

Thienyltriazine based porous organic polymers with nitrogen rich moieties: Synthesis and gas selectivity study

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Experimental section

General Instrumentation

^1H and ^{13}C NMR spectra of the monomers and precursors were recorded at room temperature using a Jeol JNM-ECS 400 spectrometer (400 MHz ^1H , 100 MHz ^{13}C) or Bruker Avance 500 (500 MHz ^1H , 125 MHz ^{13}C) spectrometer with tetramethylsilane as the internal reference. Chemical shifts (δ) are expressed in parts per million (ppm). The spectra were processed using MestReNova v5 and referenced to residual protonated solvent signals (CDCl_3 : ^1H 7.26 ppm, ^{13}C 77.16 ppm). Fourier transform infrared spectroscopy (FTIR) spectra were recorded in the range of 4000-400 cm^{-1} using the KBr pellet technique on a Perkin-Elmer RX1 IR Spectrometer. The thermal properties of CPPs were measured by a thermogravimeter analyzer (Mettler Toledo, TGA/SDTA 851) from 40 $^\circ\text{C}$ to 800 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C min}^{-1}$ under a nitrogen atmosphere. A Rigaku (Mini Flex II, Japan) powder X-ray diffractometer equipped with Cu $\text{K}\alpha$ ($\lambda = 1.54059 \text{ \AA}$) radiation was used to record the X-ray diffraction (XRD) patterns. Solid-state UV-vis absorption spectra were obtained using a JASCO V-670 spectrophotometer. Elemental analysis was performed using a Perkin Elmer CHN analyzer. N_2 adsorption-desorption isotherms were obtained on a Micromeritics Gemini VII surface area analyzer at 77.3 K and analyzed using the Barrett-Joyner-Halenda surface/volume pore analysis. Samples were degassed at 120 $^\circ\text{C}$ under a N_2 atmosphere for 12 hours. The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method. A Carl Zeiss SUPRA 55VP microscope was used to obtain the field-emission scanning electron microscopy (FESEM) images after coating the sample with Au film. Transmission electron microscopy (TEM) images were recorded using a JEOL JEM-2100F microscope at the Department of Science and Technology, Fund for Improvement of S&T Infrastructure in Higher Educational Institutions (DST-FIST) facility of IISER Kolkata. The ^1H - ^{13}C CP/MAS NMR spectra were recorded on a Bruker AVANCE 500-MHz type (^1H , 500 MHz; ^{13}C , 125 MHz) spectrometer at a spinning speed of 8 KHz and a relaxation delay of 10 seconds. UV-visible absorption spectra were recorded using an Agilent Cary60 UV-Vis spectrophotometer. CO_2 sorption data were recorded for pressures in the range 0–1.2 bar by the volumetric method using a BELSORP MAXinstrument. Isothermic heats of adsorption (Q_{st}) were calculated using the Clausius-Clapeyron equation based on pure-component isotherms collected at three different temperatures of 263 K, 273 K, and 298 K. These calculations were performed using

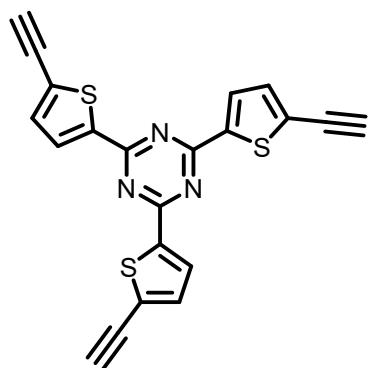
the “Heat of Adsorption” function embedded in the Belsorp Adsorption/Desorption DataAnalysis software version 6.3.1.0.

Materials

The reagents obtained from commercial sources (Sigma Aldrich, Spectrochem, Merck and Alfa Aesar) were used as received, without further purification unless otherwise specified. Toluene and Tetrahydrofuran (THF) were dried over sodium/benzophenone before use. Dry reactions were conducted in oven-dried glassware, utilizing a standard Schlenk line under an inert atmosphere of dry nitrogen. Dimethylformamide (DMF) for polymerization reactions was dried over calcium hydride followed by distillation under vacuum. Triethylamine was dried over potassium hydroxide (KOH) flakes. Dichloroethane (DCM) and chloroform (CHCl_3) were dried over calcium chloride. Solvents for Soxhlet extraction were used directly as obtained from commercial sources.

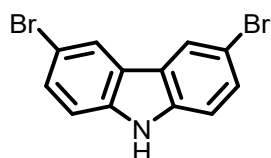
Procedure for the synthesis of precursors and polymers

Synthesis of 2,4,6-tris(5-ethynylthiophen-2-yl)-1,3,5-triazine (TE-TT)



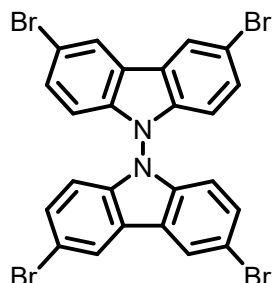
2,4,6-tris(5-ethynylthiophen-2-yl)-1,3,5-triazine (**TT-TE**) was synthesized from 2-cyanothiophene according to the procedure reported by Misra and group.¹ ^1H data was consistent with the reported values. ^1H NMR of **TE-TT** (400 MHz, Jeol, CDCl_3): δ ppm 8.04 (d, 1H, $J = 4$ Hz); 7.30 (d, 1H, $J = 4$ Hz); 3.52 (s, 1H).

Synthesis of 3,6-dibromo-9H-carbazole (CBz)



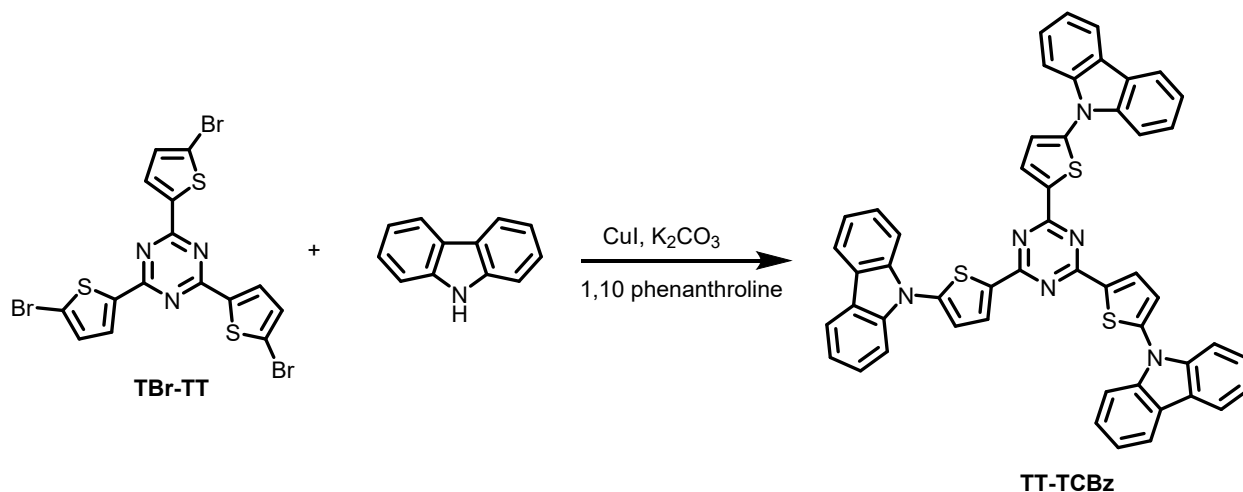
3,6-dibromo-9*H*-carbazole was synthesized by using the method reported by Faulkner.²

Synthesis of 3,3',6,6'-tetrabromo-9,9'-bicarbazole (BCBz)



3,3',6,6'-tetrabromo-9,9'-bicarbazole was synthesized by using the method reported by Chen and co-workers.³

Synthesis of 9,9'-((6-(5-(1,2,3,4-tetrahydro-9*H*-carbazol-9-yl)thiophen-2-yl)-1,3,5-triazine-2,4-diyl)bis(thiophene-5,2-diyl))bis(9*H*-carbazole) (TT-TCBz)

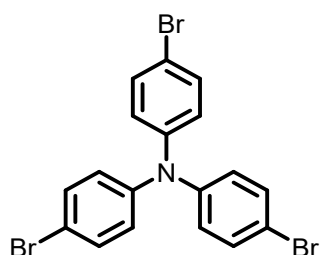


Scheme S1. Synthesis of **TT-TCBz**

TT-TCBz was synthesized using an approach used by Han and group for the synthesis of a monomer, in which thienyltriazine is replaced by benzene.⁴ Under a nitrogen atmosphere, a 250 mL flask was charged potassium carbonate (20.0 mmol), copper iodide (4.0 mmol), 1,10-phenanthroline (0.4 mmol), carbazole (16 mmol), 1,3,5-tribromobenzene (4.0 mmol), and dry *N,N*-dimethylformamide (80 mL). The reaction mixture was stirred for 30 minutes at room temperature and then heated to 110 °C for 3 days. After cooling to room temperature, water was added under

stirring, and the suspension was filtered. The solid was washed with water, then with an excess amount of petroleum, and finally with methanol. A bright yellow-colored solid, **TT-TCBz** was obtained in around 70% yield. ^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 7.33-7.36 (m, 3H); 7.49 (t, 2H, $J = 8$ Hz), 7.68-7.71 (m, 2H), 8.13 (d, 2H, $J = 8$ Hz), 8.40-8.42 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ (ppm): 110.38, 120.33, 121.20, 123.83, 125.04, 126.52, 131.27, 137.65, 141.03, 145.43, 167.27; HRMS: m/z calculated: $(\text{M}+\text{Na})^+$ i.e. $\text{C}_{51}\text{H}_{34}\text{N}_6\text{S}_3\text{Na}$ 849.1905, found: 849.1901.

