

Electronic Supplementary Information (ESI) for
**Nanoporous covalent organic polymers incorporating Tröger's base
functionalities for enhanced CO₂ capture**

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TABLE OF CONTENTS

A. Supplementary Method	2
B. Supplementary Discussions	4
C. Supplementary Figures	6
D. Supplementary Tables	18
E. Supplementary References	21

A. Supplementary Methods

1. Materials and methods

All reagents and solvents that are commercially available were used without further purification. The starting materials for tröger's base linked covalent organic polymers (TB-COPs) – Tetraanilyladamantane (TAA) and Tetraanilylmethane (TAM) were synthesized following procedures reported in the literatures^{1, 2}. ¹H NMR spectra of monomers were obtained on a Bruker DMX 300 MHz NMR spectrometer. Solid-state cross-polarization magic angle spinning (CP/MAS) spectra of TB-COPs were acquired in solid-state using a Bruker DSX 400 MHz NMR system (in KBSI Daegu Center). FT-IR spectra were obtained on KBr disks using a Perkin-Elmer FT-IR spectrometer. X-ray diffraction patterns of the samples were acquired from 10 to 80° by a Rigaku D/MAX-2500 Multi-purpose High Power X-ray diffractometer. Field-Emission Scanning Electron Microscope (FE-SEM) images were obtained by FEI Nova 230. Element analysis (CHNO) was acquired by a sFLASH 2000 series of Thermo Scientific. Thermogravimetric analysis (TGA) was performed on a NETZSCH-TG 209 F3 instrument by heating the samples up to 700°C at 10°C min⁻¹ in N₂ and air atmosphere. Nitrogen adsorption isotherms were obtained with a Micromeritics Triflex accelerated surface area and porosimetry analyzer at 77 K after the samples were degassed at 150°C for 5 h under vacuum. The surface area of the samples was calculated by *Brunauer-Emmett-Teller* (BET) method. Low-pressure CO₂ and N₂ adsorption-desorption isotherms were measured at 273 K and 298 K using a Micromeritics Triflex system.

2. Synthesis of Tröger–Covalent Organic Polymers (TB–COPs)

TB–COP–1: Tetraanilyladamantane (0.2 g, 0.4 mmol) was dissolved in dimethoxymethane (0.35 mL, 4 mmol) under N₂ atmosphere at 0°C. Trifluoroacetic acid (1.53 mL, 20 mmol) was added dropwise over 5 min, and the solution was stirred vigorously for 1 h at room temperature. After 1 h, the solution was solidified and became a firm solid and the solid was roughly ground into several pieces with mortar. The obtained solids were combined and added into ammonium hydroxide solution and stirred for 2 h. The solids were filtered and washed with chloroform and methanol several times. Finally, the solids were refluxed in methanol for 24 h, for complete solvent exchange. Afterwards, the solids were filtered and dried at 80°C under vacuum condition for 12 h to give TB-COP-1 (0.37 g, 81 %) as an orange solid.

TB–COP–2: Tetraanilylmethane (0.2 g, 0.5 mmol) was dissolved in dimethoxymethane (0.47 mL, 5 mmol) under N₂ atmosphere at 0°C. Trifluoroacetic acid (2 mL, 25 mmol) was added dropwise over 5 min, and the solution was stirred vigorously for 1 h at room temperature. After 1 h, the solution was solidified and grounded into several pieces with mortar. The obtained solids were combined and added into ammonium hydroxide solution and stirred for 2 h. The solids were filtered and washed with chloroform and methanol several times. Finally, the solids were refluxed in methanol for 24 h, for complete solvent exchange. Afterwards, the solids were filtered and dried at 80°C under vacuum for 12 h to give TB-COP-2 (0.38 g, 80 %) as a dark purple solid.

B. Supplementary Discussions

1. Ideal Adsorbed Solution Theory (IAST)

IAST calculations can be carried out by fitting adsorption isotherms with a Single-site Langmuir model or a Dual-site Langmuir model. These models were fitted only on the basis of deriving the best fit with adjusted r^2 values exceeding 0.999. The Origin Pro v8.5 program has been used to calculate the following equations.

