23460
C25	0.41893	0.65313	0.44934	H67	0.13855	0.39608	0.21870
C26	0.48557	0.68064	0.42871	H68	0.28393	0.37762	0.67665
C27	0.27995	0.50195	0.47366	H69	0.34682	0.48369	0.71363
C28	0.22030	0.47586	0.34032	H70	0.48932	0.60514	0.64038
C29	0.18399	0.41502	0.32748	H71	0.59821	0.65110	0.61287
C30	0.20662	0.37893	0.44383	H72	0.61052	0.81112	0.21860
C31	0.26588	0.40466	0.57967	H73	0.49997	0.76430	0.23280
C32	0.30199	0.46543	0.59678	H74	0.69751	0.73522	0.51510
C33	0.51458	0.64947	0.53569	H75	0.12345	0.29735	0.30080
C34	0.57718	0.67598	0.52513	H76	0.06572	0.20650	0.48117
C35	0.61246	0.73440	0.41273	H77	0.01383	0.10044	0.44908
C36	0.58400	0.76597	0.30767	H78	0.18419	0.10496	0.52490
C37	0.52110	0.73933	0.31649	H79	0.23638	0.21264	0.54955
C38	0.67860	0.76137	0.41567	H80	0.78784	0.76898	0.26078
C39	0.16817	0.31483	0.41769	H81	0.89746	0.82259	0.30120
C40	0.15556	0.21771	0.50613	H82	0.89553	0.98466	0.39494
C41	0.77805	0.84564	0.32235	H83	0.78480	0.92983	0.36221
C42	0.09238	0.18528	0.48312				

Table S8. Fractional atomic coordinates for the unit cell of TPT-COF-6 with AA-stacking

Space group: P3 (No. 143)							
a = b = 25.40160 Å, c = 3.50762 Å, $\alpha = \beta = 90^{o}$, $\gamma = 120^{o}$							
R_{wp} = 10.04%, R_p = 8.25%							
N1	0.15567	0.83995	0.50893	C15	0.32178	0.80510	0.42394
N2	0.27385	0.64359	0.46693	C16	0.29787	0.84278	0.42168
N3	-2.02993	0.94002	1.52920	C17	0.31009	0.70334	0.46695
C4	0.06332	0.93693	0.52705	C18	-2.06042	-0.03027	0.52929
C5	0.03291	0.87462	0.49761	H19	-0.01507	0.84982	0.47642
C6	0.06422	0.84381	0.49265	H20	0.04037	0.79592	0.46843
C7	0.12619	0.87422	0.51492	H21	0.20450	0.96149	0.58097
C8	0.15685	0.93650	0.55035	H22	0.15025	1.01538	0.58248
C9	0.12567	0.96747	0.55463	H23	0.24243	0.90682	0.40816
C10	0.21218	0.86018	0.45980	H24	0.15191	0.73930	0.54043
C11	0.23651	0.81961	0.46320	H25	0.19359	0.67298	0.54246
C12	0.19937	0.75803	0.50679	H26	0.36928	0.82413	0.38993
C13	0.22319	0.72027	0.50747	H27	0.32730	0.89011	0.38686
C14	0.28472	0.74337	0.46627				

