

Supporting Information

Facile fabrication of cost-effective porous polymer networks for selective CO₂ capture

Lin-Bing Sun,^{a,*} Ai-Guo Li,^a Xiao-Dan Liu,^a Xiao-Qin Liu,^a Dawei Feng,^b Weigang Lu,^b
Daqiang Yuan^b and Hong-Cai Zhou^{b,*}

^a *State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical
Engineering, Nanjing Tech University, Nanjing 210009, China. Email: lbsun@njtech.edu.cn.*

^b *Department of Chemistry, Texas A&M University, College Station, Texas 77842-3012, United States.
Email: zhou@chem.tamu.edu.*

Experimental Section.

Chemicals

Mesitylene and ethylene diamine were purchased from Alfa Aesar Chemicals. Paraformaldehyde, sodium chloride, zinc chloride, anhydrous magnesium sulfate, concentrated hydrochloric acid, dichloromethane, tetrahydrofuran, potassium hydroxide, and the triblock copolymer P123 (EO₂₀PO₇₀EO₂₀) were obtained from Sigma-Aldrich. All chemicals were used directly without further purification.

Synthesis

The monomer 2,4,6-tris(chloromethyl)mesitylene (M1) was prepared according to the method reported previously.¹ The porous polymer networks were synthesized by a nucleophilic substitution reaction of 2,4,6-tris(chloromethyl)mesitylene (namely M1) with ethylene diamine (namely M2). In a typical process, M1 (0.561 g, 2 mmol) was dissolved in THF (50 mL) followed by the addition of M2 (0.180 g, 3 mmol). The obtained solution was then heated in a nitrogen atmosphere at 63 °C for 24 h. After cooling to room temperature, the reaction mixture was centrifuged to remove solvent, and the precipitate was treated with an ethanol/water (20 mL/20 mL) solution of KOH (0.504 g) at 50 °C for 12 h. The material was then washed with an ethanol/water solution for 3 times and dried at room temperature. The obtained white powder was denoted as PPN-80. In a similar process, PPN-81 was synthesized by the addition of triblock copolymer P123 (0.5 g) to the initial solution containing monomers. No catalysts were used at all for the synthesis of PPNs.

Characterization

Fourier transform infrared (IR) spectra were recorded on a shimadzu IRAffinity-1 spectrometer. Solid state ¹³C cross-polarization (CP) magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were measured on a Bruker AVANCE 400 spectrometer using densely packed powders of porous polymer networks in 4 mm ZrO₂ rotors. Elemental analysis was carried out on

an Elementar Vario EL elemental analyzer. Thermogravimetric (TG) analysis was performed using a thermobalance (Shimadzu TGA-50). About 10 mg of sample was heated from room temperature to 800 °C in a flow of N₂ (25 mL·min⁻¹). The N₂ adsorption-desorption isotherms were measured using a Micromeritics ASAP 2020 system at 77 K. The samples were degassed at 100 °C for 6 h before analysis. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) and Langmuir models. The total pore volumes were derived from the amount adsorbed at the relative pressure of about 0.99.

Adsorption Test

Static adsorption experiments of CO₂, CH₄, and N₂ were conducted using an ASAP 2020 system. Adsorption-desorption isotherms of CO₂, CH₄, and N₂ at 273 K were measured in an ice-water bath, while isotherms at 283 and 295 K were measured in a water bath. The isosteric heats of CO₂ adsorption (Q_{st}) were calculated from the CO₂ adsorption isotherms at temperatures of 273, 283, and 298 K, the data were simulated with a Virial-type expression composed of parameters a_i and b_i that are independent of temperature according to equation 1. Generally, a nonlinear curve was obtained displaying the connection between $\ln P$ and adsorption quantity (N), from the fitting parameters results of a_i , the Q_{st} was calculated according to equation 2.²

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i \quad (1)$$

$$Q_{st} = -R \sum_{i=0}^m a_i N^i \quad (2)$$

To investigate the adsorption selectivity of CO₂ over CH₄ or N₂ on porous polymer networks, the selectivity is defined as $S = (x_1/y_1)/(x_2/y_2)$, where x_1 and y_1 (x_2 and y_2) are the molar fractions of component 1 (component 2) in the adsorbed and bulk phases, respectively.³ The ideal adsorption solution theory (IAST) of Myers⁴ has been reported to predict binary gas mixture adsorption in porous materials accurately, so far many theoretical models combined with the IAST have been proposed to descript the adsorption data, such as Langmuir model, Dual-Site Langmuir mode,

