

Electronic Supplementary Information

Rational design of functionalized covalent organic frameworks and their performance towards CO₂ capture

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Section 1. Methods

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AV 400MHz spectrometer (Bruker). Solid-state ^{13}C NMR spectra were recorded on a Bruker AVIII 500MHz spectrometer. Thermogravimetric analysis (TGA) was performed under N_2 on a NETZSCH STA449F3 with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker model VERTEX 70 infrared spectrometer. The powder X-ray diffraction data were collected on a D/Max2550 VB/PC diffractometer (40 kV, 200 mA) using a $\text{Cu K}\alpha$ as the radiation. Elemental analysis was conducted on an elemental analyzer (Vario EL III). The morphology of samples was characterized by scanning electron microscope (SEM, JSM-6360LV).

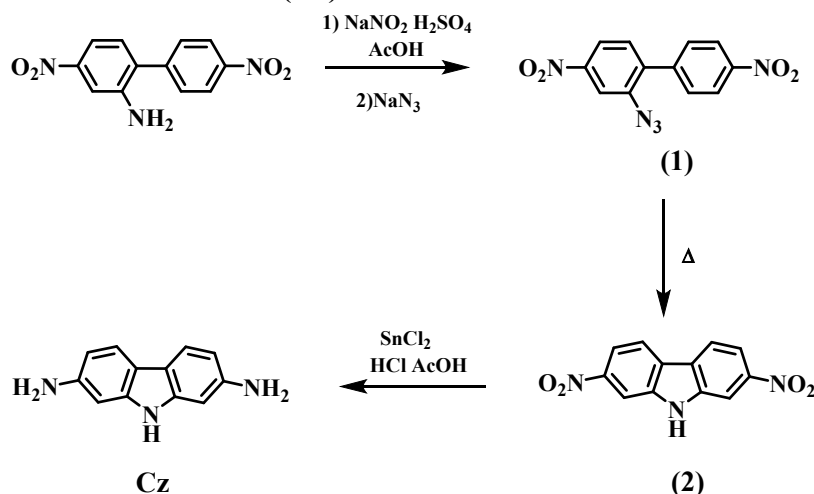
Molecular modeling and Pawley refinement were carried out using the Reflex module in Material Studio 7.0. The unit cell dimensions for COFs were taken from the DFTB calculation and the space group for both COFs was selected as $P6$. Then we performed Pawley refinement to optimize the lattice parameters and simulated the PXRD patterns using the Reflex module until the R_{wp} value converges.

Both of gas adsorption and desorption isotherms of COFs were measured using a Micromeritics ASAP 2020 static volumetric analyzer at the setting temperature. Prior to each adsorption experiment, the samples were degassed for 12 h at $120\text{ }^\circ\text{C}$ ensuring that the residual pressure fell below 1×10^{-5} Torr and then cooled down to the target temperatures, followed by introduction of a single component gas (CO_2 or N_2) into the system. Once the adsorption process finished, the desorption experiment was automatically initiated. In the desorption stage, gas pressure gradually decreased and the corresponding amount of residue adsorbed gas was measured and calculated by the instrument.

Section 2. Materials and experimental procedures

Solvents, reagents and chemicals were purchased from Aldrich and TCI. All were used without any further purification. 1,3,5-triformylbenzene (TFB)¹ and 2,4,6-triformylphloroglucinol (Tp)² were synthesized according to the literatures.

Synthesis of 2,7-diaminocarbazole (Cz)³:



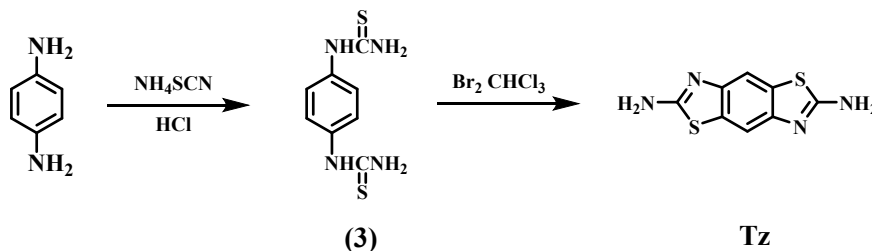
4,4-dinitro-2-azidobiphenyl (1): To a solution of 10.0 g (38.6 mmol) of 4,4-dinitro-2-biphenylamine in a mixture of 200 mL of acetic acid and 40 mL of sulfuric acid at 0 °C was added dropwise 5.32 g (77.1 mmol) of sodium nitrite. The mixture was stirred at 5-10°C for 2 h after approximately 5.00 g of urea (to destroy the excess of nitrous acid), 500 mL of ice-water and 5.00 g of activated carbon were added. The mixture was stirred again for 20 min and filtrated rapidly through a Buchner funnel into a flask immersed in an ice bath. A solution of 5.07 g (78.0 mmol) of sodium azide in 100 mL of water was added dropwise to the clear yellow filtrate. The resulting solution was stirred at 0 °C for 1 h and at room temperature for 24 h. The mixture was quenched with 500 mL of a solution of NaHCO₃ in water and extracted three times with ethyl acetate. The organic layer was dried over magnesium sulfate and the solvent was removed under vaccum. Recrystallization from ethanol afforded 7.42 g (Yield: 72 %) of the title product as a yellow solid. ¹H NMR (400 MHz, Acetone-*d*₆, ppm): 8.37 (d, 2H, *J* = 8.8 Hz); 8.20 (d, 1H, *J* = 2.2 Hz); 8.16 (dd, 1H, *J* = 10.3 and 2.2 Hz); 7.89 (dd, 2H, *J* = 8.8 and 2.8 Hz); 7.79 (d, 1H, *J* = 8.1 Hz).