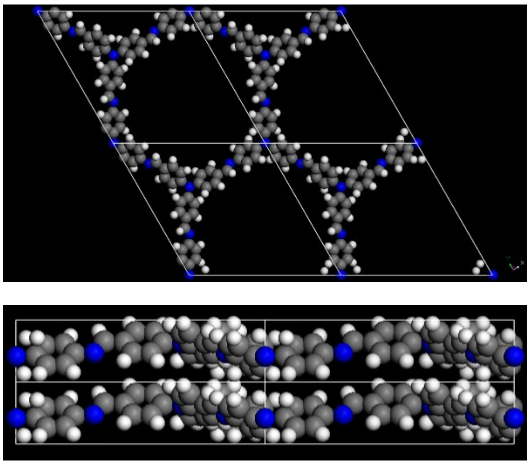
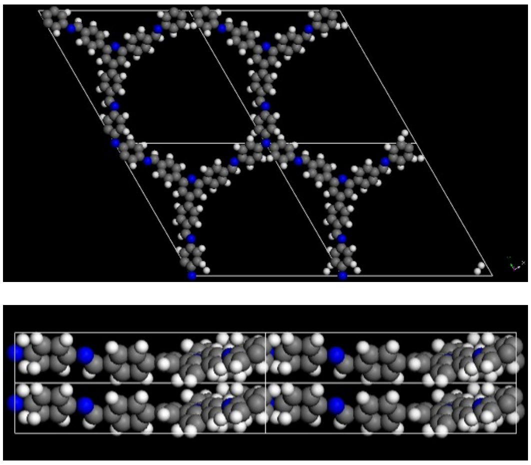
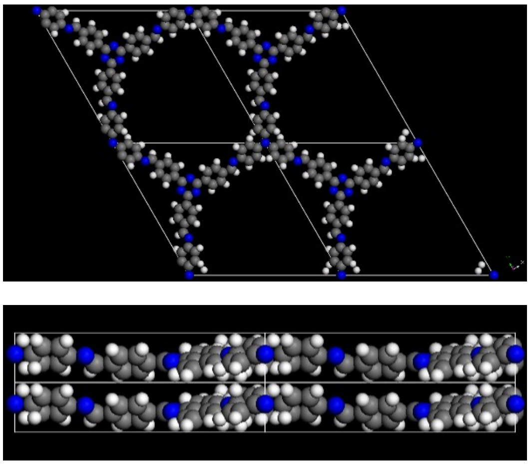
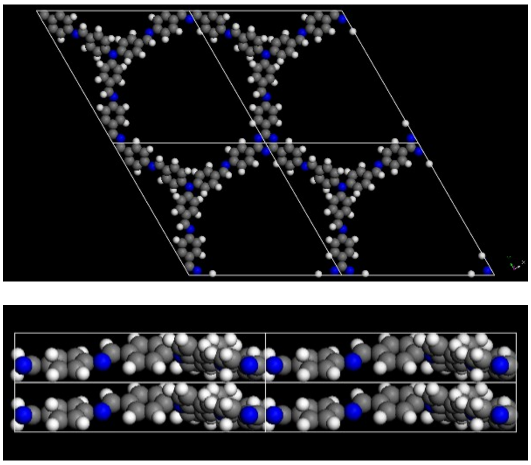
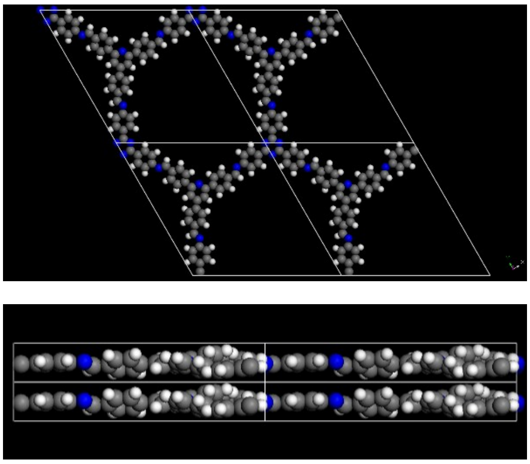
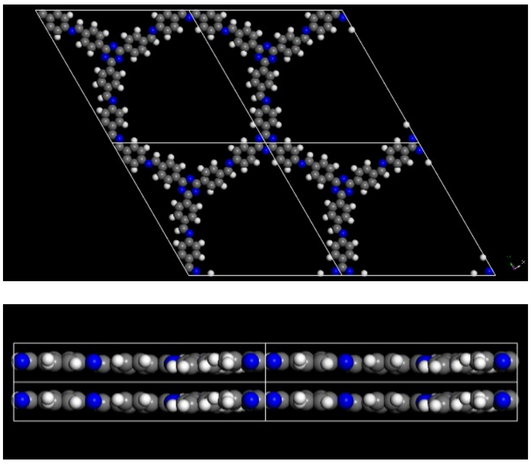
TPA-COF-1	TPA-COF-2
	
TPA-COF-3	TPT-COF-4
	
TPT-COF-5	TPT-COF-6
	

Figure S29. Simulated structures of TPA-COFs to TPT-COFs (top views along the *c* axis and down views along the *a* axis).