Synthesis of tris(4-bromophenyl)amine (TPA)



tris(4-bromophenyl)amine was synthesized by using the method reported by Yoshizawa and co-workers.⁵

Synthesis of polymers **TT-CBz**, **TT-BCBz**, **TT-TPA** by Sonogashira-Hagihara Coupling Reaction

Polymers **TT-CBz**, **TT-BCBz**, and **TT-TPA** were synthesized by using standard Sonogashira-Hagihara coupling reaction. A 50 mL oven-dried three-neck round bottom flask fitted with a reflux condenser and a nitrogen purger on the top was charged with a small magnetic stirring bar. The reaction vessel was degassed and purged with nitrogen multiple times. Then, the flask was charged with bromo precursor and 2,4,6-tris(5-ethynylthiophen-2-yl)-1,3,5-triazine (**TE-TT**). 7 mL anhydrous dimethylformamide (DMF) and 7 mL anhydrous triethylamine (Et_3N) were added to the flask under nitrogen, followed by the addition of tetrakis(triphenylphosphine)palladium, i.e., $\text{Pd}(\text{PPh}_3)_4$ (5 mol%) and copper(I)iodide (CuI), (5 mol%). The reaction mixture was stirred at 130 °C for 72 hours under a nitrogen atmosphere. The mixture was then cooled to room temperature, and the precipitated polymer was filtered and washed three times with dichloromethane, water, methanol and acetone (100 mL each) to remove

any unreacted monomers or catalyst residues. Further purification of the polymer was done by Soxhlet extraction with methanol, chloroform, tetrahydrofuran, and acetone for 24 hours each.

The amount of the reactants used are given below

For polymer TT-CBz: Acetylene derivative of thienyltriaizne, **TE-TT:** 0.300 g, 0.75 mmol, 1 equivalent and 3,6-dibromo-9*H*-carbazole: 0.243 g, 0.75 mmol, 1 equivalent. Color: brown, Yield: 93%

For polymer TT-BCBz: Acetylene derivative of thienyltriaizne, **TE-TT:** 0.350 g, 0.87 mmol, 1 equivalent and 3,3',6,6'-tetrabromo-9,9'-bicarbazole: 0.422 g, 0.65 mmol, 0.75 equivalent; Color: brown, Yield: 90%

For polymer TT-TPA: Acetylene derivative of thienyltriaizne, **TE-TT:** 0.250 g, 0.625 mmol, 1 equivalent and tris(4-bromophenyl)amine: 0.422 g, 0.65 mmol, 0.75 equivalent, Color: brown, Yield: 95%

Synthesis of polymers TT-TCBz-(a-g)

Polymers belonging to **TT-TCBz-(a-g)** series were synthesized under different reaction conditions to study the effect of reaction conditions on FeCl₃-mediated polymerization. The reactions were done under three different types of polymerizations: Oxidative Polymerization (OP), Friedel-Crafts polymerization (FCP) and Competitive Oxidative/Friedel-Crafts Polymerization (CO/FC-P). The detailed reaction conditions are provided below and summarized in **Table S1**.

a) Oxidative Polymerization (OP)

Synthesis of polymer **TT-TCBz-a**

A 250 mL two-necked round-bottomed flask was charged with compound **TT-TCBz** (1.2 g, 1.45 mmol, 1 equivalent). The flask was thoroughly evacuated and then filled with nitrogen. This was then followed by the addition of dry CHCl₃ (75 mL). The mixture was stirred for 5 minutes. In a separate single-necked flask, FeCl₃ (9.4 g, 58 mmol, 40 equivalent) was dissolved in CHCl₃ (10 mL). This mixture was added to the flask containing **TT-TCBz**. The mixture was then stirred at room temperature for 72 hours. The reaction was quenched by the addition of methanol. The resulting solid was filtered and thoroughly washed with water, tetrahydrofuran, methanol and

6 N HCl aq. Washing was continued until the filtrate was colorless. This precipitate was then subjected to Soxhlet extraction with methanol, dichloromethane, tetrahydrofuran, and acetone for 24 hours per solvent. The polymer **TT-TCBz-a** was obtained as a yellow color solid in 89% yield.

Synthesis of polymer **TT-TCBz-b**

A 250 mL two-necked round-bottomed flask was charged with compound **TT-TCBz** (1.2 g, 1.45 mmol, 1 equivalent). The flask was thoroughly evacuated and filled with nitrogen. This was then followed by the addition of dry CHCl_3 (75 mL). The mixture was stirred for 5 minutes. In a separate single-necked flask FeCl_3 (9.4 g, 58 mmol, 40 equivalent) was dissolved in MeNO_2 (30 mL). This mixture was added to the flask containing **TT-TCBz**. The mixture was then stirred at room temperature for 72 hours. The reaction was then quenched by the addition of methanol. The resulting solid was filtered and thoroughly washed with water, tetrahydrofuran, methanol and 6 N HCl aq. Washing was continued until the filtrate was colorless. This precipitate was then subjected to Soxhlet extraction with methanol, dichloromethane, tetrahydrofuran, and acetone for 24 h per solvent. The polymer **TT-TCBz-b** was obtained as a yellow color solid with 89% yield.

Synthesis of polymer **TT-TCBz-c**

A 100 mL two-necked round-bottomed flask was charged with compound **TT-TCBz** (600 mg, 0.73 mmol, 1 equivalent). The flask was thoroughly evacuated and filled with nitrogen. This was then followed by the addition of dry dichloroethane (35 mL). The mixture was stirred for 5 minutes. In a separate single-necked flask, FeCl_3 (4.6 g, 29 mmol, 40 equivalent) was dissolved in dichloroethane (10 mL). This mixture was added to the flask containing **TT-TCBz**, and the temperature of the flask was raised to 80 °C. The mixture was stirred for 72 hours under this condition. The reaction was then quenched by the addition of methanol. The resulting solid was filtered and washed thoroughly with water, tetrahydrofuran, methanol and 6 N HCl aq. Washing was continued until the filtrate was colorless. This precipitate was then subjected to Soxhlet extraction with methanol, dichloromethane, tetrahydrofuran, and acetone for 24 h per solvent. The polymer **TT-TCBz-c** was obtained as a yellow color solid in 93% yield.

Synthesis of polymer **TT-TCBz-d**

A 100 mL two-necked round-bottomed flask was charged with compound **TT-TCBz** (600 mg, 0.73 mmol, 1 equivalent). The flask was then thoroughly evacuated and filled with nitrogen.

This was then followed by the addition of dry dichloroethane (35 mL). The mixture was stirred for 5 minutes. In a separate single-necked flask, FeCl₃ (4.6 g, 29.16 mmol, 40 equivalent) was dissolved in MeNO₂ (10 mL). This mixture was added to the flask containing **TT-TCBz**. The mixture was stirred for 72 hours under this condition. The reaction was then quenched by the addition of methanol. The resulting solid was filtered and thoroughly washed with water, tetrahydrofuran, methanol and 6 N HCl aq. Washing was continued until the filtrate was colorless. This precipitate was subsequently subjected to Soxhlet extraction with methanol, dichloromethane, tetrahydrofuran, and acetone for 24 h per solvent. The polymer **TT-TCBz-d** was obtained as a yellow color solid in 90% yield.

Synthesis of polymer **TT-TCBz-e**

A 100 mL two-necked round-bottomed flask was charged with compound **TT-TCBz** (600 mg, 0.73 mmol, 1 equivalent). The flask was then thoroughly evacuated and filled with nitrogen. This was then followed by the addition of dry CHCl₃ (35 mL). The mixture was stirred for 5 minutes. In a separate single-necked flask FeCl₃ (4.6 g, 29.16 mmol, 40 equivalent) was dissolved in MeNO₂ (10 mL). This mixture was added to the flask containing **TT-TCBz**, and the temperature of the mixture was raised to 60 °C. The mixture was stirred for 72 hours under this condition. The reaction was then quenched by the addition of methanol. The resulting solid was filtered and thoroughly washed with water, tetrahydrofuran, methanol and 6 N HCl aq. Washing was continued until the filtrate was colorless. This precipitate was then subjected to Soxhlet extraction with methanol, dichloromethane, tetrahydrofuran, and acetone for 24 h per solvent. The polymer **TT-TCBz-e** was obtained as a yellow color solid in 90% yield.

b) Friedel-Crafts polymerization (FCP)


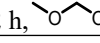
A two-necked round-bottomed flask was charged with a stirring bar, **TT-TCBz** (600 mg, 0.17 mmol, 1 equivalent) and FeCl₃ (4.6 g, 29.16 mmol, 40 equivalent). The flask was thoroughly evacuated and filled with nitrogen. Dry dichloroethane (20 mL) was introduced, and the mixture was stirred for 5 minutes. While stirring, the color of the mixture changed to purple-red. This was followed by the slow addition of dimethoxyethane (2.23 g or 2.5 mL, 29.16 mmol, 40 equivalent) through a syringe with continuous stirring. During this process, the colour of the mixture changed to light brown. The mixture was stirred for 72 hours under this condition. The reaction was then

quenched by adding methanol. The resulting solid was filtered and thoroughly washed with water, tetrahydrofuran, methanol, and 6 N HCl aq. Washing was continued until the filtrate was colorless. This precipitate was then subjected to Soxhlet extraction with methanol, dichloromethane, tetrahydrofuran, and acetone for 24 hours per solvent. The polymer **TT-TCBz-f** was obtained as a yellow-colored solid with 94% yield.

c) Competitive Oxidative/Friedel-Crafts Polymerization (CO/FC-P)

A two-necked round-bottomed flask was charged with a stirring bar, **TT-TCBz** (600 mg, 0.17 mmol, 1 equivalent) and FeCl₃ (4.6 g, 29.16 mmol, 40 equivalent). The flask was thoroughly evacuated and then filled with nitrogen. Dry dichloroethane (20 mL) was introduced, and the mixture was stirred for 5 minutes. While stirring, the color of the mixture changed to purple-red. This was followed by the gradual addition of dimethoxyethane (2.23 g or 2.5 mL, 29.16 mmol, 40 equivalent) through a syringe with continuous stirring. During this process, the color of the mixture changed to light brown. The reaction mixture was stirred under these conditions for 15 minutes, after which the temperature was raised to 80 °C. The mixture was stirred for 72 hours under this condition. The reaction was then quenched by the addition of methanol. The resulting solid was filtered and thoroughly washed with water, tetrahydrofuran, methanol and 6 N HCl aq. Washing was continued until the filtrate was colorless. This precipitate was then subjected to Soxhlet extraction with methanol, dichloromethane, tetrahydrofuran, and acetone for 24 hours per solvent. The polymer **TT-TCBz-g** was obtained as a yellow color solid with 88% yield.

