Supporting Information

Thiazolothiazole-Linked Porous Organic Polymers

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Experimental Details

Materials and Methods

Solvents, reagents and chemicals were purchased form Aldrich and TCI America. Tetraphenylmethane and 1,3,5-triformylbenzene were purchased form Matrix Scientific. All were used without any further purification. Tetrakis(4-formylphenyl)methane was synthesized using published procedures.¹ Thermogravimetry analyses (TGA) were performed under N₂ on a SII Nanotechnology TGA 2950, with a heating rate of 10 °C min⁻¹. ¹³C NMR measurements were performed on a 9.4 T Bruker Avance spectrometer at a Larmor frequency of 100.6 MHz. Measurements were made with a 4 mm MAS probe spinning at 7 kHz. Chemical shifts were externally referenced to TMS ($\delta = 0$ ppm). The X-ray powder diffraction (XRD) data was collected on a PANalytical Empyrean diffractometer. FT-IR data were obtained using a Bio-Rad Excalibur FTS-3000 spectrometer.

Elemental analysis was determined using a Vario EL III Elemental Analyzer (Elementar, Germany). Carbon content of TzTz-POP-1 and TzTz-POP-2 was 45.75% and 57.89%, respectively. Hydrogen content of the TzTz-POP-2 is found to be 4.20% and higher than that of TzTz-POP-1 (2.98%).

Nitrogen adsorption isotherms were measured at -196 °C using Micromeritics ASAP 2020 static volumetric analyzer. Before adsorption measurements the polymers were degassed at 120 °C. The Brunauer-Emmett-Teller surface area was calculated within the relative pressure range 0.01 to 0.1. Total volume was calculated at P/P_{θ} =0.99. Nonlocal density functional theory pore size distributions obtained using CO₂ as the adsorbate isotherms were collected from the Quadrasorb SI analyser.²

Synthesis

The synthesis of tetrakis(4-formylphenyl)methane was following the published procedures and shown in **Scheme S1**.¹ The final light yellow solid was obtained in 30% yield. The ¹HNMR spectrum of tetrakis(4-formylphenyl)methane was shown in **Fig. S8**.



Scheme S1 The synthesis of tetrakis(4-formylphenyl)methane.

1,3,5-triformylbenzene derived thiazolothiazole-linked porous organic polymer (TzTz-POP-1): A pyrex tube was charged with 1,3,5-triformylbenzene (M1, 143 mg, 0.882 mmol) and dithiooxamide (160 mg, 1.3 mmol) and anhydrous DMF (5 ml) and the mixture was sonicated for 2 minutes, degassed through three freeze-pump-thaw cycles, sealed under vacuum, heated at 160 °C for 24 h. The reaction mixture was cooled to room temperature and the yellow precipitate was collected by centrifugation. The crude polymer was thoroughly washed by Soxhlet extraction with CHCl₃ for 24 h, and dried under vacuum at 120 °C for 12 h to afford yellow powder (230 mg) in 76% isolated yield. Tetrakis(4-formylphenyl)methane derived TzTz-POP-2: A pyrex tube was charged with tetrakis(4-formylphenyl)methane (M2, 96.6 mg, 0.22 mmol) and dithiooxamide (54 mg, 0.44 mmol) and anhydrous DMF (3 ml) and the mixture was sonicated for 2 minutes, degassed through three freeze-pump-thaw cycles, sealed under vacuum, heated at 160 °C for 24 h. The reaction mixture was cooled to room temperature and the yellow precipitate was collected by centrifugation. The crude polymer was thoroughly washed by Soxhlet extraction with CHCl₃ for 24 h, and dried under vacuum at 120 °C for 12 h to afford yellow powder (121 mg) in 80% isolated yield.

CO₂/N₂ Uptake

The gas adsorption isotherms of TzTz-POPs 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 $5*10^{-3}$ mbar and then cooled down to the target temperatures, followed by introduction of a single component gas (CO₂ or N₂) into the system.³ CO₂ adsorption cycle experiments were measured under the same condition.

Heat of CO₂ Adsorption Calculation⁴

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

$$\ln\left(\frac{P_1}{P_2}\right) = \Delta H_{ads} \times \frac{T_2 - T_1}{R \times T_1 \times T_2}$$

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_{ads}) of a gas as a function of the quantity of gas adsorbed.

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

$$Q = \frac{Q_m \times B^{\binom{t}{t}}P_1}{(1 + B \times P)^{\frac{t}{t}}}$$

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.

Figures



Fig. S1 FT-IR spectra of starting material (dithiooxamide) and TzTz-POPs.



Fig. S2 Thermogravimetric analysis for TzTz-POPs (measured under N_2).



Fig. S3 X-ray powder diffraction patterns of TzTz-POPs.



Fig. S4 TEM imags of TzTz-POP-1 (A) and TzTz-POP-2 (B).



Fig. S5 NLDFT pore size distributions of TzTz-POPs obtained using both N_2 (A and B) and CO₂ (C and D) as the adsorbates.



Fig. S7 Five cycles of CO₂ uptake at 273 K for TzTz-POP-2.



Fig. S7 The selectivity of TzTz-POPs for CO_2 over N_2 isotherms obtained from the initial slope method.



Fig. S8 ¹HNMR spectrum of tetrakis(4-formylphenyl)methane (in CDCl₃).

РОР	SA_{BET} (m ² g ⁻¹)	CO ₂ uptake (mmol g ⁻¹)	T (K)	Selectivity (obtained from the initial slope method)	Q _{st} (kJ mol ⁻¹)	Ref.
TzTz-POP-1	298.5	1.9	273	54	32	This work
TzTz-POP-2	488.4	2.5	273	35	30	This work
CMP-1-NH ₂	710	1.64	273		29.5	5
		0.95	298			
azo-COP-2	729	2.56	273	109.6	24.8	6
		1.53	298	130.6		
CPOP-1	2220	4.82	273	25	27	7
Py-1	437	2.70	273	117	36	8
BILP-4	1135	5.34	273	79	28.7	9
		3.59	298	32		
ALP-1	1235	5.37	273	35	29.2	10
PPN-6-SO ₃ H	1254	3.6	295		30.4	3
PPN-6-SO ₃ Li	1186	3.7	295		35.7	3
PPN-6- CH ₂ DETA	555	4.3	295		56	11
PPN-6- SO ₃ NH ₄	593	1.7 (15% CO ₂)	295		40	12

Table S1 Summary of surface area, CO_2 uptake, selectivity (CO_2/N_2) (at 273 and 298 K) and isosteric heat (Q_{st}) in selected POPs (with excellent reported results).

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