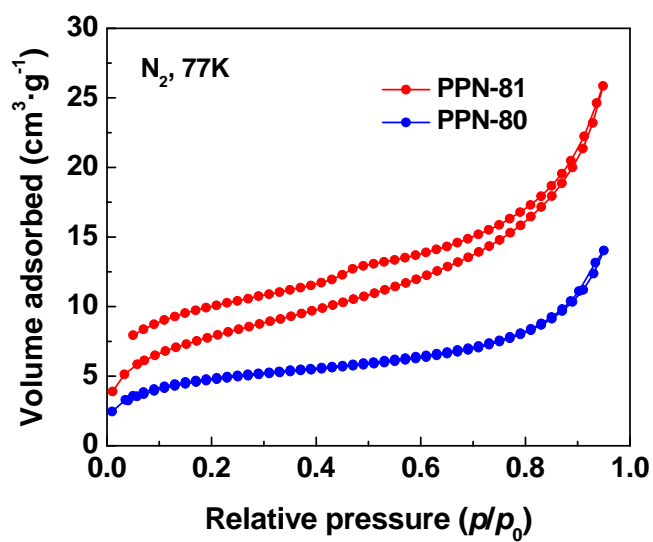
and Dual-Site Langmuir-Freundlich model. Herein, Langmuir model was chosen to fit the adsorption isotherms, and then Langmuir-IAST was utilized to estimate CO₂/N₂ and CO₂/CH₄ selectivities of porous polymer networks. In the calculation, a CO₂/N₂ ratio of 15/85 and a CO₂/CH₄ of 50/50 were used, which are typical composition of flue gas emitted from coal-fired power plants and general feed composition of landfill gas, respectively. After the adsorbent was saturated with CO₂, regeneration was performed by evacuating at 60 °C. The adsorption capacity of regenerated adsorbent was measured again.

References

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- 2 J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 1304.
- 3 W.-J. Jiang, Y. Yin, X.-Q. Liu, X.-Q. Yin, Y.-Q. Shi and L.-B. Sun, *J. Am. Chem. Soc.*, 2013, **135**, 8137.
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Table S1 Elemental analysis of PPN-80 and PPN-81

Element	Theoretical content (%)	Measured content (%)	
		PPN-80	PPN-81
C	73.13	71.67	71.66
H	9.82	8.99	9.24
N	17.06	13.12	13.96
Cl		0.68	0.30

**Fig. S1** N₂ adsorption-desorption isotherms of PPN-80 and PPN-81 at 77 K.

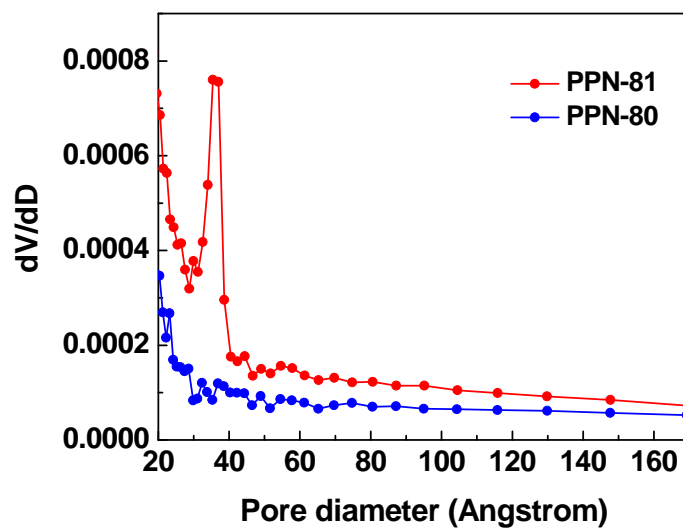


Fig. S2 Pore size distributions of PPN-80 and PPN-81 materials.

