Supporting Information

Efficient CO_2 Capture by a Task-Specific Porous Organic Polymer Bifunctionalized with Carbazole and Triazine Groups

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Experimental Details

Methods

Solvents, reagents and chemicals were purchased form Aldrich and TCI America. All were used without any further purification. Thermogravimetry analyses (TGA) were performed under N_2 on a SII Nanotechnology TGA 2950, with a heating rate of 10 °C min^{-1}. ^{13}C 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 15 kHz. Chemical shifts were externally referenced to TMS (δ = 0 ppm) using the methyl resonance of hexamethylbenzene (17.5 ppm relative to TMS). The X-ray powder diffraction (XRD) data was collected on a PANalytical Empyrean diffractometer. Nitrogen adsorption isotherms were measured at -196 ºC using Micromeritics ASAP 2020 static volumetric analyzer. Before adsorption measurements the polymer was degassed at 120 ºC. 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_0=0.99. 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).

Synthesis

Carbazole derived task-sepcific polymer (TSP-1): To a solution of carbazole (M1, 20 mmol) and FDA (40 mmol) in anhydrous 1, 2-dichloroethane (DCE, 20ml), anhydrous ferric chloride ($FeCl_3$, 40 mmol) was added under nitrogen atmosphere. The mixture was heated at 80 °C for 24h. The crude polymer was collected and thoroughly washed by *Soxhlet* extraction with methanol for 24 h. The product was then dried at 120 °C under vacuum to give TSP-1 (yield 90%) as a brown solid.

Triazine and carbazole bifunctionalized task-sepcific polymer (TSP-2): Triazine-containing monomer 2,4,6-Tricarbazolo-1,3,5-triazine (M1, 2.5 mmol) and FDA (15 mmol) were dispersed in anhydrous 1, 2-dichloroethane (DCE, 10ml) for 10 minutes. Anhydrous ferric chloride ($FeCl_3$, 15 mmol) was then added under nitrogen atmosphere. The mixture was heated at 80°C for 24h. The brown crude polymer was collected and thoroughly washed by *Soxhlet* extraction with methanol and chlorobenzene for 24 h, respectively, to remove unreacted monomers. The solid was then dried at 120 °C under vacuum to give TSP-2 (yield 60%).

CO_2/N_2 Uptake

The gas adsorption isotherms of TSPs 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 (CO_2 or N_2) into the system.[1]

Heat of CO_2 Adsorption Calculation [2]

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 CO_2 adsorbed was determined by the Toth model for the isotherms.

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

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 Ideal Adsorption Solution Theory (IAST) calculations[1, 3]

The pure component isotherms of CO_2 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 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% CO_2 and 85% N_2, which is typical of flue gases.

Figures

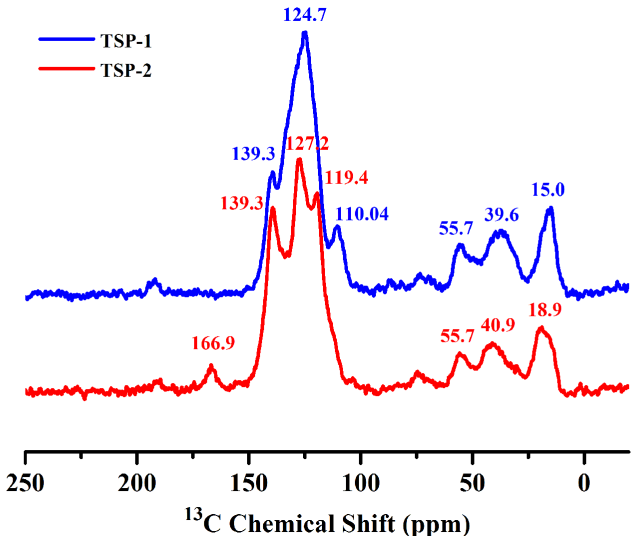

Fig. S1 Solid state ^{13}CNMR of carbazole based TSPs.

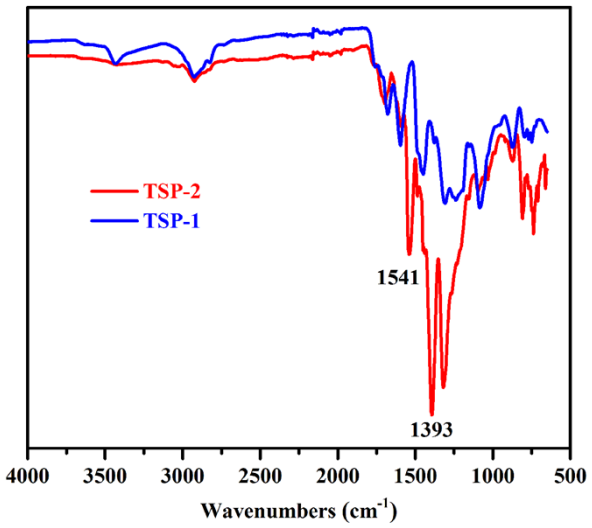

Fig. S2 FTIR spectra of carbazole based TSPs.