Section J. SEM analysis

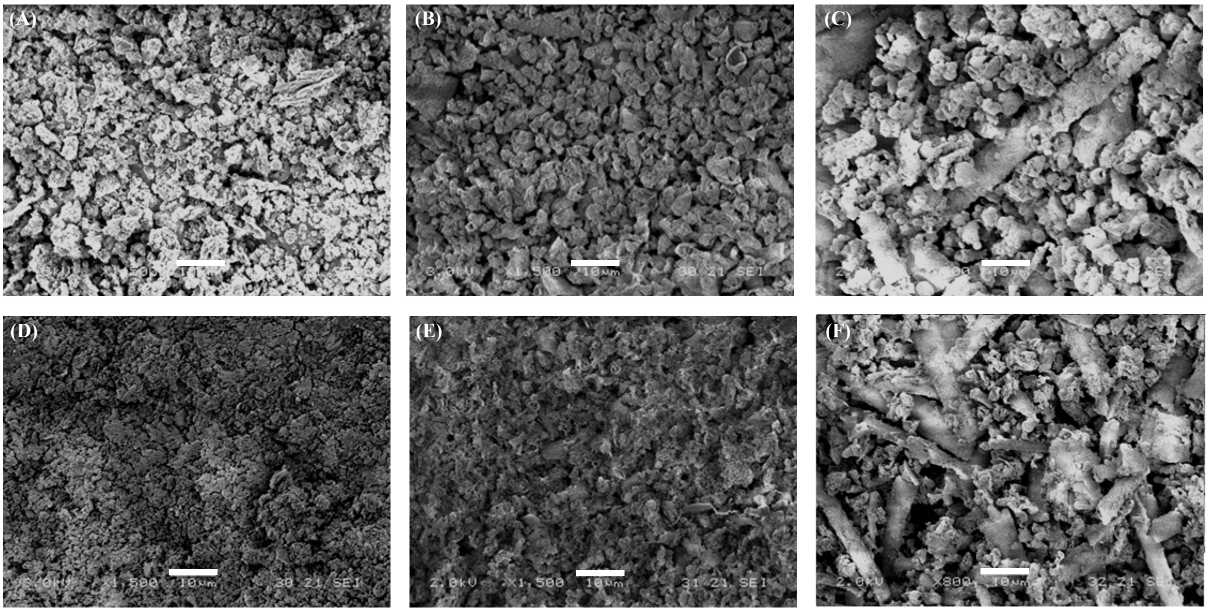


Figure S30. SEM images of the TPA-COFs: (A) TPA-TPA-COF (TPA-COF-1), (B) TPA-TPP-COF (TPA-COF-2), and (C) TPA-TPT-COF (TPA-COF-3); and the TPT-COFs: (D) TPT-TPA-COF (TPT-COF-4), (E) TPT-TPP-COF (TPT-COF-5), and (F) TPT-TPT-COF (TPT-COF-6).