Single-site Langmuir model can be defined as,

$$q = \frac{q_{sat}bp}{1 + bp}$$

Dual-site Langmuir model can be defined as,

$$q = q_A + q_B = \frac{q_{sat,A}b_Ap}{1 + b_Ap} + \frac{q_{sat,B}b_Bp}{1 + b_Bp}$$

Where, q is a molar loading of adsorbate; q_{sat} is a saturation loading; b is coefficient in the pure component Langmuir adsorption isotherm; A and B refer to two different sites on the molecules. The IAST selectivity (S) for the $CO_2:N_2$ (15:85 v/v %) gas mixtures was derived using the following equation.

$$S = \frac{q_1q_2}{p_1p_2}$$

Where, q_1 and q_2 refer to the quantity adsorbed of component 1 and 2, and p_1 and p_2 represents the partial pressure of the component 1 and 2.

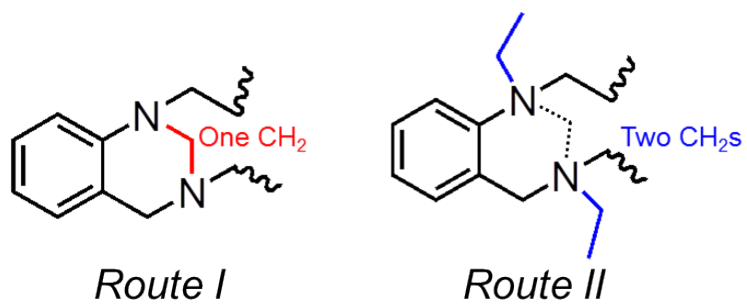
2. Isothermic heats of adsorption

Isothermic heats of adsorption (Q_{st}) were derived from the adsorption data using Clausius-Clapeyron equation,

$$\Delta H = R \left[\partial \ln P / \partial \left(\frac{1}{T} \right) \right]_{\theta}$$

Where, R is the universal gas constant [kJ/K/mol], θ is the fraction of the adsorbed sites at a pressure P and temperature T.

C. Supplementary Figures



Scheme S1. Higher C/N ratio because of the additional methylene -CH₂- bridges per two nitrogens.

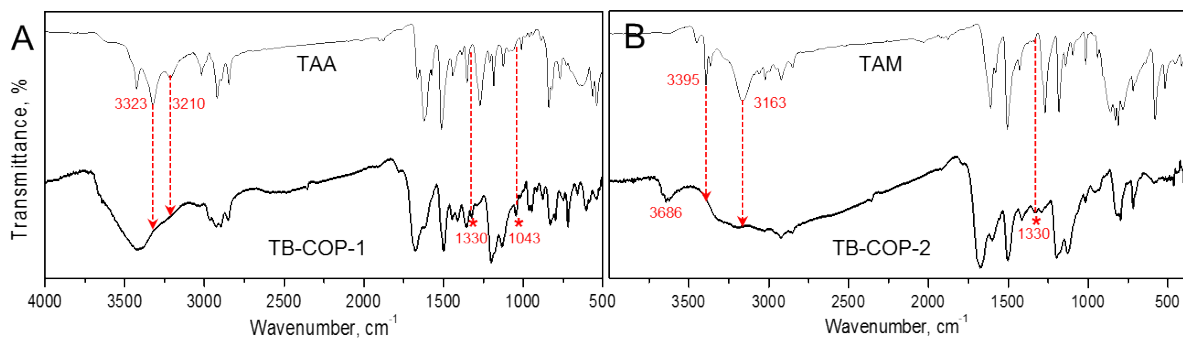


Figure S1. FTIR spectra for (A) TB-COP-1 and (B) TB-COP-2 with their precursors. Asterisk (*) shows the stretching from C-N bond.