Table S1. Synthesis of polymer of **TT-TCBz** under different reaction conditions to give polymers **TT-TCBz-a**, **TT-TCBz-b**, **TT-TCBz-c**, **TT-TCBz-d**, **TT-TCBz-e**, **TT-TCBz-f**, and **TT-TCBz-g**, respectively.

Polymer	Polymerization type	Reaction conditions	Color of polymer	Yield
TT-TCBz-a	OP	CHCl ₃ , FeCl ₃ , rt, 72 h	Yellow	89%
TT-TCBz-b	OP	CHCl ₃ , MeNO ₂ , FeCl ₃ , rt, 72 h	Yellow	89%
TT-TCBz-c	OP	DCE, FeCl ₃ , 80 °C, 72 h	Yellow	93%
TT-TCBz-d	OP	DCE, MeNO ₂ , FeCl ₃ , 80 °C, 72 h	Yellow	90%
TT-TCBz-e	OP	CHCl ₃ , MeNO ₂ , FeCl ₃ , 60 °C, 72 h	Yellow	90%
TT-TCBz-f	FCP	DCE, FeCl ₃ , rt, 72 h, 	Yellow	94%
TT-TCBz-g	CO/FCP	DCE, FeCl ₃ , 80 °C, 72 h, 	Yellow	88%

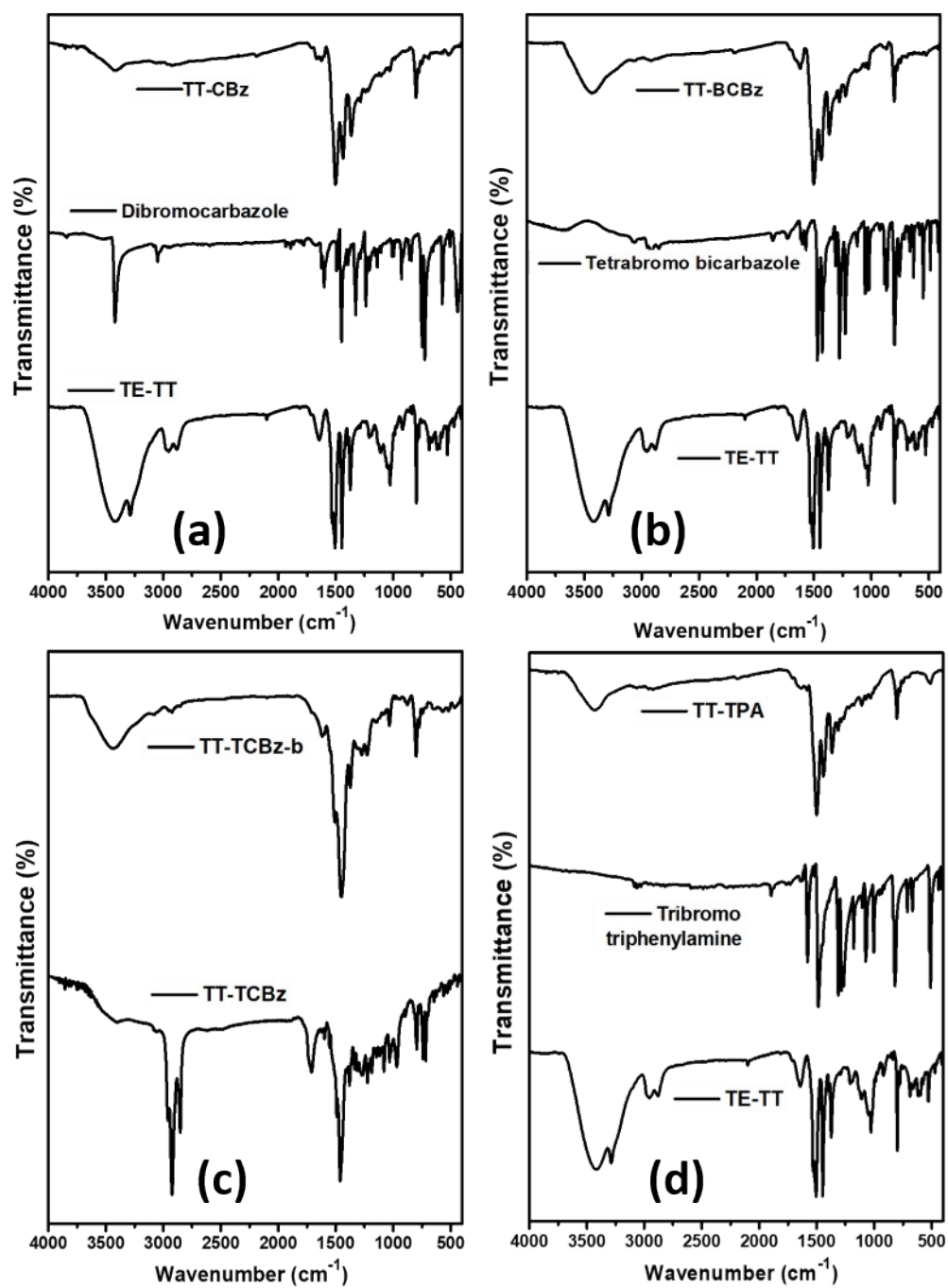


Figure S1. Stacked FT-IR Spectra of polymer precursors and porous polymers.

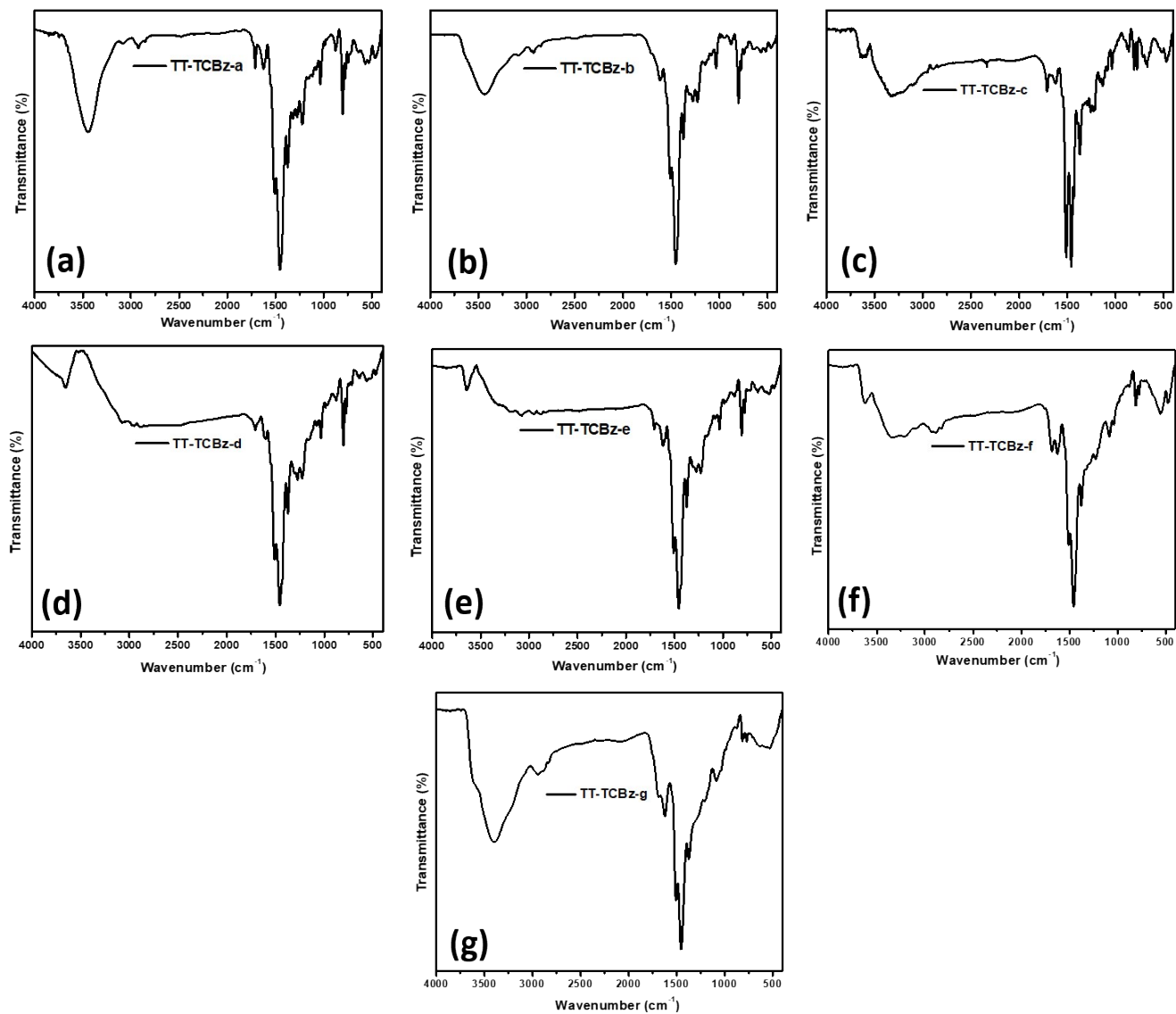


Figure S2. FT-IR Spectra of (a) TT-TCBz-a, (b) TT-TCBz-b, (c) TT-TCBz-c, (d) TT-TCBz-d, (e) TT-TCBz-e, (f) TT-TCBz-f, and (g) TT-TCBz-g, respectively.