Section K. CO_2 isosteric heats of adsorption

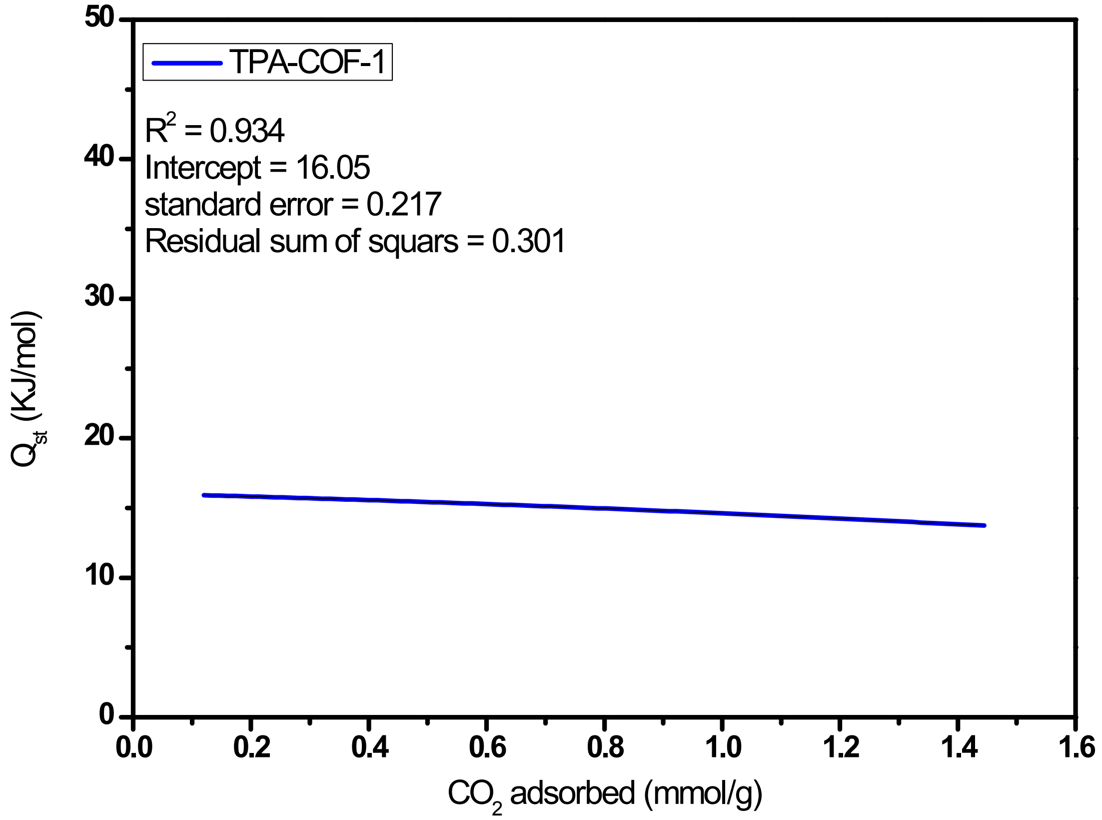


Figure S31. Isosteric heat of adsorption (Q_{st}) for TPA-COF-1 obtained from the CO_2 uptake isotherms collected at 298 and 273 K.

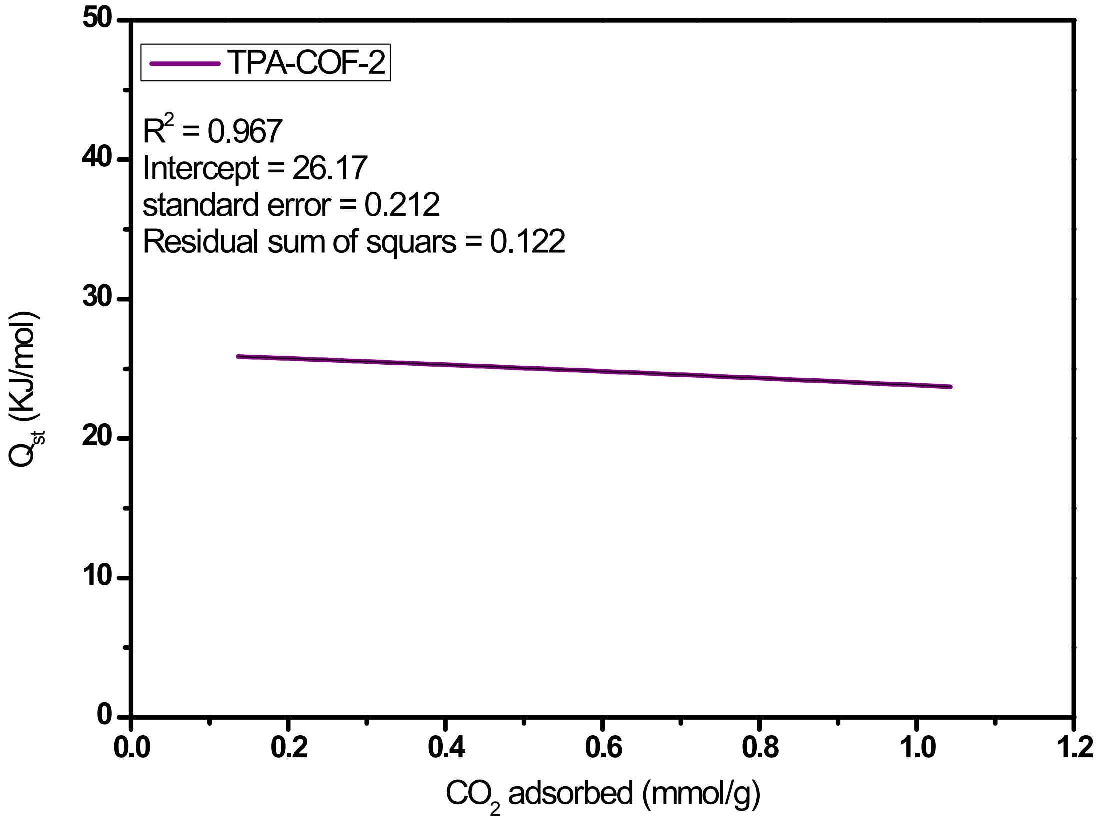


Figure S32. Isosteric heat of adsorption (Q_{st}) for TPA-COF-2 obtained from the CO_2 uptake isotherms collected at 298 and 273 K.