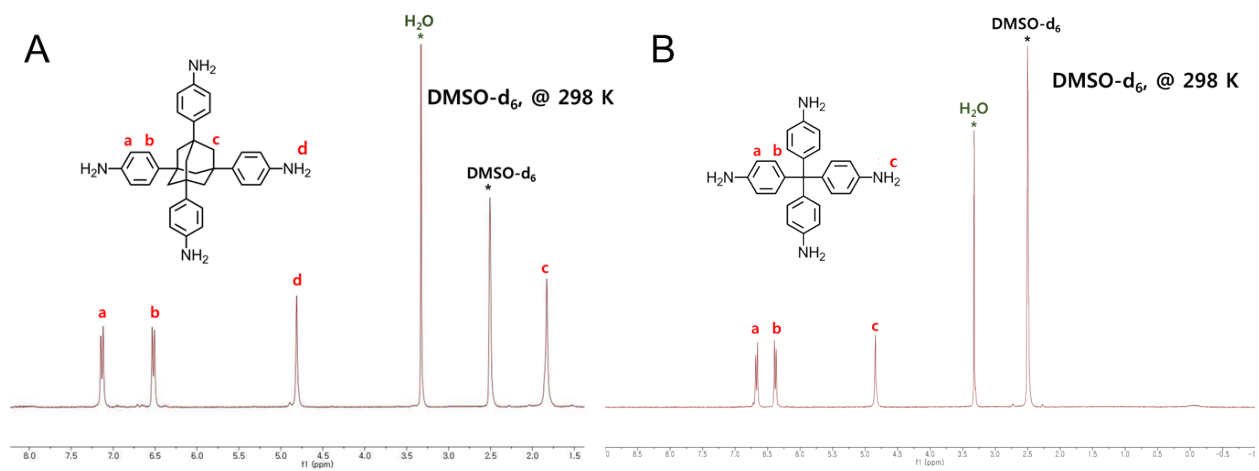


Figure S2. ^1H NMR spectra of (A) Tetraanilyladamantane and (B) Tetraanilylmethane which prepared following procedure reported in the literatures^{1,2}.

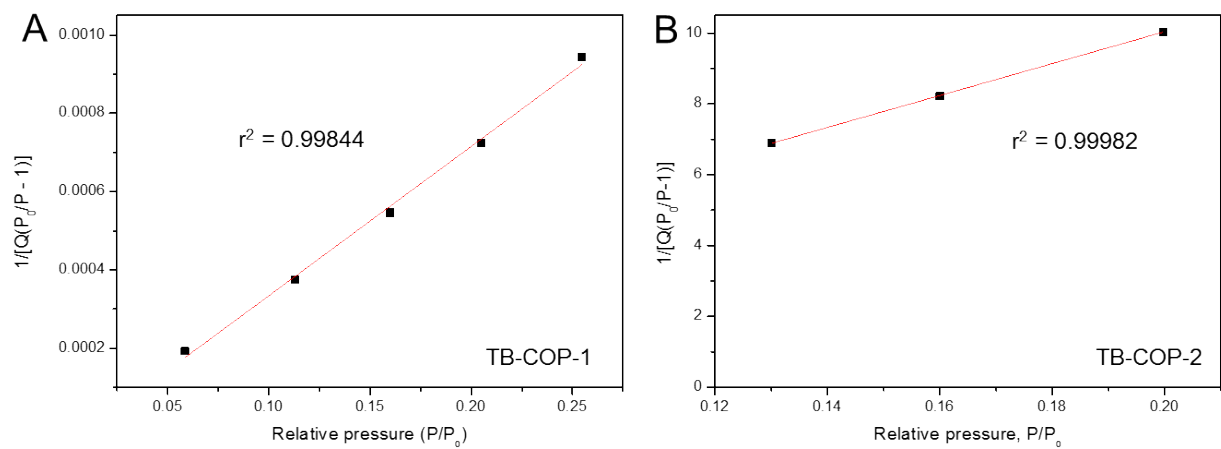


Figure S3. BET plot of (A) TB-COP-1 ($P/P_0 = 0.05 - 0.25$) and (B) TB-COP-2 ($P/P_0 = 0.1 - 0.2$) from N_2 isotherm at 77 K.