2,7-dinitrocarbazole (2): To 600 mL of boiling kerosene (first washed with concentrated sulfuric acid) was added very slowly 6.00 g (21.0 mmol) of compound 1. The solution was

maintained to reflux for 1 h. After cooling, the solution was kept at 0 °C for 24 h. The precipitate was filtered through a Buchner funnel and the solid was washed with petroleum ether. Final purification was obtained by recrystallization from ethanol to afford 3.38 g (Yield: 66 %) of the title product. ¹H NMR (400 MHz, Acetone-*d*₆, ppm): 11.14 (s, 1H); 8.55 (d, 2H, *J* = 2.2 Hz); 8.49 (d, 2H, *J* = 8.8 Hz); 8.15 (dd, 2H, *J* = 8.8 and 2.2 Hz).

2,7-dinitrocarbazole (Cz): To a solution of compound 2 (6.00 g, 23.3 mmol) in a mixture of acetic acid (200 mL) and hydrochloric 16 N (35 mL) was added 44.3 g (0.23 mmol) of tin (II) chloride. The mixture was refluxed for 24 h under argon. After cooling, the precipitate was separated from the solvent by filtration and washed several times with cold acetic acid. The resulting diammonium salt was dissolved in water followed by addition of sodium hydroxide until the pH reached a value of 10. The precipitate was collected by filtration and dried under reduced pressure. Recrystallization in ethanol afforded 3.6 g (Yield: 78 %) of the title product Cz as a shiny gray solid. The purified product was characterized by ¹H NMR (Figure S1).

Synthesis of 2,6-Diaminobenzo[1,2-d:4,5-d]bisthiazole (Tz)⁴:



p-Phenylenebis(thiourea) (3): To a 100 mL flask were added 3.4 g (31.4 mmol) of p-phenylenediamine, 28 mL of deionized water, 6.14 mL of concentrated hydrochloric acid, and 220 mg of activated carbon. The mixture was warmed to 50 °C and transferred with filtration into another 100 mL flask. Ammonium thiocyanate (9.68 g, 127.2 mmol) was added and the mixture was stirred at a pot temperature of 100 °C for 24 h. The yellow, granular product began to precipitate after 2 h of reaction. The mixture was allowed to cool, and the product was collected by filtration. The product was washed with *ca.* 100 mL of hot water and then dried at 100 °C under reduced pressure. The yield was 6.8 g (95.6%) of a light yellow, granular solid of purity suitable for the next step.

2,6-Diaminobenzo[1,2-d:4,5-d]bisthiazole (Tz): To a stirred suspension of 3.0 g (13.25 mmol)

of **3** in 14 mL of dry chloroform was added a solution of 4.9 g (30.7 mmol of Br₂) of bromine in 2 mL of chloroform such that the pot temperature did not rise above 50 °C. The orange slurry was stirred at room temperature overnight and then heated at reflux for 24 h. The mixture was allowed to cool under a slow stream of argon. The granular orange solid was then collected by filtration. The crude product was washed with 6 mL of chloroform, dried in air, and stirred with aqueous sodium bisulfite (2 g of NaHSO₃ / 30 mL of water). The yellow solid was collected by filtration, washed with 5 mL of concentrated ammonium hydroxide, and then washed with 10 mL of water. The crude Tz was recrystallized twice from 140 mL of glacial acetic acid. After drying to constant weight at 85 °C under reduced pressure, 1.6 g (Yield: 54.3%) of Tz was obtained as feathery needles. The purified product was characterized by ¹H NMR (Figure S2).