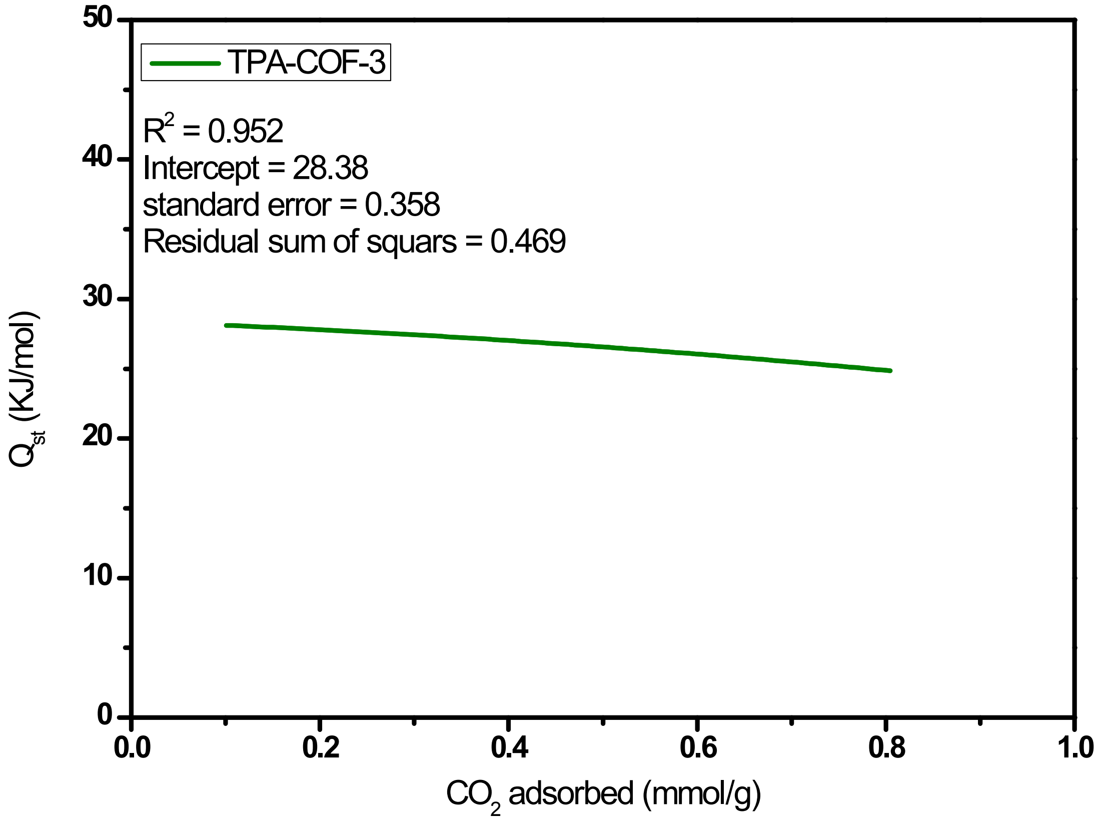


Figure S33. Isosteric heat of adsorption (Q_{st}) for TPA-COF-3 obtained from the CO_2 uptake isotherms collected at 298 and 273 K.