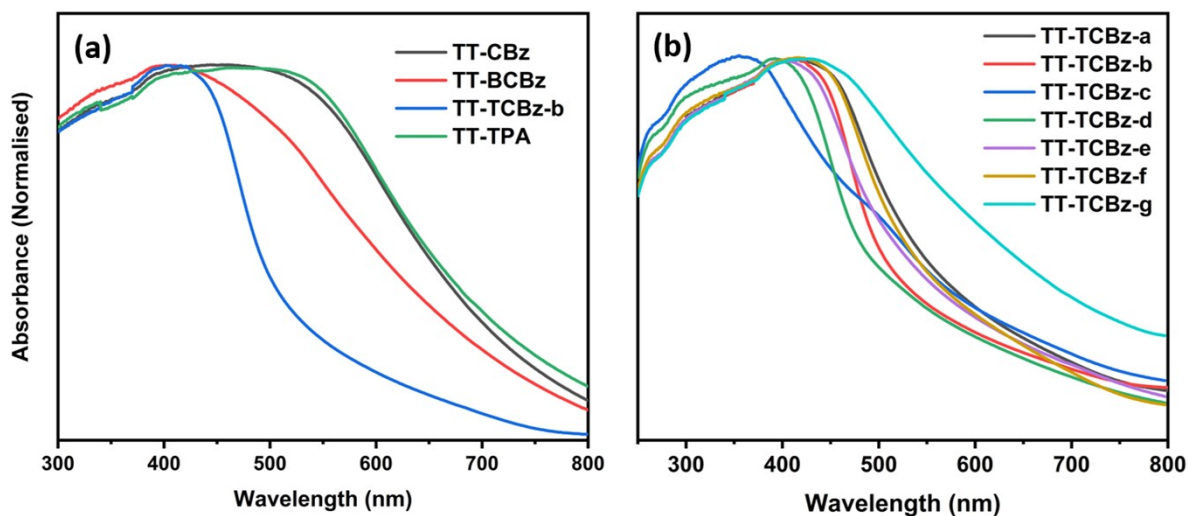


Figure S3. (a) Stacked solid-state UV-visible spectra of TT-CBz, TT-BCBz, TT-TCBz-b and TT-TPA, (b) Stacked solid-state UV-visible spectra of TT-TCBz-(a-g)

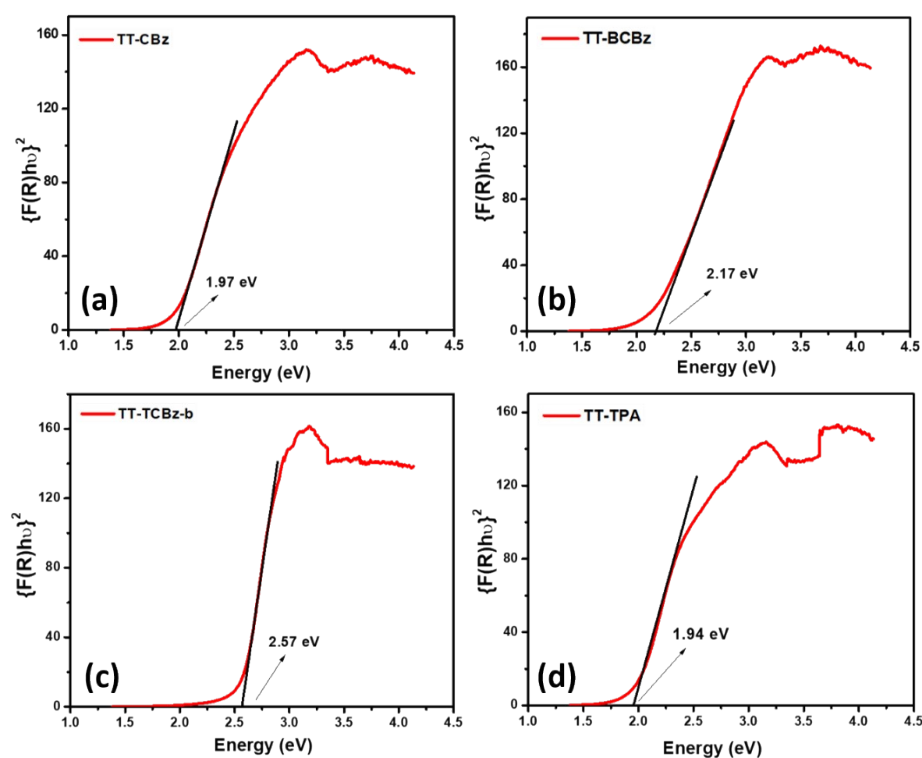


Figure S4. Kubelka-Munk plot for the band gap calculation of TT-CBz, TT-BCBz, TT-TCBz-b and TT-TPA

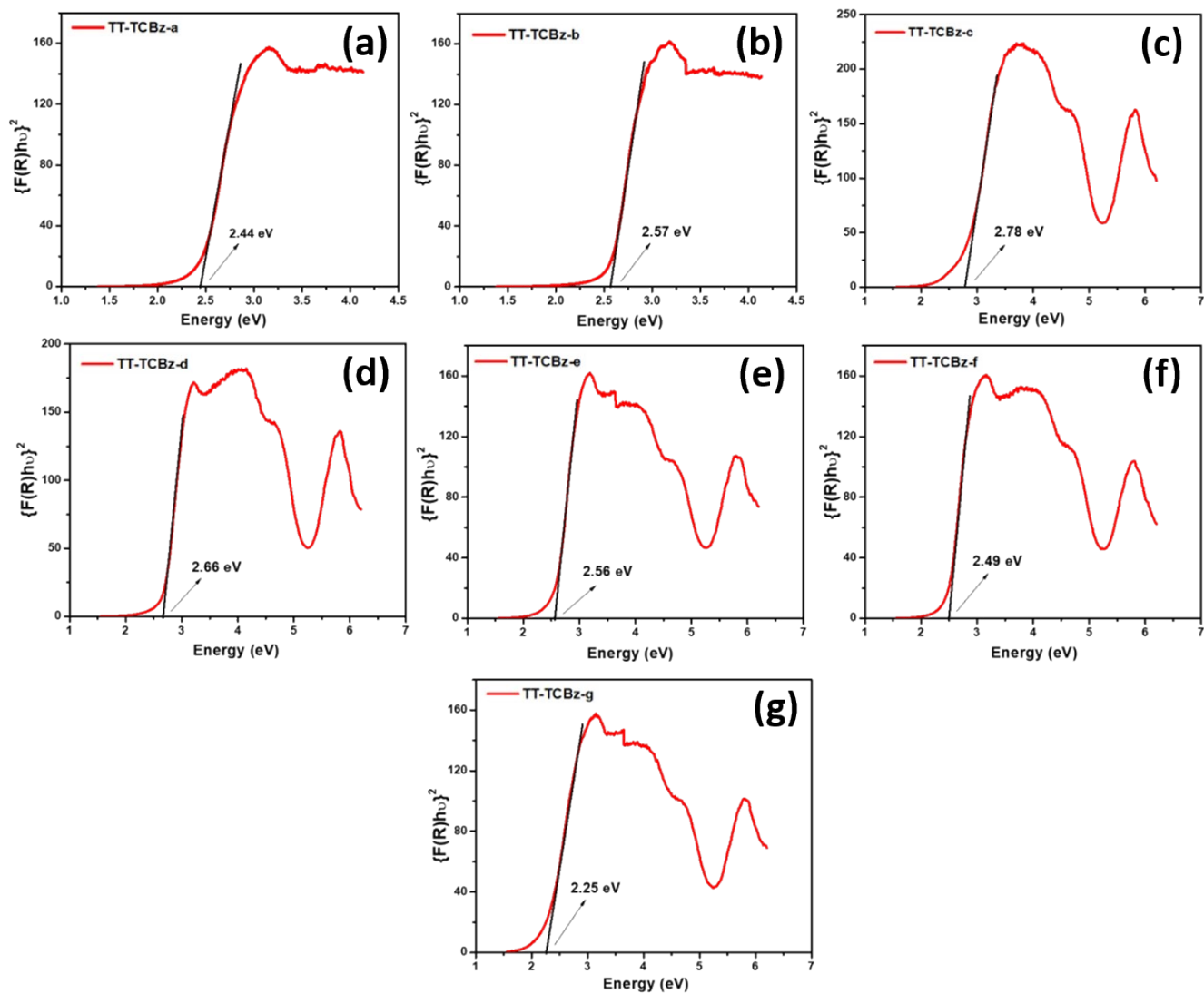


Figure S5. Kubelka-Munk plot for the band gap calculation of TT-TCBz (a-g)