Synthesis of Cz-COF

A Pyrex tube measuring o.d. × i.d. = 10 × 8 mm² was charged with Cz (29.7 mg, 0.15 mmol) and 1,3,5-triformylbenzene (TFB, 15.8 mg, 0.10 mmol) in a solution of 0.75 mL dioxane, 0.75 mL mesitylene and 0.1 mL 3 M aqueous acetic acid. The mixture was then sonicated for 10 min. The tube was subsequently flash frozen at 77 K (LN₂ bath), degassed by three freeze-pump-thaw cycles and then flame sealed. Upon sealing the length of the tube was reduced to ca. 13 cm. The reaction mixture was heated at 120°C for 3 days to afford a yellow precipitate which was isolated by filtration and washed with anhydrous tetrahydrofuran. The product was immersed in anhydrous tetrahydrofuran for 8 h, during which the activation solvent was decanted and freshly replenished for four times. The solvent was removed under vacuum at 80 °C to afford Cz-COF as a yellow powder (32 mg, 85%). Anal. Calcd for C₁₈H₁₁N₃: C, 80.29; H, 4.09; N, 15.61. Found: C, 81.05; H, 3.89; N, 15.06.

Synthesis of Tz-COF

A Pyrex tube measuring o.d. × i.d. = 10 × 8 mm² was charged with Tz (19.6 mg, 0.089 mmol) and triformylphloroglucinol (Tp, 12.5 mg, 0.059 mmol) in a solution of 1.0 mL dioxane and 0.2 mL 3 M aqueous acetic acid. The mixture was then sonicated for 10 min. The tube was subsequently flash frozen at 77 K (LN₂ bath), degassed by three freeze-pump-thaw cycles and then flame sealed. Upon sealing the length of the tube was reduced to ca. 13 cm. The reaction mixture was heated at 120°C for 3 days to afford a red precipitate which was isolated by

filtration and washed with anhydrous tetrahydrofuran. The product was immersed in anhydrous tetrahydrofuran for 8 h, during which the activation solvent was decanted and freshly replenished for four times. The solvent was removed under vacuum at 80 °C to afford Tz-COF as a red powder (24 mg, 84%). Anal. Calcd for C₁₄H₆N₄O₂S₂: C, 51.53; H, 1.84; N, 17.18. Found: C, 51.35; H, 2.09; N, 16.98.

CO₂/N₂ Uptake

The gas adsorption isotherms of Cz-COF and Tz-COF were measured using a Micromeritics ASAP 2020 static volumetric analyzer at the setting temperature. Prior to each adsorption experiment, the samples were degassed for 12 h at 120 °C ensuring that the residual pressure fell below 1 × 10⁻⁵ Torr and then cooled down to the target temperatures, followed by introduction of a single component gas (CO₂ or N₂) into the system.

Heat of CO₂ Adsorption Calculation

Pressure as a function of the amount of CO₂ adsorbed was determined by the Toth model for the isotherms.

$$Q = \frac{Q_m \times (B \times P)^{1/t}}{(1 + B \times P)^{1/t}}$$

where Q = moles adsorbed, Q_m = moles adsorbed at saturation, P = pressure; B and t = constants; which can be used to calculate the pressure P .

The isosteric heat of adsorption values were calculated using the Clausius-Clapeyron equation:

$$\ln\left(\frac{p_1}{p_2}\right) = \Delta H\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where P_i is pressure for isotherm i , T_i is temperature for isotherm i , R is 8.315 J K⁻¹ mol⁻¹; which was used to calculate isosteric heat of adsorption (ΔH) of a gas as a function of the quantity of gas adsorbed.

The Ideal Adsorption Solution Theory (IAST) calculations

The pure component isotherms of CO₂ and N₂ measured at 273 and 298 K were fitted with the single-site Langmuir model:

$$q_i = q_{i,sat} \times \frac{b_i p_i}{1 + b_i p_i}$$

Where, b_i is parameter in the pure component Langmuir isotherm (Pa⁻¹), p_i is bulk gas phase

pressure of species i (Pa), p_t is total bulk gas phase pressure of mixture (Pa), q_i is molar loading of species i (mol kg⁻¹), $q_{i,sat}$ is saturation capacity of species i (mol kg⁻¹).

Pure-component isotherm fitting parameters were then used for calculating Ideal Adsorbed Solution Theory (IAST) binary-gas adsorption selectivities, S_{ads} , defined as:

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$

The IAST calculations were carried out for binary mixture containing 15% CO₂ and 85% N₂, which is typical of flue gases.