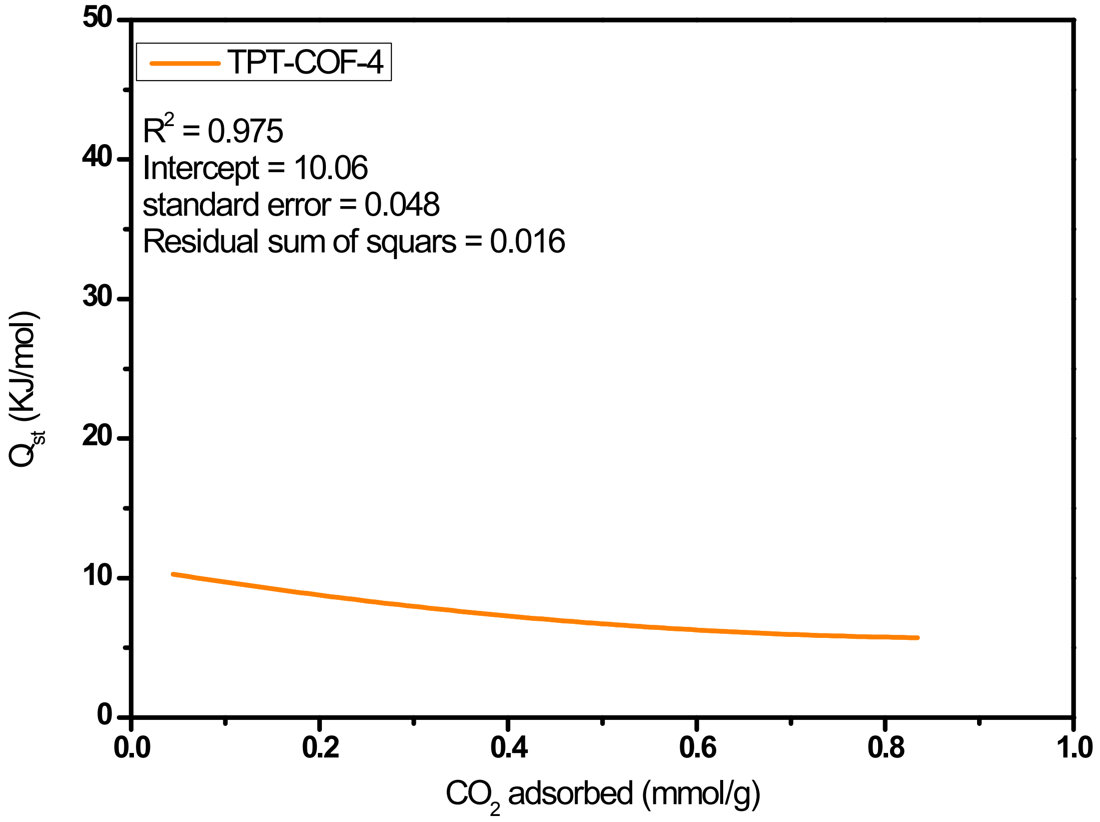


Figure S34. Isosteric heat of adsorption (Q_{st}) for TPT-COF-4 obtained from the CO_2 uptake isotherms collected at 298 and 273 K.