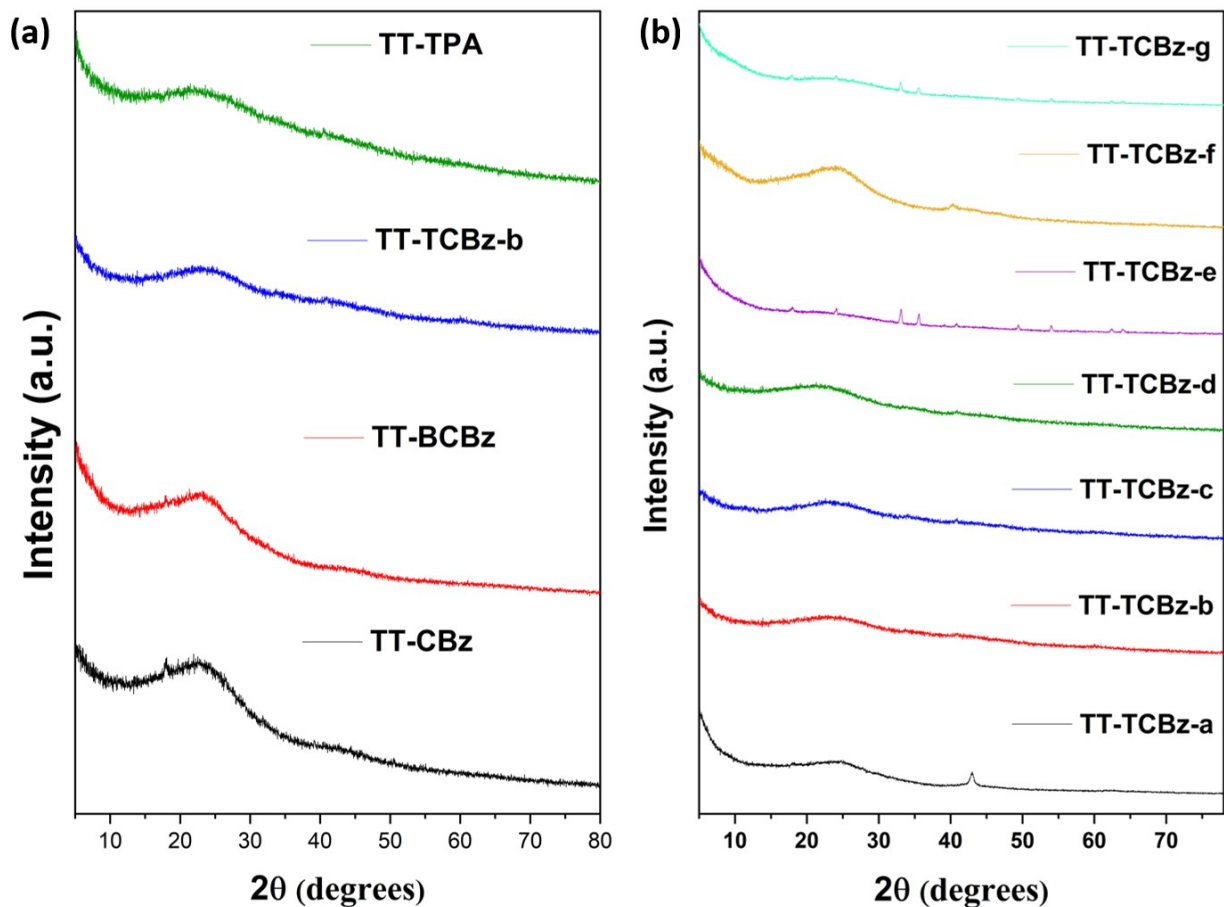


Figure S6. (a) Stacked powder X-ray patterns of TT-CBz, TT-BCBz, TT-TCBz-b and TT-TPA
 (b) Stacked powder X-ray patterns of TT-TCBz (a-g)

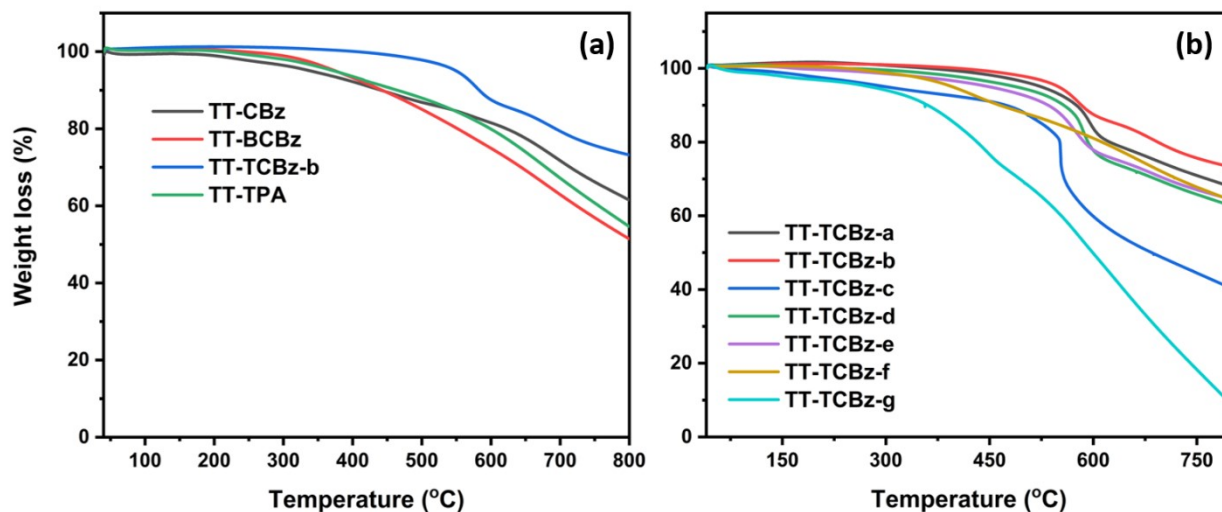


Figure S7. (a) Stacked TGA profiles of TT-CBz, TT-BCBz, TT-TCBz-b and TT-TPA. (b) Stacked TGA profiles of TT-TCBz (a-g), respectively.

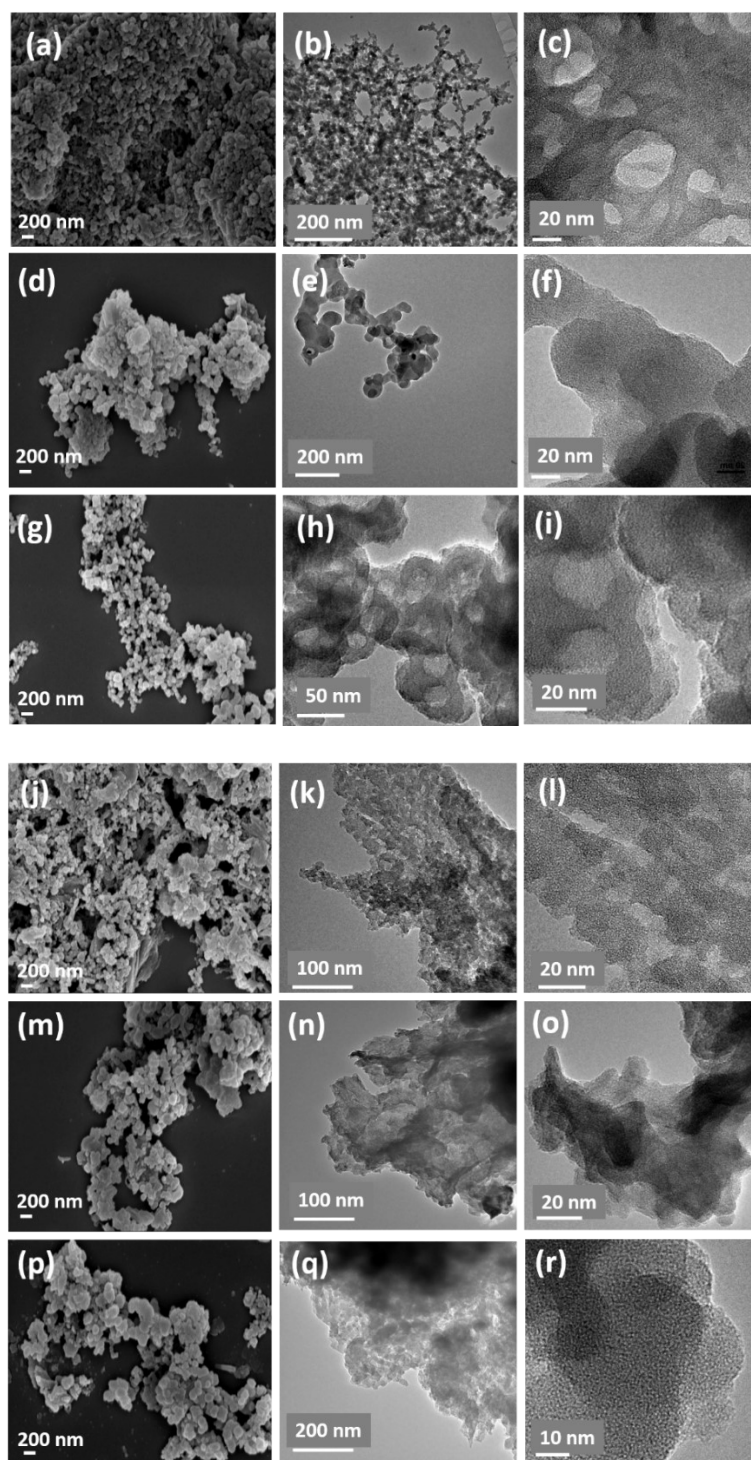


Figure S8. SEM images of (a) TT-TCBz-a (d) TT-TCBz-c, (g) TT-TCBz-d (j) TT-TCBz-e (m) TT-TCBz-f and (p) TT-TCBz-g; TEM images of (b) TT-TCBz-a (e) TT-TCBz-c (h) TT-TCBz-d (k) TT-TCBz-e (n) TT-TCBz-f and (q) TT-TCBz-g; HRTEM images of (c) TT-TCBz-a (f) TT-TCBz-c (i) TT-TCBz-d (l) TT-TCBz-e (o) TT-TCBz-f, and (r) TT-TCBz-g, respectively.