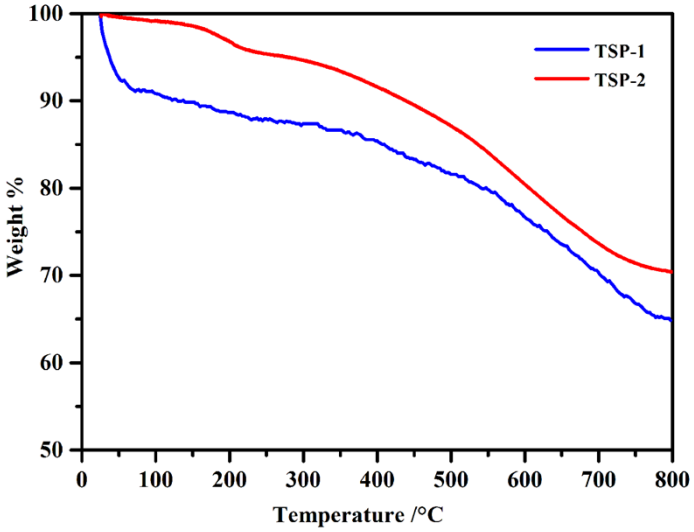

Fig. S3 Thermogravimetric analysis for TSPs (measured under N_2).

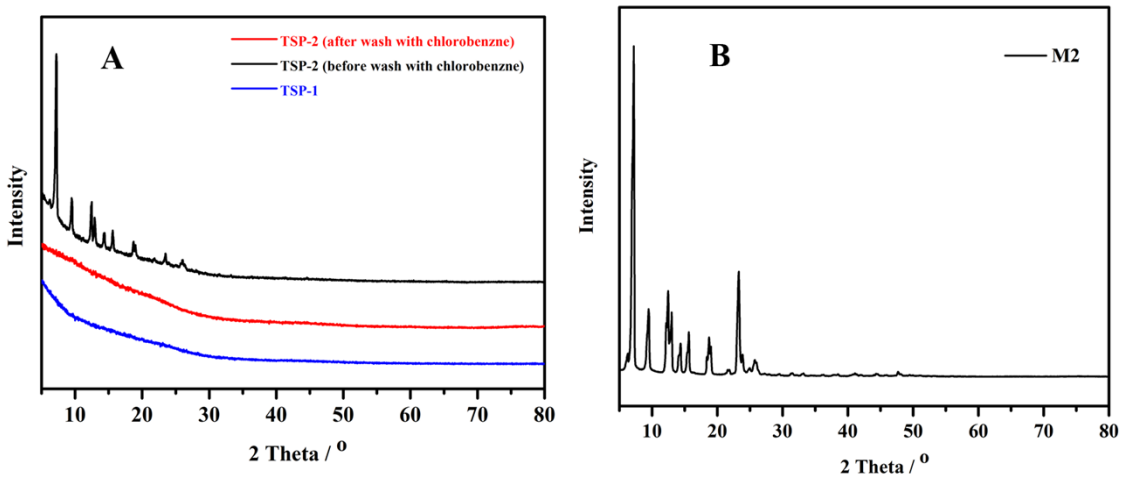

Fig. S4 X-ray powder diffraction patterns of TSPs and 2, 4, 6-Tricarbazolo-1, 3, 5-triazine (M2).

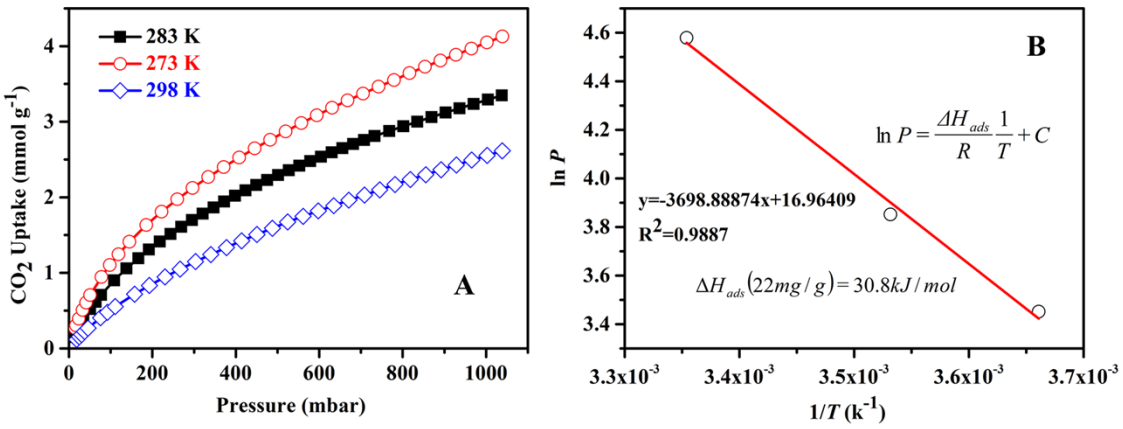

Fig. S5 A: CO_2 adsorption curves of TSP-2 at 273K, 283K and 298K; B: Heat of adsorption for TSP-2 calculated by Clausius-Clapeyron equation when the CO_2 uptake of TSP-2 is 0.5 mmol g^{-1} (22 mg g^{-1}).