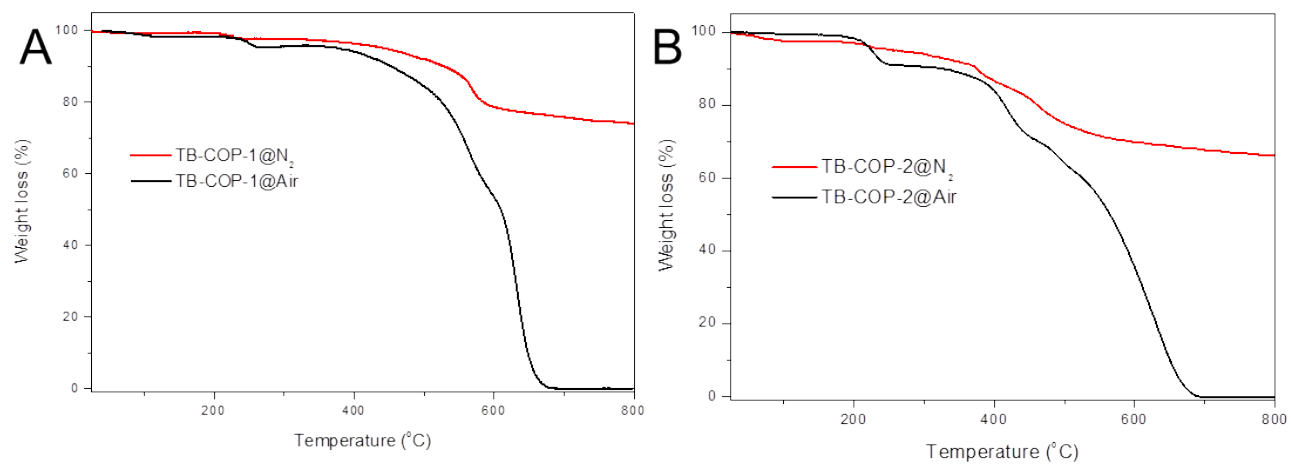


Figure S4. Thermogravimetric analysis of (A) TB-COP-1 and (B) TB-COP-2 under N₂ and air atmosphere up to 800 °C at a rate of 10 °C/min.

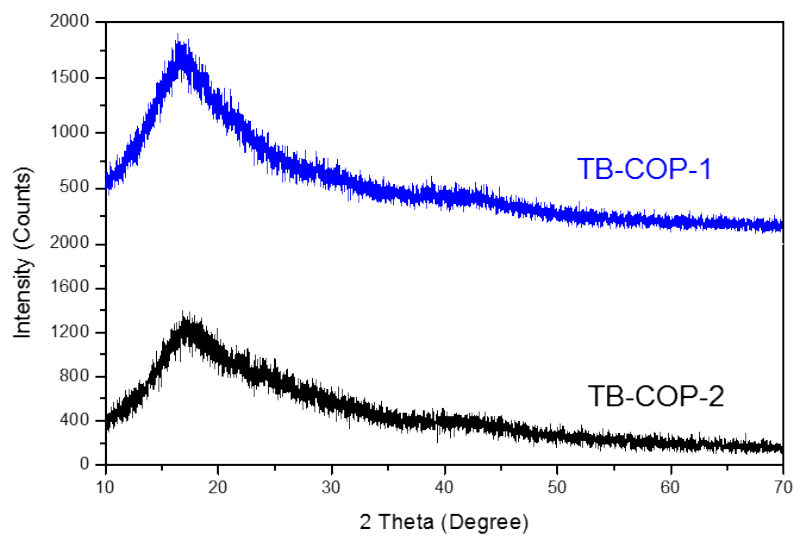


Figure S5. Powder X-ray diffraction patterns of TB-COPs with amorphous phases.

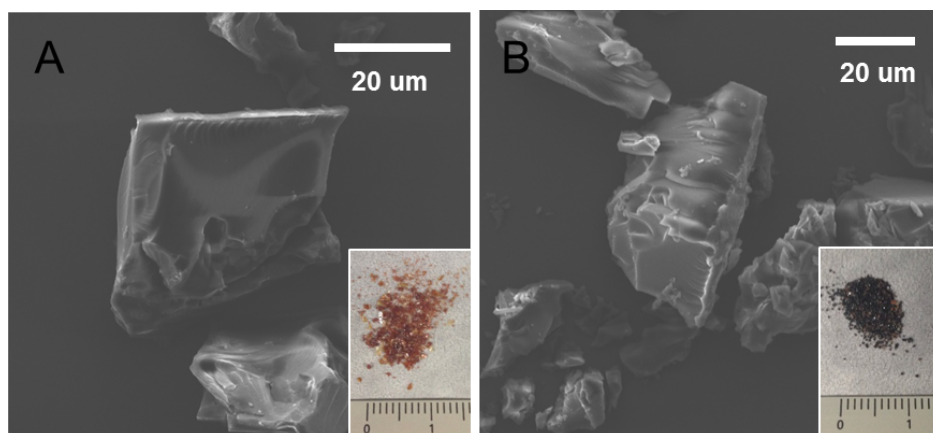


Figure S6. SEM morphology of (A) TB-COP-1 and (B) TB-COP-2 composed of micron-size particles. Inset displays graphical photographs of synthesized TB-COPs, showing that TB-COPs are glassy solids.