Section 3. Supporting Figures

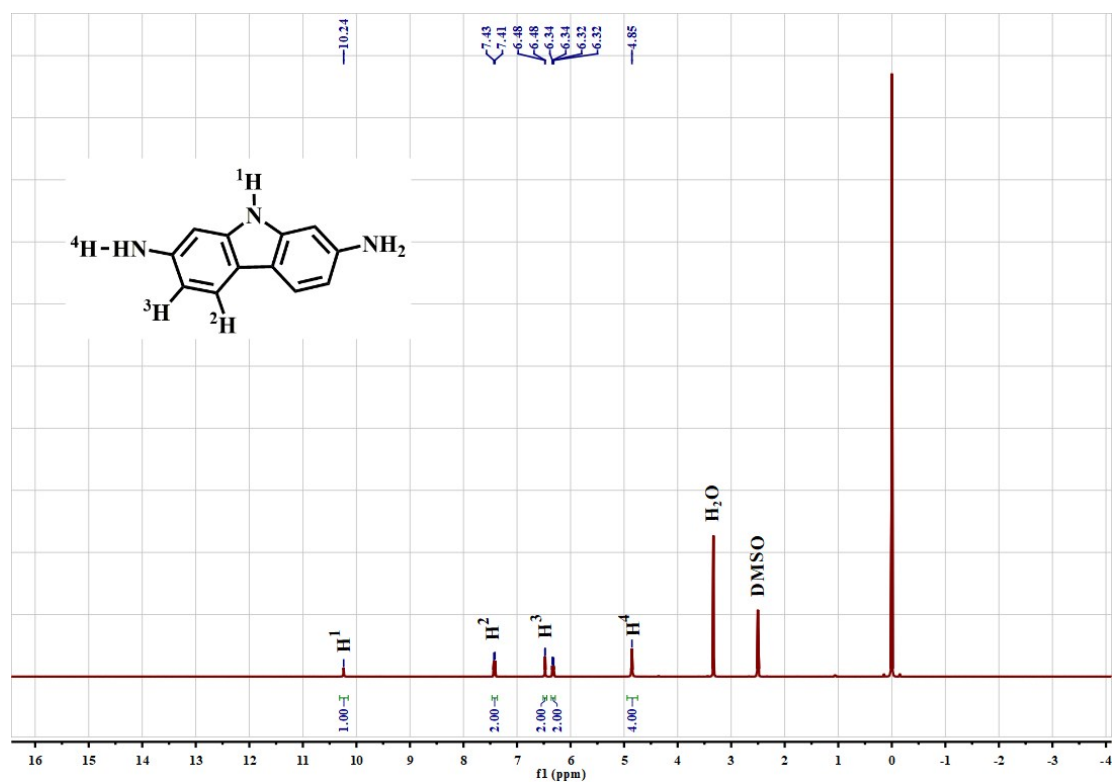


Figure S1. ^1H NMR of 2,7-diaminocarbazole in $\text{DMSO-}d_6$.

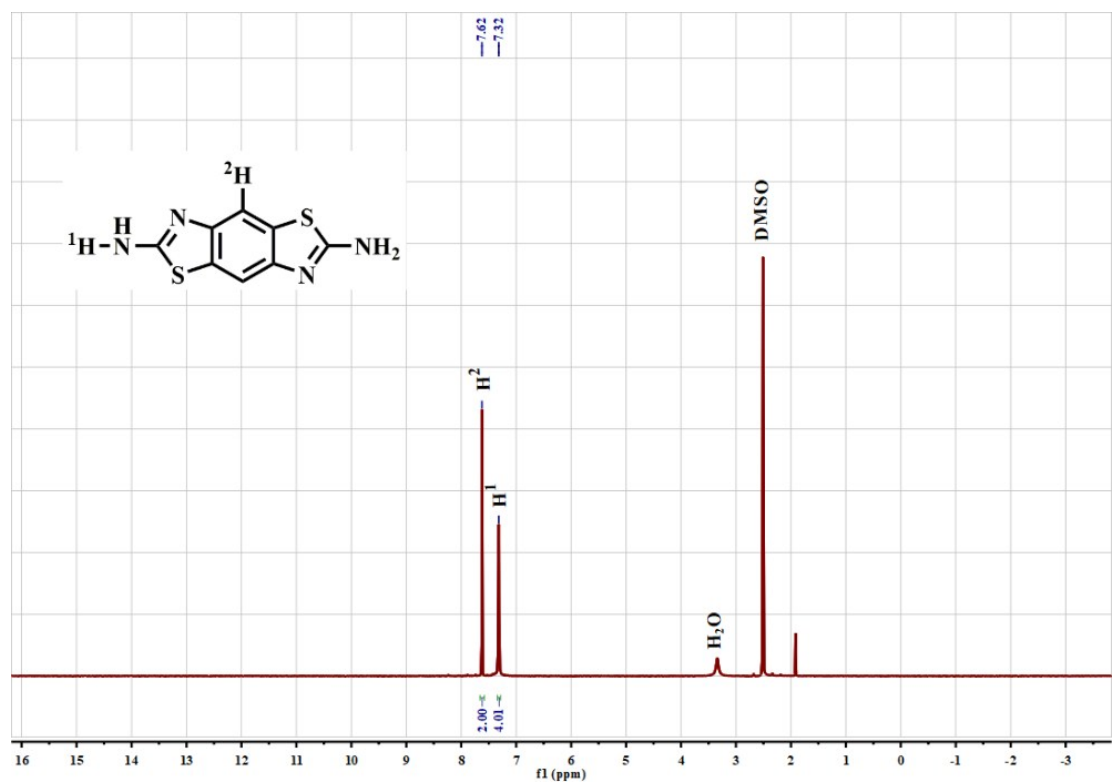


Figure S2. ^1H NMR of 2,6-Diaminobenzo[1,2-d:4,5-d]bisthiazole in $\text{DMSO-}d_6$.