Table S2. Elemental analysis of the polymers

Polymer	Theoretical values	Observed values
TT-CBz	C = 70.57, H = 2.33, N = 9.98	C = 64.78, H = 1.92, N = 8.79
TT-BCBz	C = 74.57, H = 2.50, N = 9.66	C = 69.54, H = 2.21, N = 9.12
TT-TPA	C = 73.37, H = 3.39, N = 8.56	C = 68.24, H = 2.23, N = 7.89
TT-TCBz-a	C = 74.98, H = 2.96, N = 10.29	C = 72.97, H = 2.54, N = 9.81
TT-TCBz-b	C = 74.98, H = 2.96, N = 10.29	C = 72.97, H = 2.54, N = 9.81
TT-TCBz-c	C = 74.98, H = 2.96, N = 10.29	C = 71.83, H = 2.66, N = 9.42
TT-TCBz-d	C = 74.98, H = 2.96, N = 10.29	C = 72.49, H = 2.89, N = 9.16
TT-TCBz-e	C = 74.98, H = 2.96, N = 10.29	C = 71.38, H = 2.85, N = 9.75
TT-TCBz-f	C = 76.49, H = 3.38, N = 9.39	C = 68.24, H = 3.21, N = 8.54
TT-TCBz-g	-	C = 67.42, H = 2.89, N = 8.87

**The theoretical values of elemental analysis for TT-TCBz-g have not been calculated as the exact number of methylene units is not known.

Table S3. Summary of the CO₂ adsorption capacity data of various CPPs.

Entry	Material	S _{ABET} (m ² g ⁻¹)	Temperature (K)	Pressure (bar)	Adsorption capacity (mmol g ⁻¹)	Reference
1	TT-TCBz-a	637	263	1	2.61	<i>This work</i>
			273		2.21	
			298		1.29	
	TT-TCBz-b	1059	263		3.75	
			273		3.00	
			298		1.77	
	TT-TCBz-c	523	263		2.24	
			273		1.88	
			298		1.10	
	TT-TCBz-d	854	263		3.36	
			273		2.76	
			298		1.58	
	TT-TCBz-e	832	263		3.61	
			273		2.91	
298			1.68			
TT-TCBz-f	821	263	2.66			
		273	2.19			
		298	1.33			
TT-TCBz-g	848	263	3.77			
		273	3.11			
		298	1.92			
2	TT-CPP1	545	263	1	2.62	<i>Mater. Adv.</i> , 2021 , <i>2</i> , 7473-7481.
			273		2.18	
			298		1.27	
	TT-CPP2	511	263		1.75	
			273		1.63	
			298		1.08	
	TT-CPP3	491	263		1.42	
			273		1.22	
			298		0.76	

3	DAT-2 DAT-1	971 1105	273 298 313 273 298 313	30	20.6 9.9 8.3 73.3 18.1 12.6	<i>J. CO2. Util</i> , 2022 , <i>65</i> , 102236.
4	CNOP-1 CNOP-2	1374 1546	273 298 273 298	1	3.7 2.0 4.0 2.2	<i>Ind. Eng. Chem. Res.</i> , 2022 , <i>61</i> , 13453-13460.
5	Sf-PTOTCz	852	273 298	1	3.29 1.83	<i>J. Solid State Chem.</i> , 2020 , <i>287</i> , 121327.
6	CPOP-1	2220	273	1	4.82	<i>J. Am. Chem. Soc.</i> , 2012 , <i>134</i> , 6084-6087.
7	CMP-LS1 CMP-LS2 CMP-LS3	493 1576 643	273 298 273 298 273 298	1	1.37 0.74 3.90 2.08 1.85 1.05	<i>New J. Chem.</i> , 2018 , <i>42</i> , 9482-9487.
8	SN@CMP-1 SN@CMP-2 SN@CMP-3 SN@CMP-4 SN@CMP-5 SN@CMP-6 SN@CMP-7	89 590 804 1143 1356 1172 804	273 273 273 273 273 273 273	1.05	1.08 1.53 2.38 2.64 2.89 3.86 2.72	<i>New J. Chem.</i> , 2019 , <i>43</i> , 6838-6842.
9	FcCMP-1 FcCMP-2	638 422	273 273	1	2.2 1.6	<i>Polymers</i> , 2020 , <i>12</i> , 719.
10	Py-azo-COP	700	273	1 15.5	1.93 4.14	<i>ACS Omega</i> , 2017 , <i>2</i> , 3572–3582.
11	COP-3 COP-3-rt COP-3C COP-3-600 COP-3-rt-600 COP-3C-600	1980 1490 940 1860 1370 950	273 273 273 273 273 273	1	4.6 3.5 2.1 5.2 5.4 4.3	<i>Polym. Chem.</i> , 2016 , <i>7</i> , 1290-1296.
12	Zn-CMP	791	298	1.01	1.33	<i>ChemSusChem</i> , 2014 , <i>7</i> , 2110–2114.
13	CMP1 CMP2	258 567	298	1	0.46 0.67	<i>Polymer</i> , 2016 , <i>90</i> , 187–192.
14	NWPTPE NWPPYR	508 824	298	1	0.68 0.93	<i>J. Polym. Sci., Part A: Polym. Chem.</i> , 2017 , <i>55</i> , 3862–3867.
15	HCTPP HCTPA HCTPM	582 921 670	273	1	2.79 2.27 2.14	<i>New J. Chem.</i> , 2017 , <i>41</i> , 3915–3919.
16	TSP-1 TSP-2	562 913	273 298 273 298	1	3.0 1.9 4.1 2.6	<i>Chem. Commun.</i> , 2014 , <i>50</i> , 7933-7936.
17	TCMP-0 CMP-0	963 1018	273 298 273 298	1	2.38 1.34 2.1 1.21	<i>Polym. Chem.</i> , 2012 , <i>3</i> , 928–934.

	TNCMP-2	995	273		2.62	
	TCMP-3	691	298		1.45	
	TCMP-5	494	273		2.25	
			298		1.26	
			273		1.22	
			298		0.68	
18	TPB-BD-CMP	657	273	1	2.5	<i>Mater. Chem. Front.</i> , 2017 , 1, 867–872.
	TPA-BD-CMP	543			2.94	
	TPM-BD-CMP	1008			3.78	
	SPF-BD-CMP	833			3.25	
19	P1	914	273	1	3.01	<i>Chem. Eur. J.</i> , 2016 , 22, 7179–7183.
	P2	834			2.53	
	P3	873			2.12	
20	ACMP-C	629	195	1.06	11.14.	<i>Macromolecules</i> , 2010 , 43, 5508–5511.
			273		1.56	
			298		1.08	
	ACMP-C6	380	195		9.97	
			273		0.79	
			298		0.54	
	ACMP-N	46	195		11.5	
			273		1.16	
			298		0.79	
21	CMP1	767	273	1	2.94	<i>Macromolecules</i> , 2019 , 52, 3935–3941.
	CMP2	624			2.7	
	CMP3	780			2.37	
22	CMP-1-NH₂	656	273	1	1.65	<i>Polymer</i> , 2014 , 55, 321– 325.
			298		0.96	
	CMP-1-AMD1	316	273		1.51	
			298		0.96	
	CMP-1-AMD2	264	273		1.46	
			298		0.92	
	CMP-1-AMD3	119	273		1.31	
			298		0.83	
	CMP-1-AMD4	59	273		1.13	
			298		0.71	
	CMP-1-AMD5	37	273		1.1	
			298		0.64	
	CMP-1-AMD9	68	273		0.87	
			298		0.54	
23	PP_CMP@mmm	1928	273	1	2.52	<i>Chem. Commun.</i> , 2014 , 50, 2781–2783.
			298		1.36	
	PP_CMP@omp	43	273		0.82	
			298		0.43	
	PP_CMP@omom	81	273		1.05	
			298		0.66	
24	Py-BF-CMP	1306	273	1	3.21	<i>Macromolecules</i> , 2018 , 51, 3443–3449.
	TPE-BF-CMP	777	273		2.1	
	TPA-BF-CMP	590	273		1.83	
25	HP_E-CMP	662	273	1	3.58	<i>RSC Adv.</i> , 2014 , 4, 6447– 6453.
			298		1.7	
26	CMP	772	298	1.01	1.61	<i>Nat. Commun.</i> , 2013 , 4, 1960.
	Co-CMP	965			1.8	
	Al-CMP	798			1.74	
27	Cr-CMP	738	298	1.01	1.63	<i>J. Energy Chem.</i> , 2014 , 23, 22–28.