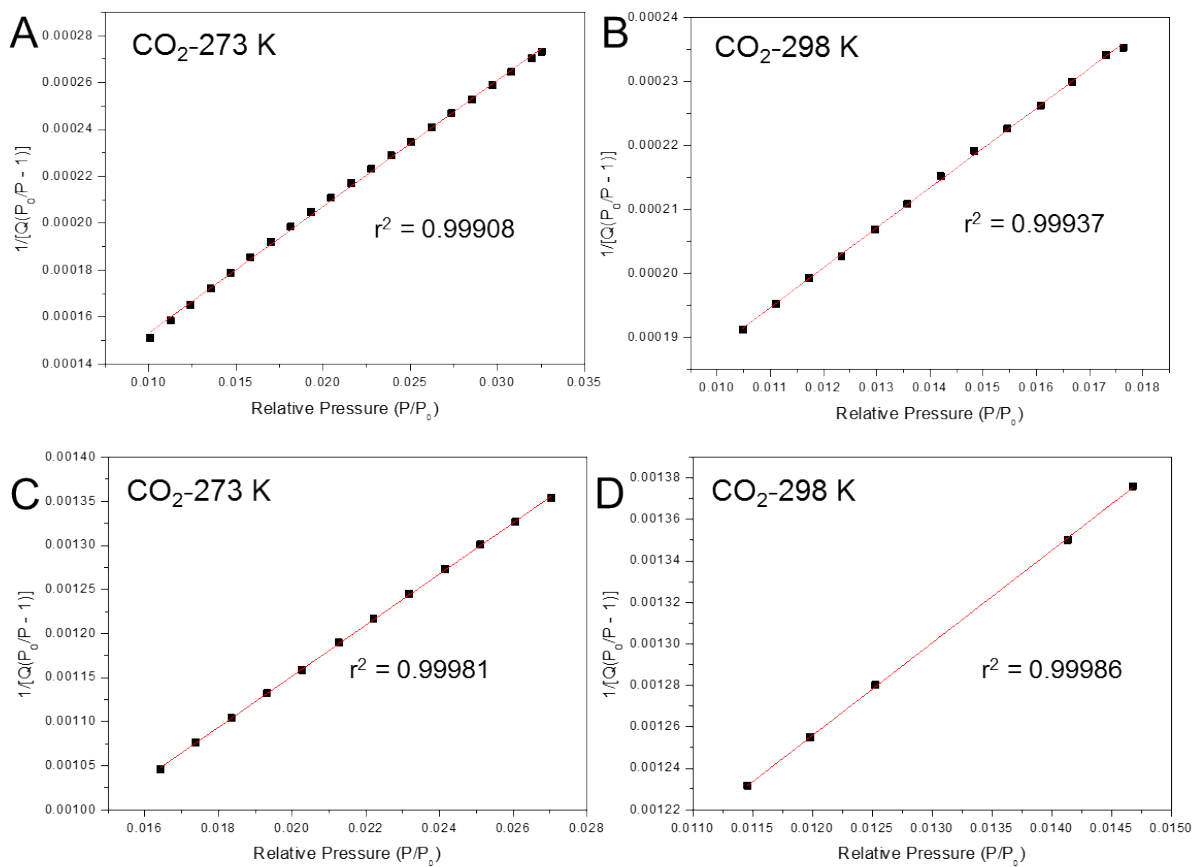


Figure S7. BET plots calculated from CO₂ isotherms for TB-COP-1 (A) at 273 K and (B) 298 K, and for TB-COP-2 (C) at 273 K and (D) 298 K.