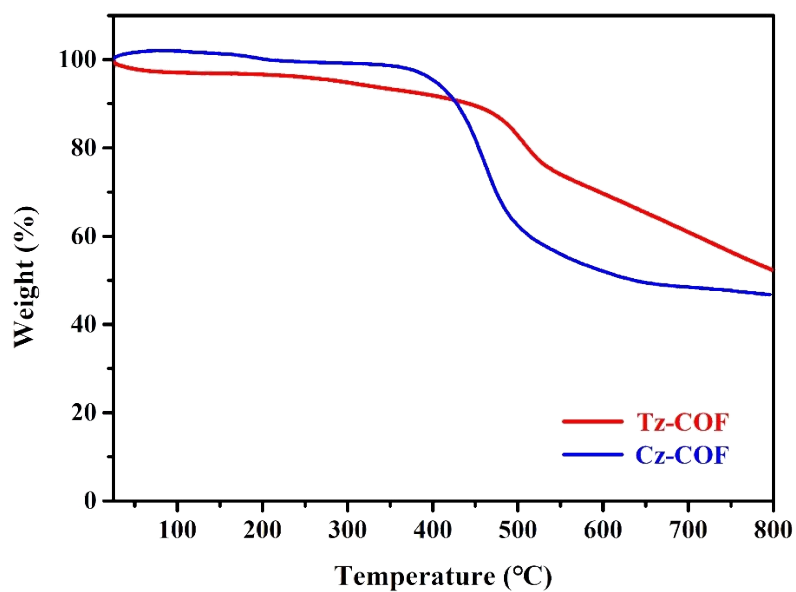


Figure S3. Thermogravimetric analysis of Cz-COF and Tz-COF (under N₂).

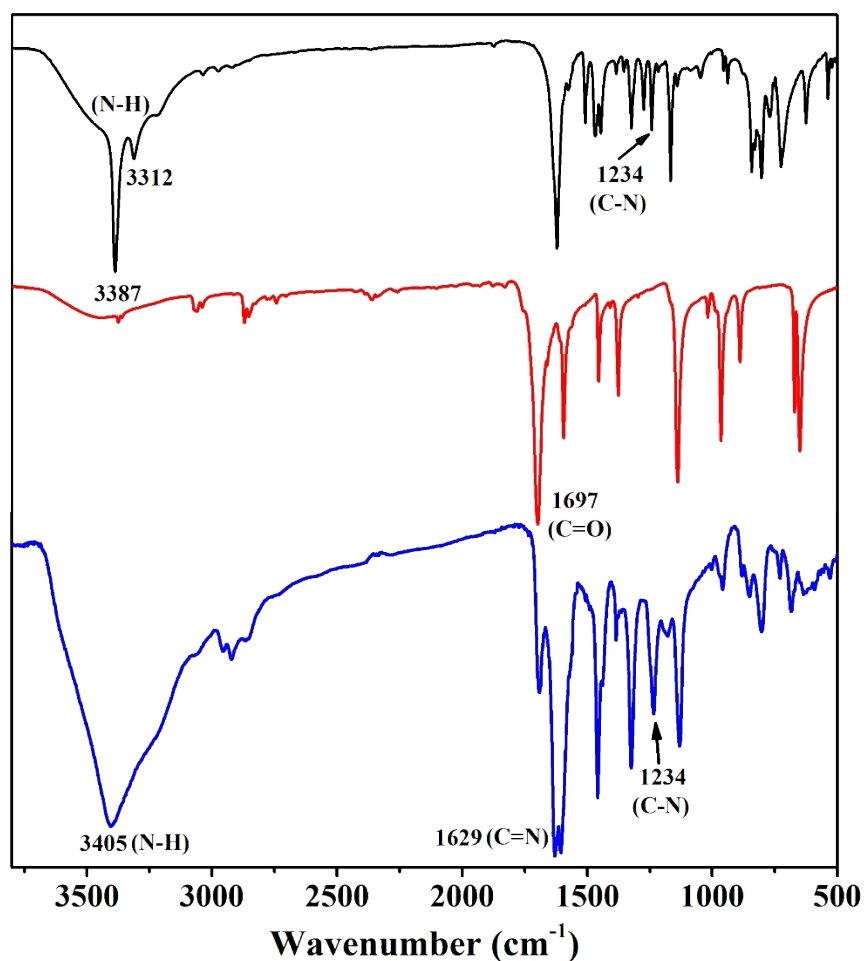


Figure S4. FT-IR spectrum of Cz-COF (blue), 1,3,5-triformylbenzene (red) and 2,7-diaminocarbazole (black).