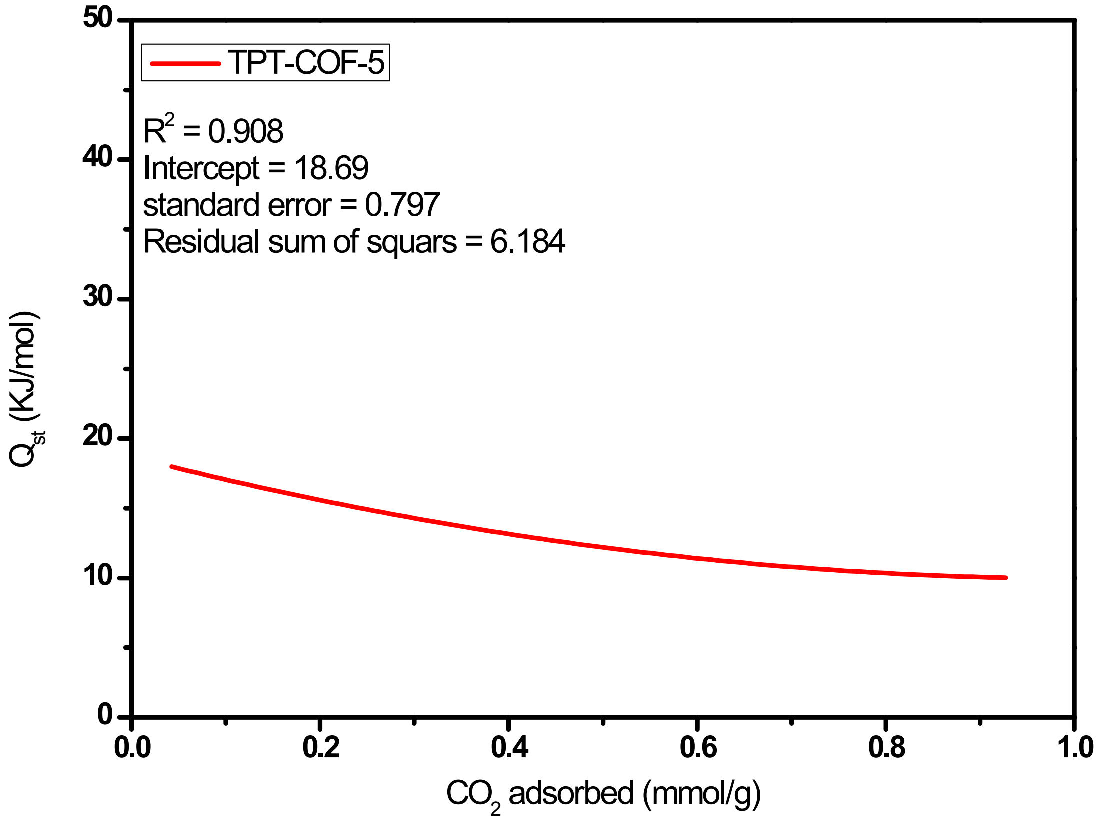


Figure S35. Isosteric heat of adsorption (Q_{st}) for TPT-COF-5 obtained from the CO_2 uptake isotherms collected at 298 and 273 K.

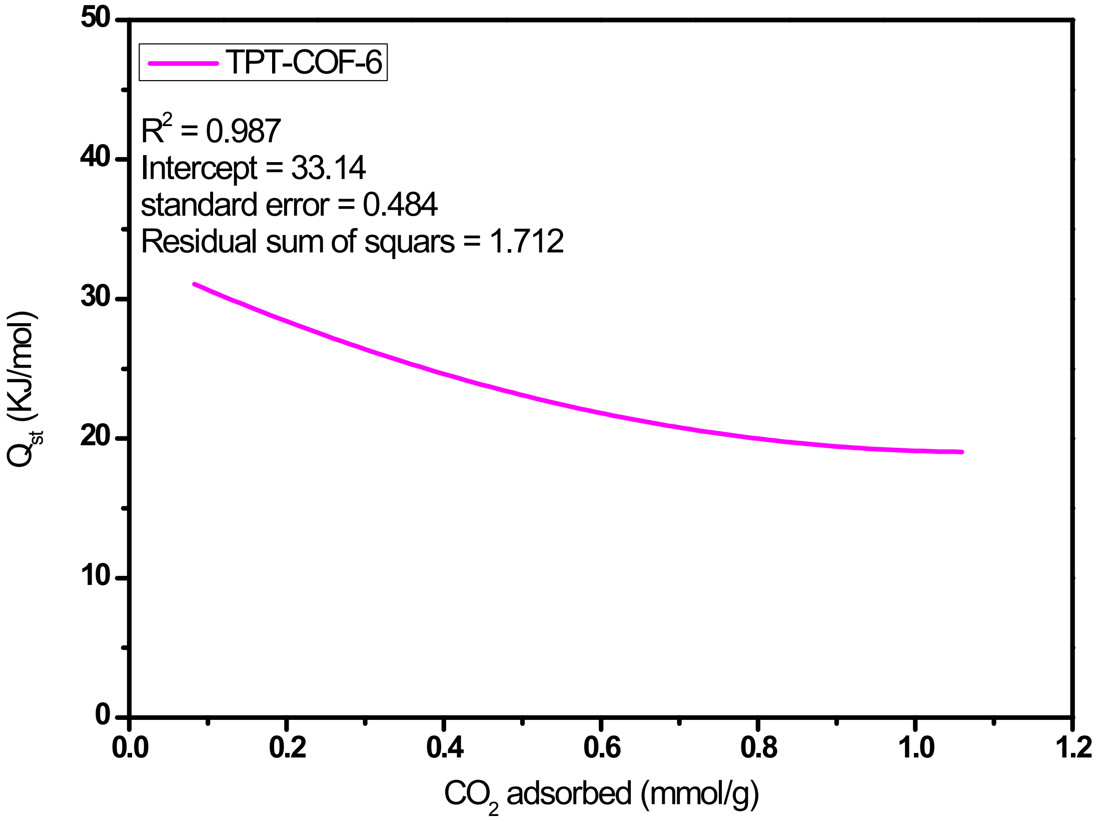


Figure S36. Isosteric heat of adsorption (Q_{st}) for TPT-COF-6 obtained from the CO_2 uptake isotherms collected at 298 and 273 K.