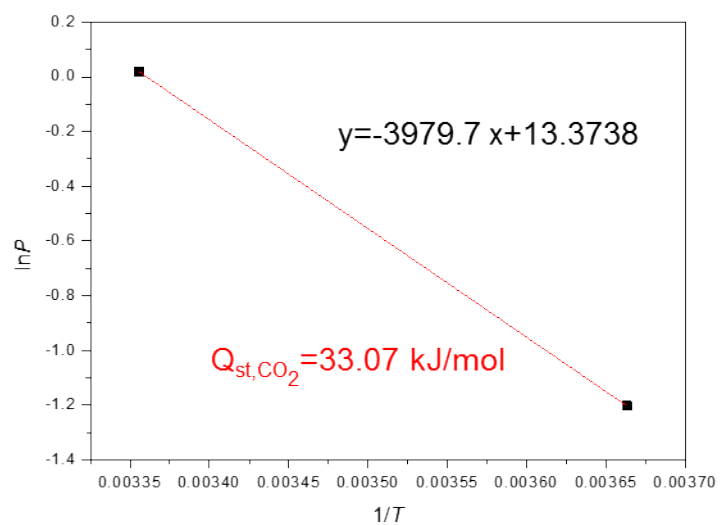


Figure S8. CO₂ adsorption data of TB-COP-2 fitted with Clausius-Clapeyron equation ($\Delta H = R[\partial \ln P / \partial (1/T)]_{\theta}$).