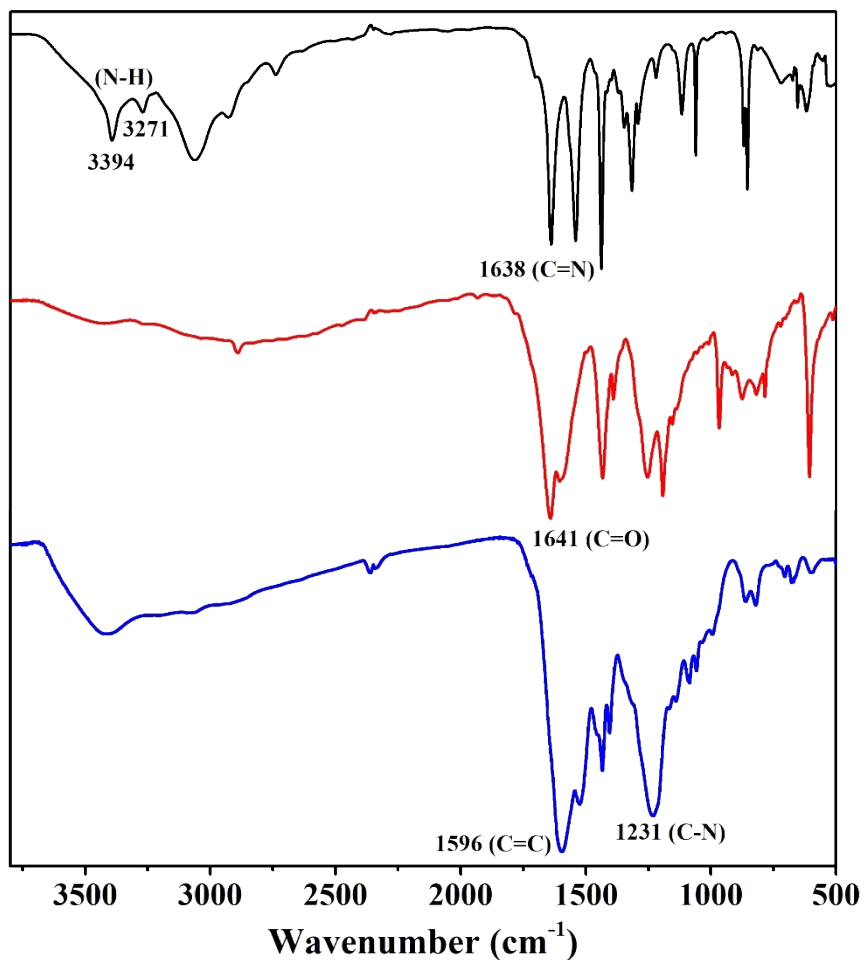


Figure S5. FT-IR spectrum of Tz-COF (blue), triformylphloroglucinol (red) and 2,6-Diaminobenzo[1,2-d:4,5-d]bisthiazole (black).

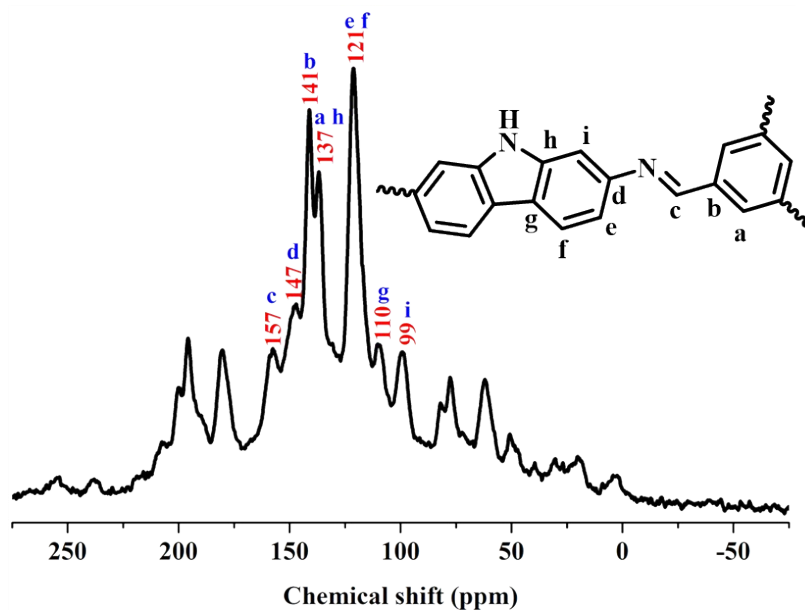


Figure S6. ^{13}C CP/MAS NMR spectra of Cz-COF.