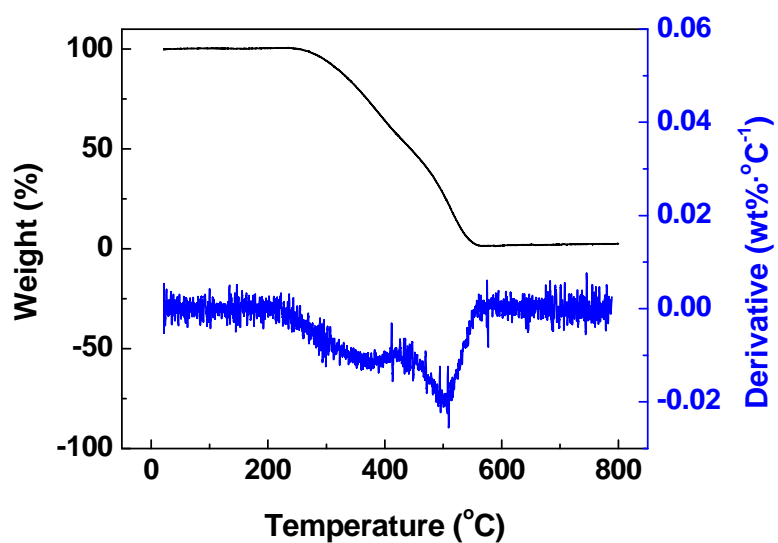


Fig. S3 TG and DTG curves of the material PPN-80.

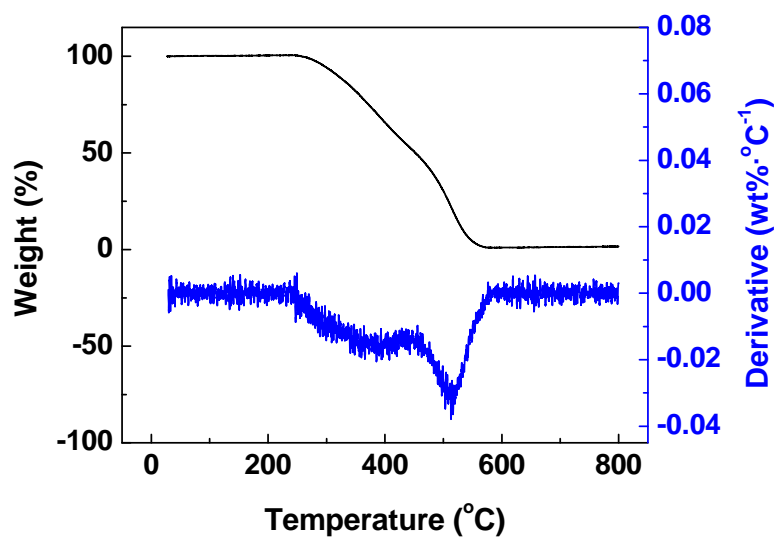


Fig. S4 TG and DTG curves of the material PPN-81.

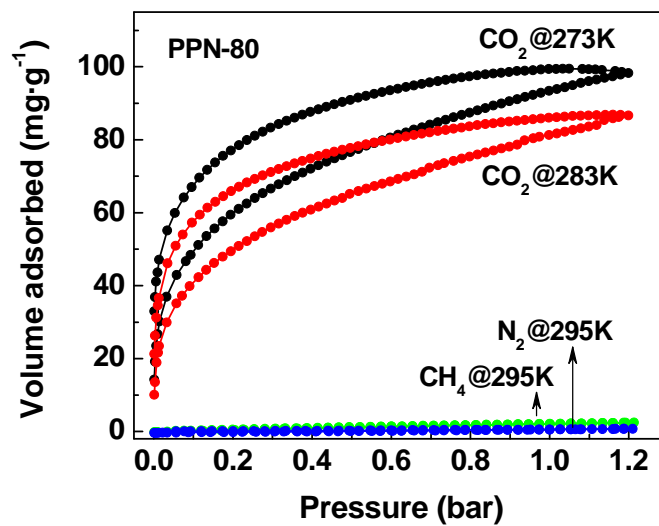


Fig. S5 CO₂, CH₄, and N₂ adsorption-desorption isotherms over PPN-80 at different temperatures.

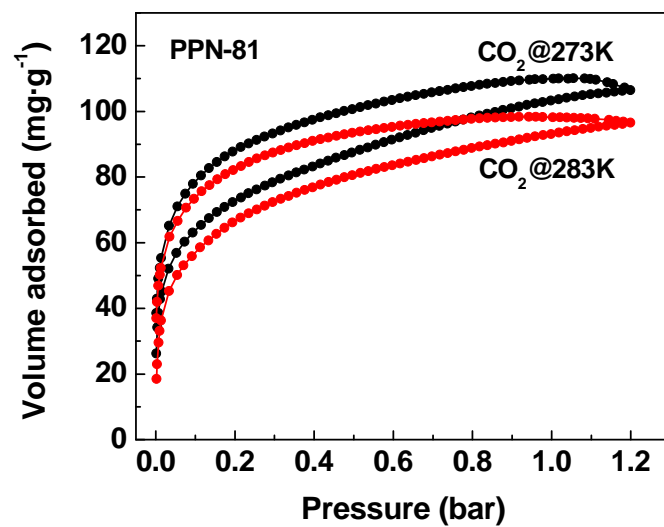


Fig. S6 CO₂ adsorption-desorption isotherms over PPN-81 at different temperatures.