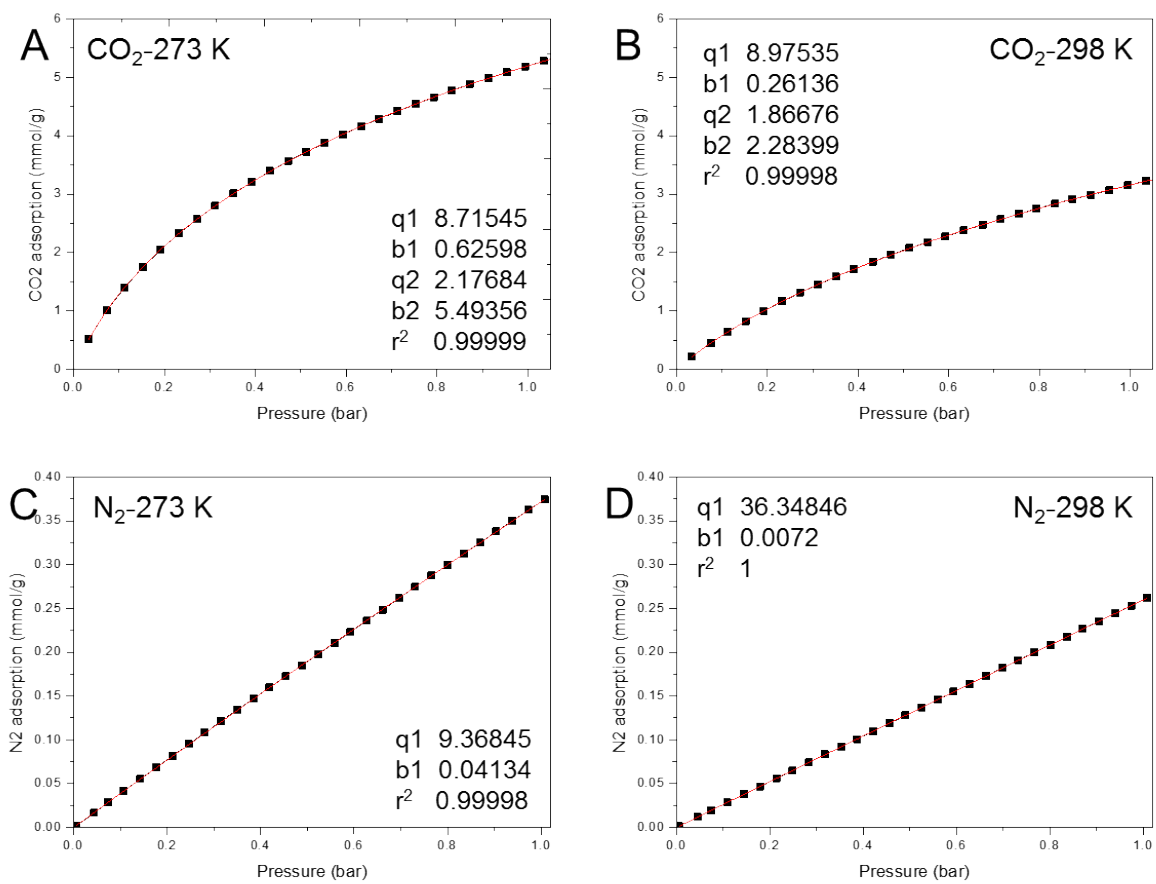


Figure S9. Dual-site Langmuir isotherm fits for CO₂ adsorption of TB-COP-1 at (A) 273 K and (B) 298 K. Single-site Langmuir isotherm fits for N₂ adsorption of TB-COP-1 at (C) 273 K and (D) 298 K. Inset tables display predicted parameters of isotherm models; in which dual-site Langmuir isotherm is defined as ‘ $y=(q_1*b_1*x)/(1+b_1*x)+(q_2*b_2*x)/(1+b_2*x)$ ’ and single-site Langmuir isotherm is defined as ‘ $y=q_1*b_1*x/(1+b_1*x)$ ’.

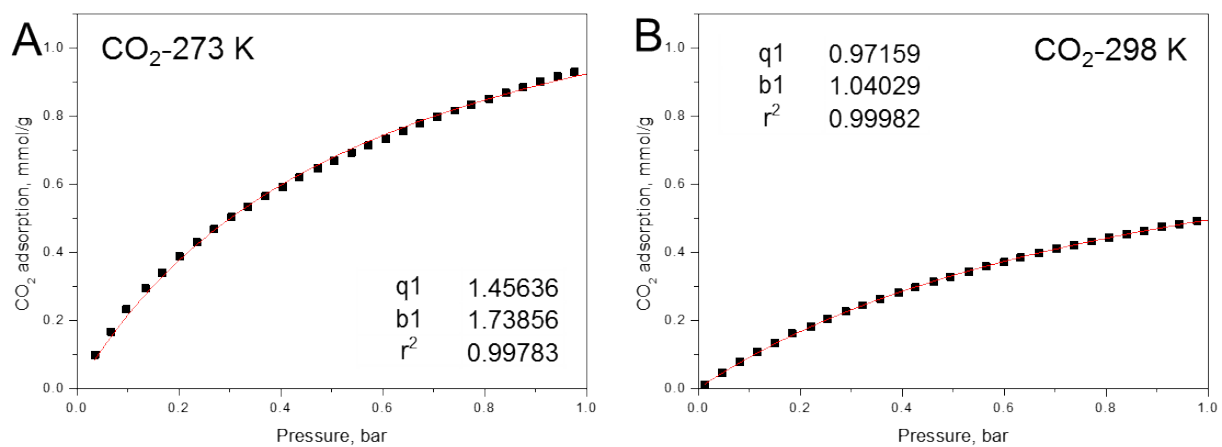


Figure S10. Single-site Langmuir isotherm fits for CO₂ adsorption of TB-COP-2 at (a) 273 K and (b) 298 K.