28	AI-CMP	839	273 298	1.01	0.98 0.62	<i>RSC Adv.</i> , 2015 , 5, 31664–31669.
29	NCMP-I NCMP-III	945 593	273 298 273 298	1	1.93 1.43 0.95 0.5	<i>Macromol. Mater. Eng.</i> , 2016 , 301, 451–456.
30	BQCMP-1 DQCMP-1	422 123	273 298 273 298	1	1.55 1.06 1.09 0.86	<i>Macromol. Mater. Eng.</i> , 2016 , 301, 1104–1110.
31	HCMP-1 HCMP-2 HCMP-3 HCMP-4	308 58 50 28	273 273 273 273	1	1.7 1.23 1.16 0.98	<i>Macromolecules</i> , 2016 , 49, 6322–6333.
32	PTEB aerogel	1701	273	1	3.47	<i>Adv. Mater.</i> , 2014 , 26, 8053–8058.
33	CMP-PM CMP-PM-Me	416 241	273 273	1.01	1.99 1.42	<i>Chem. Eur. J.</i> , 2018 , 24, 7480–7488.
34	BO-CMP-1 BO-CMP-2 oBO-CMP-1 oBO-CMP-2	440 1030 390 540	273	1	1.8 2.41 1.16 1.7	<i>Macromolecules</i> , 2018 , 51, 947–953.
35	CMP-1 CMP-1-(CH₃)₂ CMP-1-(OH)₂	837 899 1043	298	1	1.18 0.94 1.07	<i>Chem. Sci.</i> , 2011 , 2, 1173–1177.
36	BFCMP-1 BFCMP-2	1316 1470	273 298 273 298	1.13	2.45 1.39 2.77 1.64	<i>Polymer</i> , 2015 , 61, 36–41
37	PPTBC PMTBC PPETBC PMETBC	917 704 702 540	273 298 273 298 273 298 273 298	1.13	2.93 1.71 2.86 1.79 2.23 1.25 1.96 1.09	<i>Macromol. Chem. Phys.</i> , 2015 , 216, 504–510.
38	MFCMP-1	840	273	1	3.69	<i>J. Mater. Chem. A</i> , 2014 , 2, 13422–13430.
39	CMP-YA CMP-SO-1B2 CMP-SO-1B3	1410 1085 1080	273 298 273 298 273 298	1	1.25 1.9 1.19 1.92 1.22 1.89	<i>Macromolecules</i> , 2017 , 50, 4993–5003.
40	CK-COP-1 CK-COP-2	54 615	273	1	0.65 2.21	<i>J. Polym. Sci., Part A: Polym. Chem.</i> , 2017 , 55, 2383–2389.
41	ThPOP-1 ThPOP-2	1050 160	273	1	3.41 0.91	<i>Polym. Chem.</i> , 2016 , 7, 5031–5038.
42	Porp-TPE Porp-Py-CMP	547 31	273 273	1.05 1.05	2.09 1.29	<i>Polym. Chem.</i> , 2019 , 10, 819–822.
43	Por-Py-CMP	1014	273	1	3	<i>RSC Adv.</i> , 2016 , 6,

			298		1.86	75478–75481.
44	DA-CMP1	662	273	1.13	2.28	<i>J. Mater. Chem. A</i> , 2015 , 3, 21185–21193.
	DA-CMP2	603	298		1.35	
	Azo-CMP1	1146	273		1.64	
	Azo-CMP2	898	298		0.95	
			273		3.72	
			298		2.15	
			272		3.17	
			298		1.96	
45	SCMP-COOH@1	911	298	1	1.39	<i>Polym. Chem.</i> , 2016 , 7, 4599–4602.
	SCMP-COOH@2	622			1.07	
	SCMP-COOH@3	820			1.25	
46	ZnP-5N3-CMPs	711	273	1	1	<i>Chem. Commun.</i> , 2017 , 53, 11422–11425.
			298		0.59	
	ZnP-25N3-CMPs	685	273		1.23	
			298		0.7	
	ZnP-50N3-CMPs	654	273		1.98	
			298		1.11	
	ZnP-75N3-CMPs	565	273		1.64	
			298		0.98	
	ZnP-100N3-CMPs	477	273		1.57	
			298		0.91	
	ZnP-5F-CMPs	430	273		1.32	
			298		0.77	
	ZnP-25F-CMPs	352	273		1.91	
			298		1.18	
	ZnP-50F-CMPs	240	273		2.95	
			298		2.04	
47	PCZN-1	1003	273	1	2.57	<i>Polym. Chem.</i> , 2017 , 8, 7240–7247.
	PCZN-2	607			2.36	
	PCZN-3	714			2.54	
	PCZN-4	374			2.02	
	PCZN-5	707			2.29	
	PCZN-6	718			2.82	
	PCZN-7	1058			2.91	
	PCZN-8	1126			3.18	
	PCZN-9	690			2.93	
	PCZN-10	391			1.7	
48	PCTF-8	625	273	1	2.47	<i>J. Mater. Chem. A</i> , 2016 , 4, 13450–13457.
			293		1.41	
49	BCMP3	950	273	1	2.41	<i>Chem. Eur. J.</i> , 2015 , 21, 17355–17362.
			298		1.61	
50	LKK-CMP-1	467	273	1	2.22	<i>Ind. Eng. Chem. Res.</i> , 2018 , 57, 9254–9260.
			298		1.38	
51	PCTF-1	2235	273	1	3.22	<i>Chem. Commun.</i> , 2013 , 49, 3961–3963.
			298		1.84	
	PCTF-2	784	273		1.82	
			298		0.99	
52	CPOP-8	1610	273	1	3.75	<i>Macromolecules</i> , 2014 , 47, 5926–5931.
	CPOP-9	2440			4.13	
	CPOP-10	1110			3.36	
53	PTA-1	52	273	1	0.84	<i>Chem. Commun.</i> , 2014 , 50, 8002–8005.
	PTA-2	62	273		1.25	
			303		0.59	
	PTA-3	450	273		1.48	

			303		0.77	
54	BILP-101	536	298	1	2.43	<i>Chem. Commun.</i> , 2015 , <i>51</i> , 13393–13396.
55	PAF-33	821	273	1	2.16	<i>Polym. Chem.</i> , 2014 , <i>5</i> , 2266–2272.
	PAF-33-NH₂	370	298		1.25	
			273		1.19	
	PAF-33-COOH	445	298		0.75	
			273		1.94	
	PAF-34	953	298		1.21	
			273		2.5	
	PAF-34-OH	771	298	1.39		
			273	2.21		
	PAF-35	567	298	1.25		
			273	1.77		
			298	1.01		
56	Cu/BF₄/BIPLPL-1	380	273	1	2.57	<i>J. Phys. Chem. C</i> , 2015 , <i>119</i> , 8174–8182.
57	BILP-15	448	273	1	2.68	<i>Environ. Sci. Technol.</i> , 2015 , <i>49</i> , 4715–4723.
			298		1.82	
	BILP-16	435	273		2.7	
			298		1.83	
	BILP-15(AC)	862	273		3.43	
			298	2.29		
	BILP-16(AC)	843	273	3.46		
			298	2.32		
58	TBILP-1	117	273	1	2.91	<i>Macromolecules</i> , 2014 , <i>47</i> , 8328–8334.
			298		1.98	
59	BILP-10	787	273	1	4.02	<i>J. Mater. Chem. A</i> , 2014 , <i>2</i> , 12492–12500.
			298		2.52	
	BILP-11	658	273		3.09	
			298		2	
	BILP-13	677	273	2.57		
			298	1.8		
60	NPOF-1	2062	298	1	1.52	<i>J. Phys. Chem. C</i> , 2016 , <i>120</i> , 2592–2599.
	NPOF-1-NO₂	1295			2.52	
	NPOF-1-NO₂(xs)	749			2	
	NPOF-1-NH₂	1535			3.77	
	NPOF-1-NH₂(xs)	1074			2.93	
61	ALP-5	801	273	1	4.46	<i>J. Mater. Chem. A</i> , 2015 , <i>3</i> , 20586–20594.
			298		2.94	
	ALP-6	698	273		3.42	
			298		2.17	
	ALP-7	412	273		2.5	
			298		1.55	
	ALP-8	517	273		3.05	
			298		1.97	

Table S4. Summary of the CO₂/N₂: 15/85 (v/v) selectivity data of various POPs (^a at 273 K and 1 bar, ^b at 298 K and 1 bar)

Entry	Material	S _{BET} (m ² g ⁻¹)	CO ₂ uptake (mmol g ⁻¹)		CO ₂ /N ₂ selectivity	Reference
			273 K	298 K		
1	TT-TCBz-b	1059	3.00	1.77	24.5 ^b	This work
	TT-TCBz-g	848	3.11	1.92	65.0 ^b	
2	CTF-1	746	3.00	1.41	20 ^a	<i>Energy Environ. Sci.</i> , 2013 , <i>6</i> , 3684-3692.
	CTF-1-600	1553	3.82	2.25	13 ^a	
	FCTF-1	662	4.67	3.21	31 ^a	
	FCTF-1-600	1535	5.53	3.41	19 ^a	
3	F-DCBP-CTF-1	1574	5.98	3.82	31 ^b	<i>J. Mater. Chem. A.</i> , 2018 , <i>6</i> , 6370-6375.
4	CTF-3	1454	2.13	1.34	24.5 ^a	<i>J. Mater. Chem. A.</i> , 2019 , <i>7</i> , 17277-17282.
5	CQN-1g	1870	7.16	4.57	42.7 ^b	<i>Angew. Chem., Int. Ed.</i> , 2019 , <i>58</i> , 872-876.
6	BTAP-1	750.9	3.26	1.78	40 ^a	<i>Chem.</i> , 2016 , <i>1</i> , 482-493.
	BTAP-2	445.6	2.55	2.23	52 ^a	
	BTAP-3	419.9	1.58	1.41	62 ^a	
7	BTLP-4	1011	4.3	2.7	41 ^a	<i>J. Mater. Chem. A.</i> , 2017 , <i>5</i> , 258-265.
	BTLP-5	705	3.2	1.98	45 ^a	
	BOLP-4	698	3.1	2.0	79 ^a	
	BOLP-5	759	2.9	1.8	95 ^a	
8	BILP-4	1134	5.3	3.6	79 ^a	<i>Chem. Mater.</i> , 2012 , <i>24</i> , 1511-1517.
	BILP-5	599	2.9	2.0	95 ^a	
9	Th-1	726	2.88	-	39 ^a	<i>Adv. Mater.</i> , 2012 , <i>24</i> , 5703-5707.
	Py-1	437	2.71	-	117 ^a	
	Fu-1	514	2.21	-	50 ^a	
10	HMC-1	855	5.8	-	72 ^a	<i>ACS Sustain. Chem. Eng.</i> , 2016 , <i>4</i> , 3697-3703.
	HMC-2	425	6.6	-	70 ^a	
	HMC-3	566	7.1	-	23 ^a	
11	Tt-POP-1	258	0.75	0.29	30 ^a	<i>ACS Appl. Nano Mater.</i> , 2022 , <i>5</i> , 5302-5315.
	Tt-POP-2	368	0.91	0.49	26 ^a	
	Tt-POP-3	974	0.78	0.45	25 ^a	
12	TAP1	474	2.2	1.4	94 ^a	<i>ACS Appl. Polym. Mater.</i> , 2019 , <i>1</i> , 959-968.
	TAP2	772	3.2	2.3	112 ^a	
	TAP3	729	3.4	2.3	114 ^a	
13	PFPOP-1	570	2.8	1.2	43.7 ^b	<i>RSC Adv.</i> , 2015 , <i>5</i> , 71095-71101.
	PFPOP-2	630	3.4	1.5	52.1 ^b	
	PFPOP-3	530	3.9	1.7	56.5 ^b	
14	PMOP	1604	5.00	3.17	47.1 ^a	<i>ACS Appl. Mater. Interfaces</i> , 2018 , <i>10</i> , 15174-15182.
15	TBOSBL1	649	4.0	2.1	68 ^a	<i>ACS Omega</i> , 2020 , <i>5</i> , 4250-4260.
	TBOSBL2	570	3.4	2.6	106 ^a	
	TBOSBL3	493	2.8	2.2	108 ^a	
16	COP-190H-en	456	3.6	2.19	171 ^b	<i>Micropor. Mesopor. Mat.</i> , 2021 ,