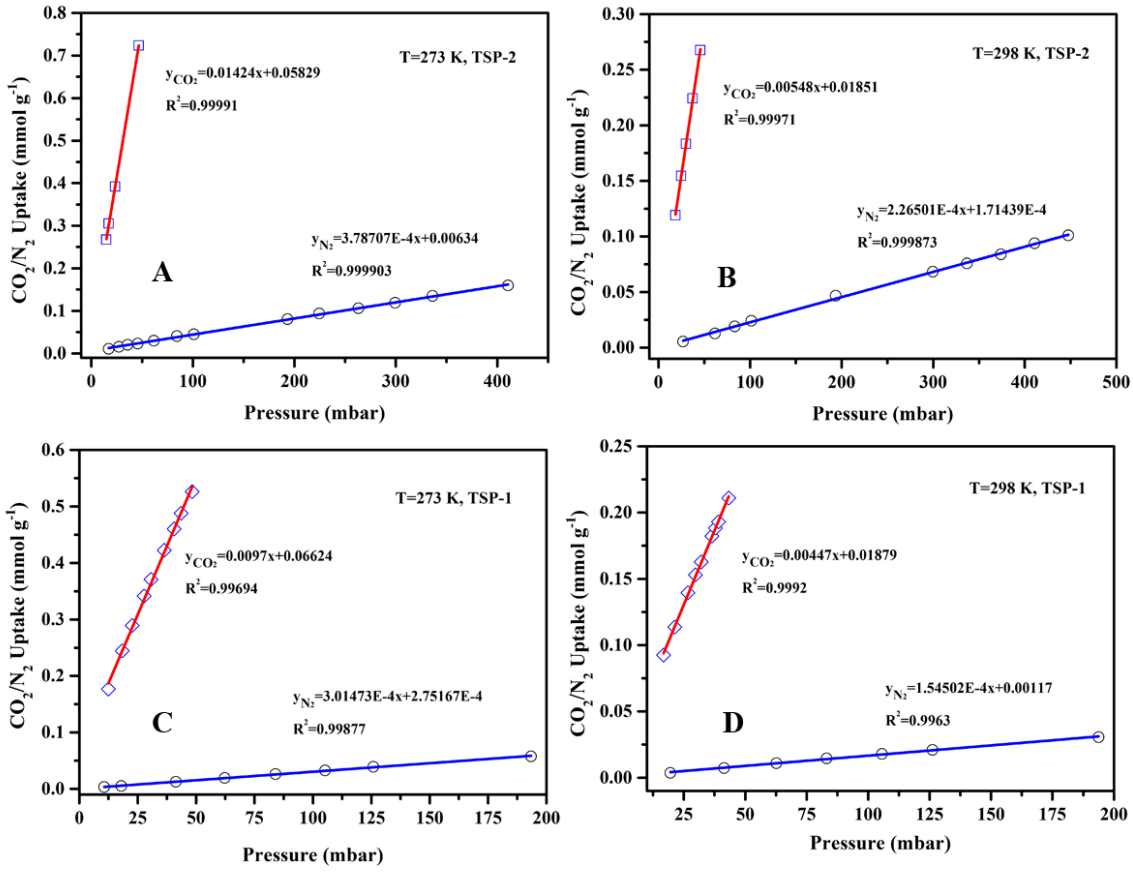

Fig. S6 The selectivity of TSPs for CO_2 over N_2 isotherms obtained from the initial slope method

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).

MOP	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.
TSP-2	913.0	4.1	273	38	30.2	This work
		2.6	298	24		
TB-MOP	694	4.05	273	45.2	29.5	2
		2.57	298	50.6		
FCTF-1-600	1535	5.53	273		30	4
		3.41	298			
CMP-1-$(OH)_2$	1043	1.80	273		27.6	5
		1.07	298			
BILP-4	1135	5.34	273	79	28.7	6
		3.59	298	32		
PECONF-3	851	3.49	273	77	26	7
		2.47	298	41		
CPOP-1	2220	4.82	273	25	27	8
azo-COP-2	729	2.56	273	109.6	24.8	9
		1.53	298	130.6		
Py-1	437	2.70	273	117	36	10
ALP-1	1235	5.37	273	35	29.2	3
PPN-6-SO_3H	1254	3.6	295		30.4	1

PPN-6-SO_3Li	1186	3.7	295	35.7	1
PPN-6-CH_2DETA	555	4.3	295	56	11
PPN-6-SO_3NH_4	593	1.7 (15% CO_2)	295	40	12

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