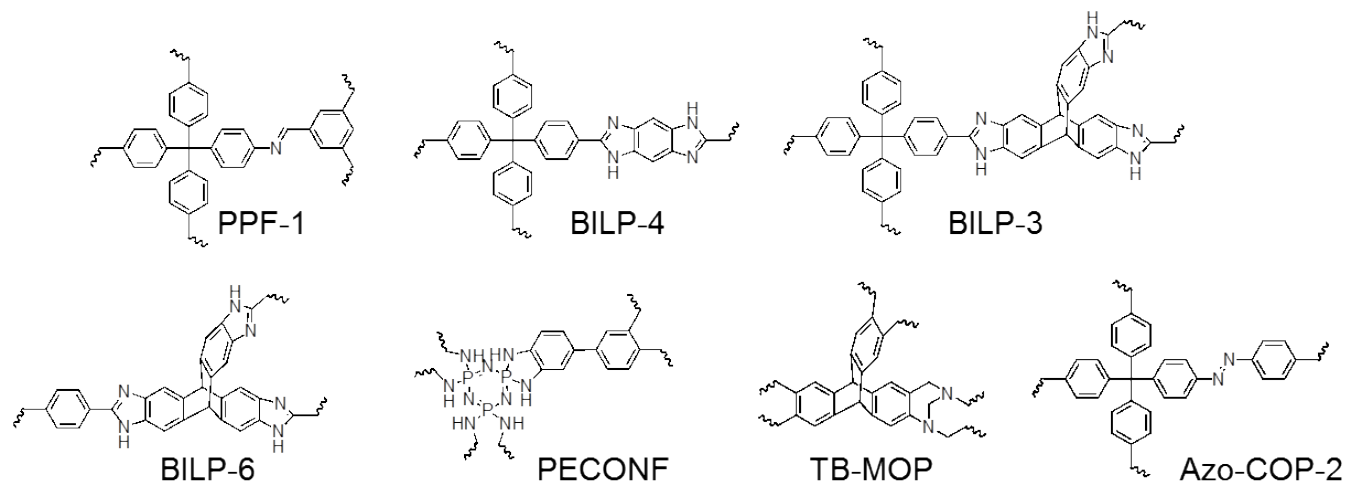


Figure S11. Structures of PPF, BILP, PECONF, TB-MOP and Azo-COP.

D. Supplementary Tables

	C/N Ratio		Carbon (C, %)		Nitrogen (N, %)		Hydrogen (H, %)		Oxygen (O, %)	
	Expected	Found	Expected	Found	Expected	Found	Expected	Found	Expected	Found
TB-COP-1	8.56	8.22	83.90	76.51	9.80	9.31	6.30	6.01	-	2.58
Omitting oxygen				83.46		10.16		6.56		-
TB-COP-2	6.64	7.21	82.30	77.39	12.40	10.73	5.30	5.21	-	2.48
Omitting oxygen				83.02		11.51		5.59		-

Table S1. Elemental analysis of TB-COPs after drying at 150 °C for 5 h. For a clear comparison, the amount of oxygen moieties that are thought to be coming from the trapped water molecules was eliminated.

	Surface area, m ² g ⁻¹			Pore distribution	
	BET (N ₂)	Micropore	BET (CO ₂) @ 273 K	Pore size, nm	Pore volume, cm ³ g ⁻¹
TB-COP-1	1340.17	772.415	694.88	1.575	0.5405
TB-COP-2	0.094	-	154.43	-	-

Table S2. Surface area and average pore size of TB-COPs. Micropore surface area of TB-COP-1 was derived from the t-plot method. Pore volume was calculated at $P/P_0 = 0.994$.

Materials	CO ₂ adsorption (@ 1 bar, mmol g ⁻¹)		N ₂ adsorption (@ 1 bar, mmol g ⁻¹)		Selectivity CO ₂ /N ₂			SA _{BET} m ² g ⁻¹	CO ₂ Q _{st} kJ mo l ⁻¹	Functionality	Ref.
	273 K	298 K	273 K	298 K	Method	273 K	298 K				
TB-COP-1	5.3	3.22	0.373	0.262	IAST	79.18	68.87	1340	25.95	Tröger's base	This work
					Henry	33.94	22.22				
TB-COP-2	0.95	0.5	-	-	-	-	-	0.094	33.07		This work
PPF-1	6.07	5.82	-	-	IAST	14.5	-	1740	25.6	Imine	3
BILP-4	5.34	3.59	0.04	0.136	Henry	79	32	1135	28.7	Benzimidazole	4
BILP-3	5.11	3.29	0.12	0.09	Henry	59	31	1306	28.6		5
BILP-6	4.79	2.75	0.243	0.24	Henry	63	39	1261	28.4		
PECONF- 2	2.85	1.98	-	-	Henry	74	44	637	31	Phosphazene	6
PECONF- 3	3.49	2.47	-	-	Henry	77	41	851	26		
TB-MOP	4.05	2.57	-	-	Henry	45.2	50.6	694	29.5	Tröger's base	7
Azo-COP- 2	2.554	1.53	0.064	0.033	IAST	109.6	130.6	729	24.8	Azo	8

Table S3. Comparison of CO₂ and N₂ uptake, CO₂/N₂ selectivity, BET surface area (SA_{BET}), and isosteric heat of adsorption (Q_{st}) of selected porous polymers.

E. Supplementary References

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