Section L. Electrochemical analysis

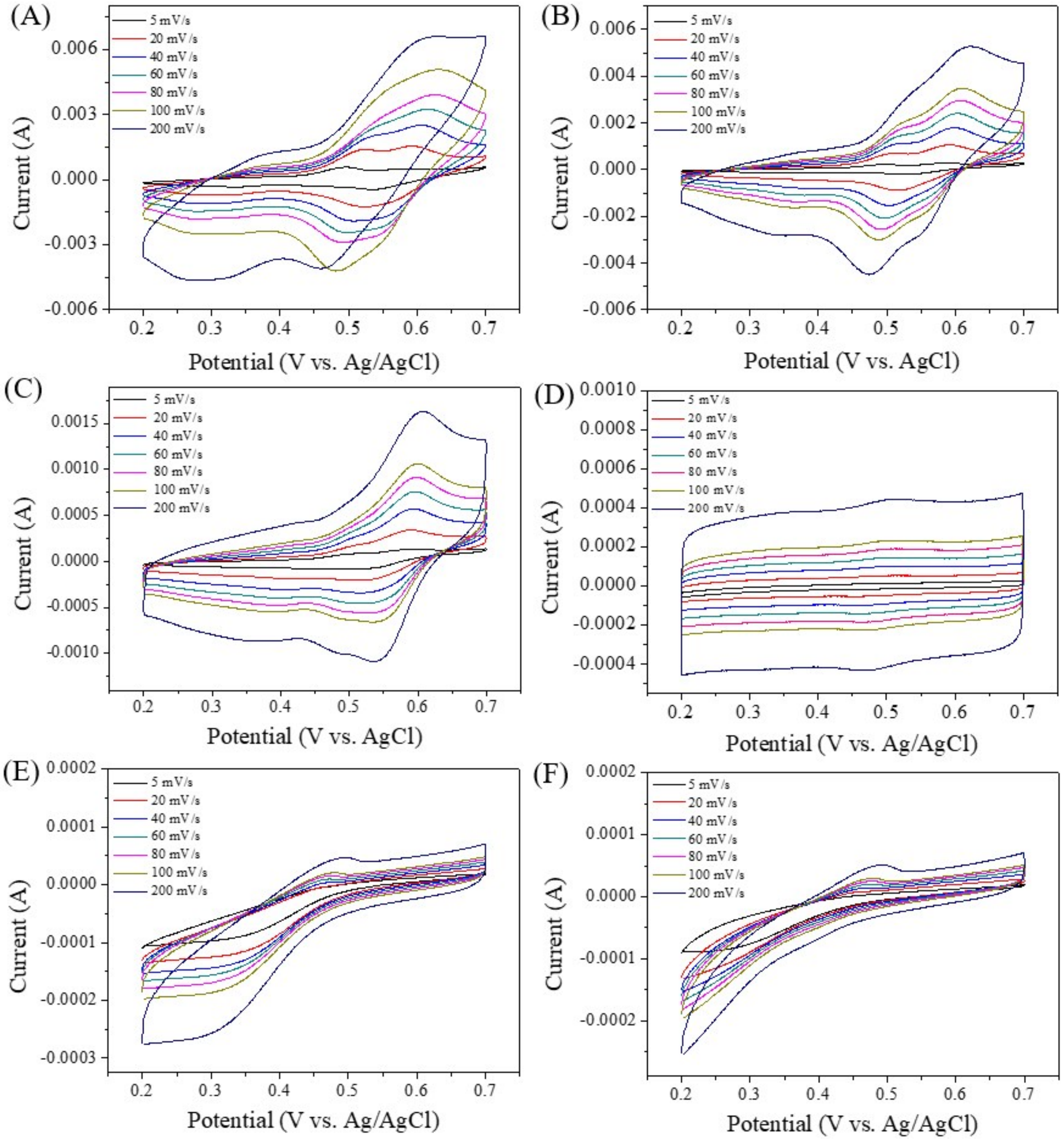


Figure S37. CV traces of the COFs, recorded at various scan rates: (A) TPA-COF-1, (B) TPA-COF-2, (C) TPA-COF-3, (D) TPT-COF-4, (E) TPT-COF-5, and (F) TPT-COF-6.