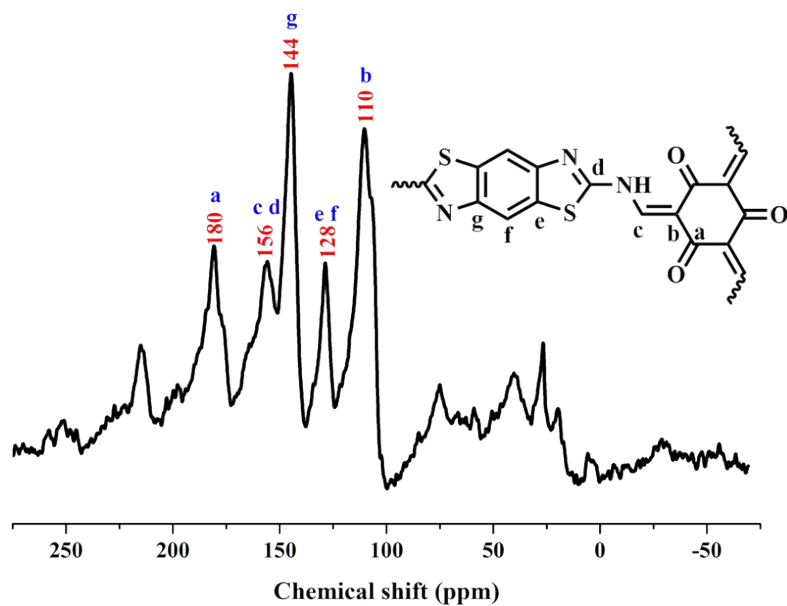


Figure S7. ^{13}C CP/MAS NMR spectra of Tz-COF.

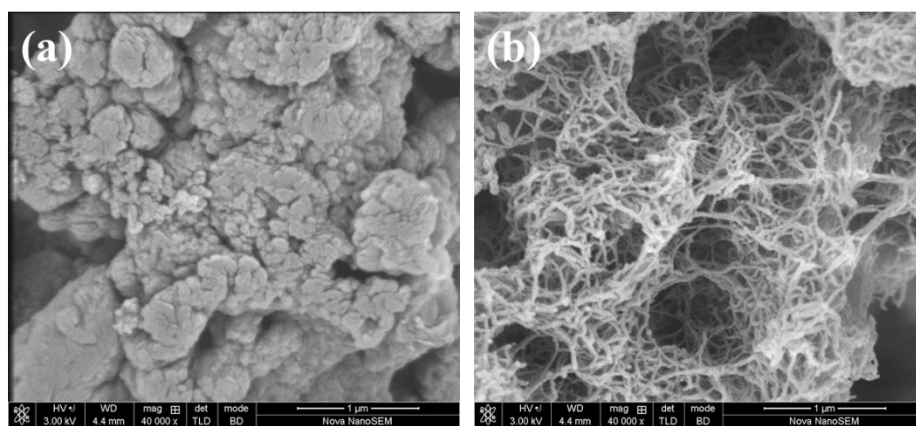


Figure S8. SEM images for (a) Cz-COF and (b) Tz-COF.

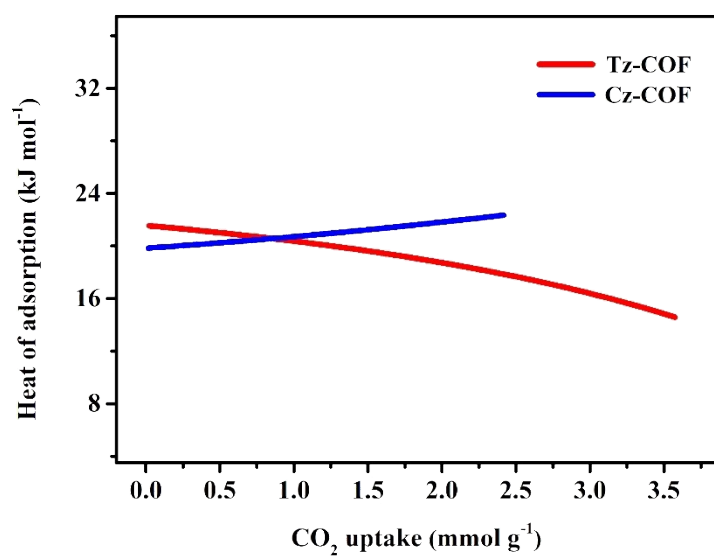


Figure S9. The isosteric heat of adsorption for Cz-COF and Tz-COF.