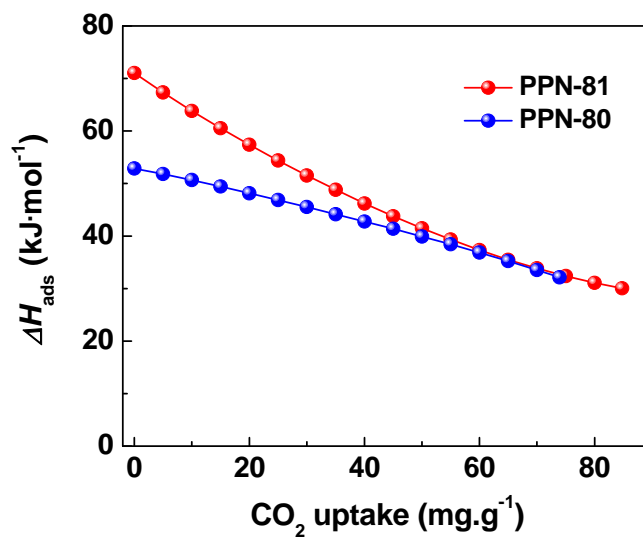


Fig. S7 Isosteric heats of adsorption calculated from the adsorption branches at three different temperatures for PPN-80 and PPN-81.

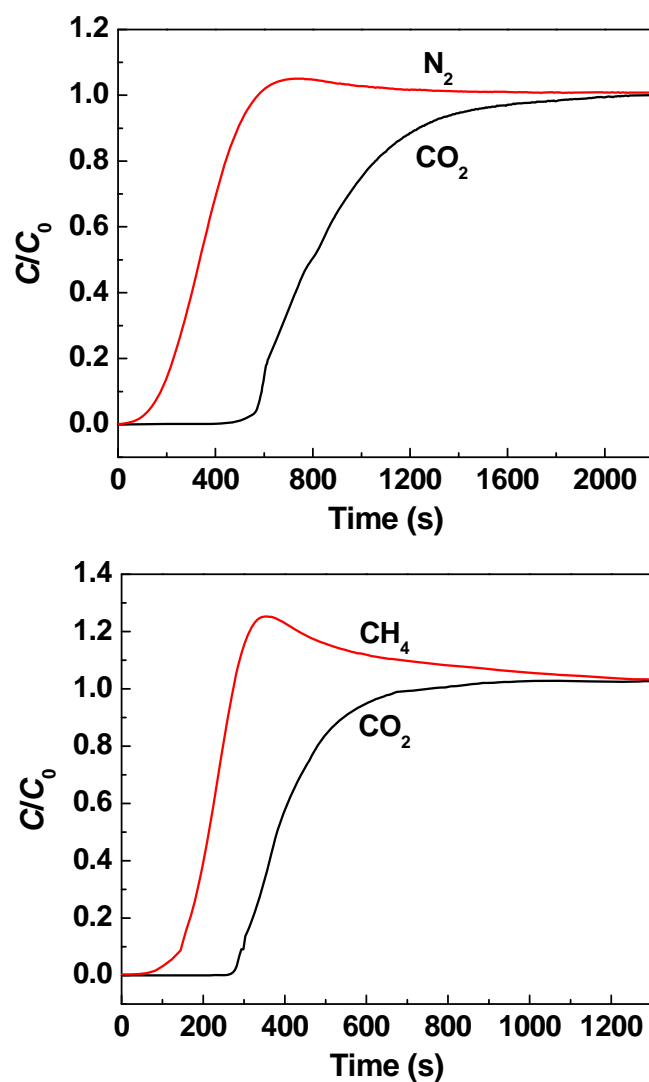


Fig. S8 Dynamic breakthrough curves of CO_2/N_2 and CO_2/CH_4 over the material PPN-81. Mixture gases were prepared with a CO_2/N_2 ratio of 15/85 and a CO_2/CH_4 ratio of 50/50.