	COP-190H0-deta	72	2.7	1.79	121 ^b	328, 111450.
	COP-190H-CN	661	3.2	2.11	91 ^b	
	COP-190H-SH	773	3.6	2.28	76 ^b	
17	CPOP-1	2220	4.82	-	25 ^a	<i>J. Am. Chem. Soc.</i> , 2012 , <i>134</i> , 6084-6087.

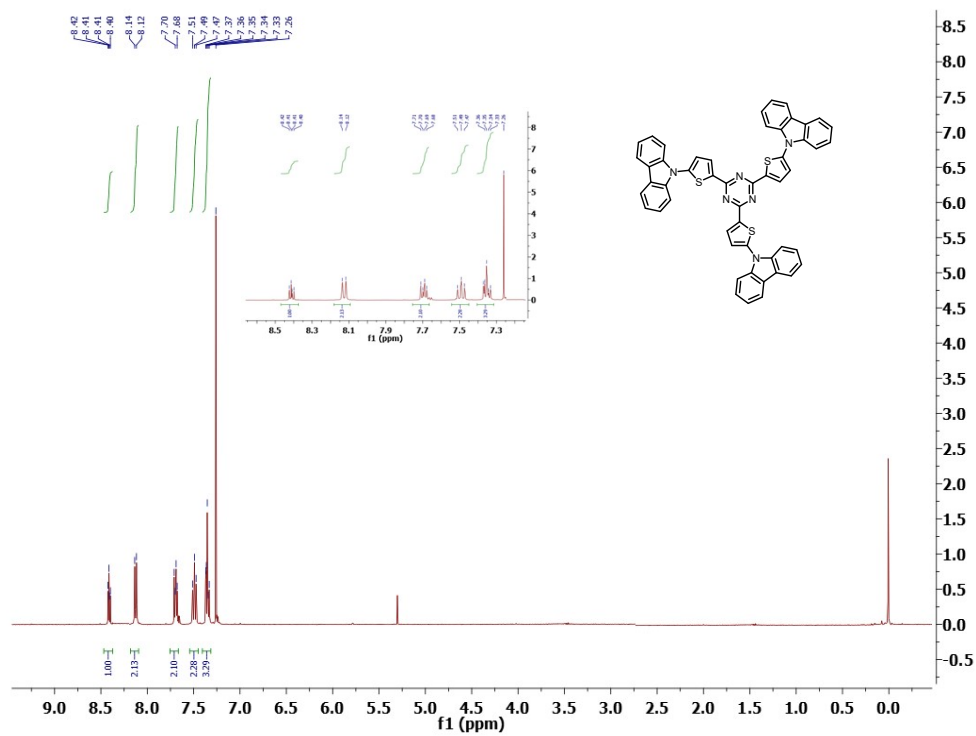


Figure S9. ¹H NMR Spectrum of TT-TCBz

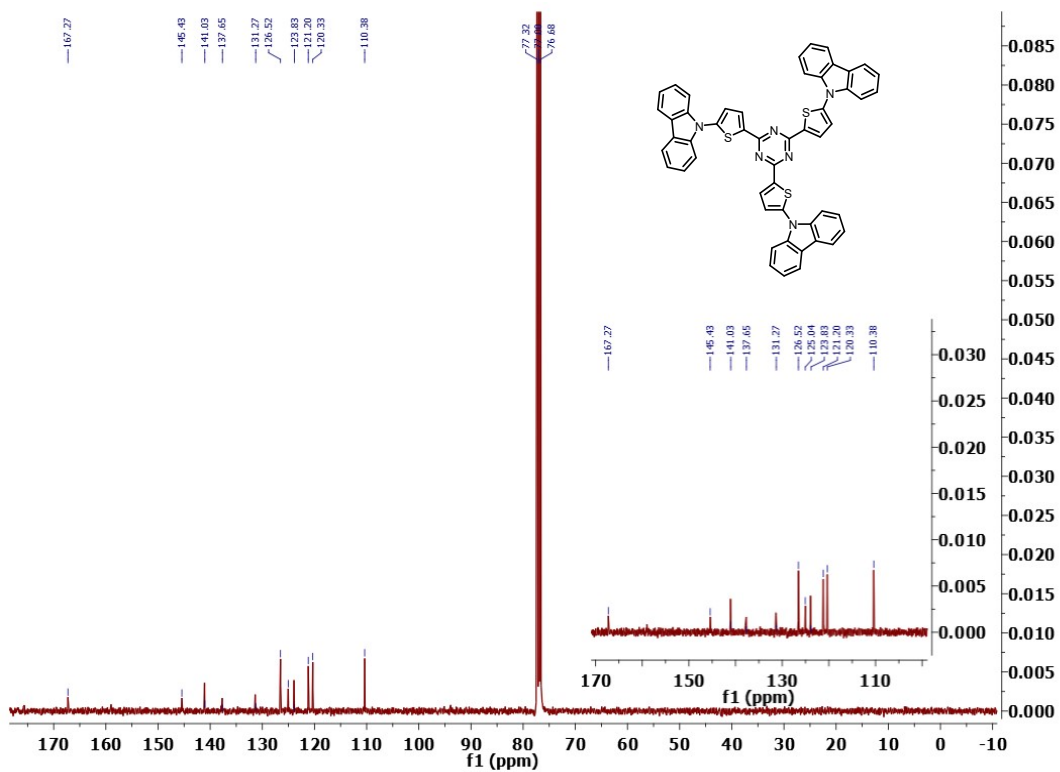


Figure S10. ^{13}C NMR Spectra of TT-TCBz

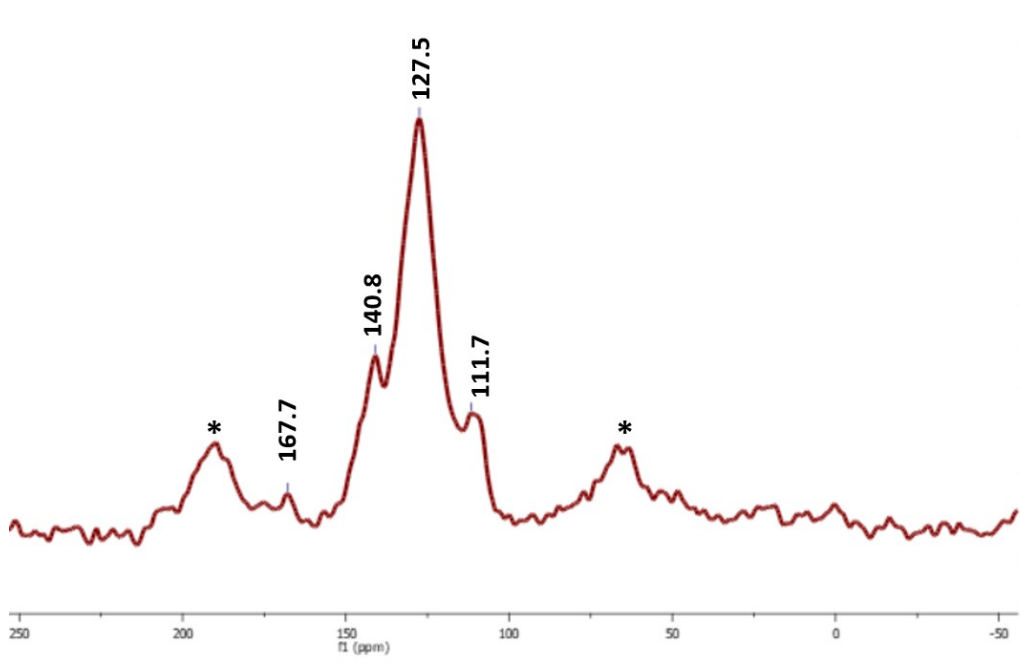


Figure S11. Solid-state ^{13}C NMR spectra of TT-TCBz-c (* mark represent the spinning sidebands)

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