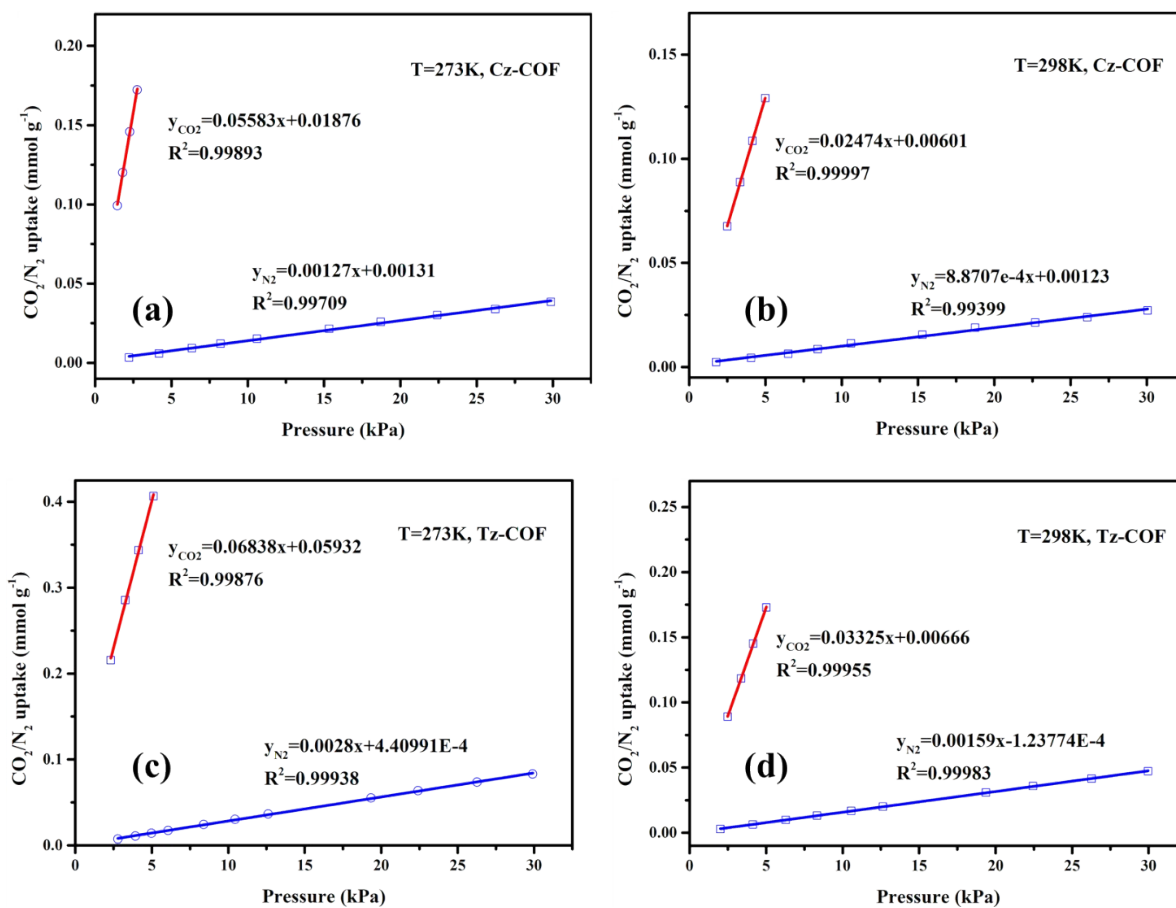


Figure S10. The selectivity of COFs for CO₂ over N₂ isotherms obtained from the initial slope method.

Section 4. Supporting Tables

Table S1. Summary of surface area, CO₂ uptake, selectivity and adsorption enthalpy (Q_{st}) in selected COFs and POPs (with excellent reported results).

Polymers	S_{BET} (m ² g ⁻¹)	T (K)	CO ₂ uptake ^a (mmol g ⁻¹)	Selectivity ^b	Q_{st} (kJ mol ⁻¹)	Ref
Tz-COF	1439	273	3.5	20	22	This work
		298	2.3	12		
Cz-COF	871	273	2.5	36	20	
		298	1.5	28		
H ₂ P-COF	1474	273	1.6		17.2	5
		298	0.9			
[HO ₂ C] _{100%}	1044	273	3.9		43.5	5
		298	1.7	77		
[EtNH ₂] ₅₀ -H ₂ P-COF	568	273	3.6		20.8	6
		298	1.9	17		
COF-103	3530	273	1.7			7
ILCOF-1	2723	273	1.4		18.3	8
TDCOF-5	2497	273	2.1		21.8	9
TpPa-COF (MW)	724	273	5.1	32	34.1	10
PAF-1	5600	273	2.1		15.6	11
PPN-6-SO ₃ H	1254	295	3.6	150	30.4	12
PPN-6-SO ₃ Li	1186	295	3.7	441	35.7	12
HAT-CTF450/600	1090	273	6.3		27.1	13
		297	4.8	110		
IBTP	328	273	1.9	51	37.4	14
Py-1	437	273	2.7	36	117	15
azo-POP-2	729	273	2.56	109.6	24.8	16
		298	1.53	130.6		
TSP-2	913	273	4.1	38	30.2	17
		298	2.6	24		

^a Measured at the pressure of 1 bar. ^b IAST selectivity (1 bar) for CO₂/N₂ (10:85 v:v).

Supporting References

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