

Electronic Supplementary Information

Micro- and mesoporous poly(schiff-base)s constructed from different building blocks and their adsorption behaviors of organic vapors and CO₂ gas

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Experimental section:

Synthesis of 1,3,5,7-Tetrakis(4-formylphenyl)adamantane (TFPA). TFPA were prepared according to the procedures described in the literature. 1,3,5,7-Tetraphenyladamantane (TPA) was prepared in reference to the procedure^{1a} with some modifications. TFPA was synthesized following the similar method as described in the literature.^{1b} Tetraphenyladamantane (3.80 g, 8.6 mmol, 1 eq.) and dichloromethane (150 mL) was added to a 250 mL three-necked round-bottomed flask with a magnetic stir-bar. Under a dried argon-flowing, the mixture was stirred rapidly and cooled to $-10\text{ }^{\circ}\text{C}$ with an ice/salt bath. Titanium tetrachloride (19.0 mL, 172.4 mmol, 20 eq.) was then added slowly to the mixture and stirred at $-10\text{ }^{\circ}\text{C}$ for 30 min. α,α -Dichloromethyl methylether (12.5 mL, 137.9 mmol, 16 eq.) was subsequently added dropwise to the mixture. The reaction was held at $-10\text{ }^{\circ}\text{C}$ for 3 h and then allowed to warm to room temperature with stirring overnight. The mixture was poured into 300mL ice-water, and 100 mL of 1M HCl was added. Then, the resulting mixture was stirred for 30 min. The two-phase mixture was separated and the aqueous phase was washed twice with 100 mL DCM. The combined organic phases were successively washed with 1M HCl, deionized water, saturated aqueous NaHCO_3 and saturated aqueous NaCl, and then dried with MgSO_4 . The solution was filtered and removed solvent by rotary evaporation. The resulted yellow solid was purified by column chromatography and then recrystallized from dioxane to give crystals of TFPA. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 10.02 (s, 1H), 7.91 (d, 2H), 7.67 (d, 2H), 2.27 (s, 3H). FTIR (KBr, cm^{-1}): 2928, 2852, 1700, 1600, 1162, 845, 756.

Synthesis of Tetrakis(4-nitrophenyl)methane (TNPM). Tetraphenylmethane (7.4 g, 23.09 mmol) was added into fuming nitric acid (40 ml) at $-40\text{ }^{\circ}\text{C}$ under vigorous stirring. Then, acetic

anhydride (12.5 ml) and acetic acid (25 ml) were slowly added and stirred for 1 h. After filtration, the resulted yellow solid was recrystallized with THF to give yellow crystals. Yield: 65 %. M.p.: 339 °C; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.22-8.25 (d, 8H, Ar-H), 7.60-7.62 (d, 8H, Ar-H); FTIR (KBr, cm⁻¹): 3070, 3100, 1605, 1591, 1519, 1493, 1347, 840, 757, 744, 711.

Synthesis of Tetrakis(4-aminophenyl)methane (TAPM). TAPM was prepared in reference to the procedure.² In a hydrogenator, dry tetrahydrofuran (40 mL), TNPM (1.6 g, 3.19 mmol) and catalysis amount of Pd/C was added and purged with nitrogen. Then, the mixture was stirred under 1.2 MPa hydrogen pressure at room temperature for 3 days. After removing the Pd/C powder and solvent, the white product was purified by recrystallization. Yield: 95 %. M.p.: 262 °C; ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 6.66-6.68 (d, 8H, Ar-H), 6.38-6.40 (d, 8H, Ar-H), 4.85 (s, 8H, -NH₂); FTIR (KBr, cm⁻¹): 3442, 3400, 3363, 3333, 3027, 3100, 1620, 1508, 1281, 1216, 1184, 820, 754, 577; HRMS calculated for C₂₅H₂₄N₄ 380.2001, found 380.2004.

Synthesis of tris(4-aminophenyl)amine (TAPA). TAPA was prepared by a similar procedure to TAPM except that the precursor compound is tris(4-nitrophenyl)amine instead of tetrakis(4-nitrophenyl)methane. Yield: 90%. M.p.: 241 °C; ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 6.60-6.62 (d, 6H, Ar-H), 6.46-6.44 (d, 6H, Ar-H), 4.68 (s, 6H, -NH₂); FTIR (KBr, cm⁻¹): 3411, 3340, 3029, 1622, 1504, 1262.

Synthesis of 1,3,5-Tris(4-nitrophenyl)benzene (TNPB). TNPB was prepared according to the literature. 4-Nitroacetophenone (25.1 g, 0.15 mol) and anhydrous ethanol (43.7 mL, 0.75 mmol) were charged in three-necked flask equipped with a magnetic stirrer. Thionyl chloride (18.2 ml, 0.25 mol) was added dropwise. Then the mixture was reacted at the refluxing temperature for additional 1 h. The solid was neutralized and washed successively with

deionized water, ethyl ether, and ethanol. The crude product was recrystallized with DMF to give yellow needle-like solid. Yield: 77%. M.p.: 325 °C; ¹H NMR (400 MHz, DMSO-d₆): δ (ppm) 8.38-8.36 (d, 6H, Ar-H), 8.27-8.29 (6H, Ar-H), 8.26 (3H, Ar-H). FTIR (KBr, cm⁻¹): 1594, 1511, 1349, 862, 843, 629.

Synthesis of 1,3,5-Tris(4-aminophenyl)benzene (TAPB). TAPB was prepared by a similar procedure to TAPM. Yield 95%. M.p.: 262 °C; ¹H NMR(400 MHz, acetone-d₆): δ (ppm) 7.59 (s, 3H, Ar-H), 7.51-7.53 (d, 6H, Ar-H), 6.77-6.79 (d, 6H, Ar-H), 4.76 (6H, -NH₂); ¹³C NMR (100 MHz, acetone-d₆): d (ppm) 149.0, 143.1, 130.7, 128.9, 122.3, 115.5; FTIR (KBr, cm⁻¹): 3442, 3360, 1620, 1593, 1516, 1283, 827.

- (1) a) Wei, Q.; Lazzeri, A.; Cuia, F. D.; Scalari, M.; Galoppini, E. *Macromol. Chem. Phys.* **2004**, 205, 2089; b) Duncan, N. C.; Hay, B. P.; Hagaman, E. W.; Custelcean, R. *Tetrahedron* **2012**, 68, 53.
- (2) Li, G. Y.; Wang, Z. G. *Macromolecules* **2013**, 46, 3058.

Table S1 Elemental analysis data of the poly(Schiff base) networks.

Materials	Theoretical value			Measured value		
	C	H	N	C	H	N
PSN-DA	85.68	6.33	7.99	83.21	6.18	7.54
PSN-TAPB	88.01	6.12	5.87	82.69	5.52	5.69
PSN-TAPA	85.41	6.01	8.58	80.16	5.45	8.37
PSN-TAPM	87.26	6.28	6.46	82.86	5.68	5.62

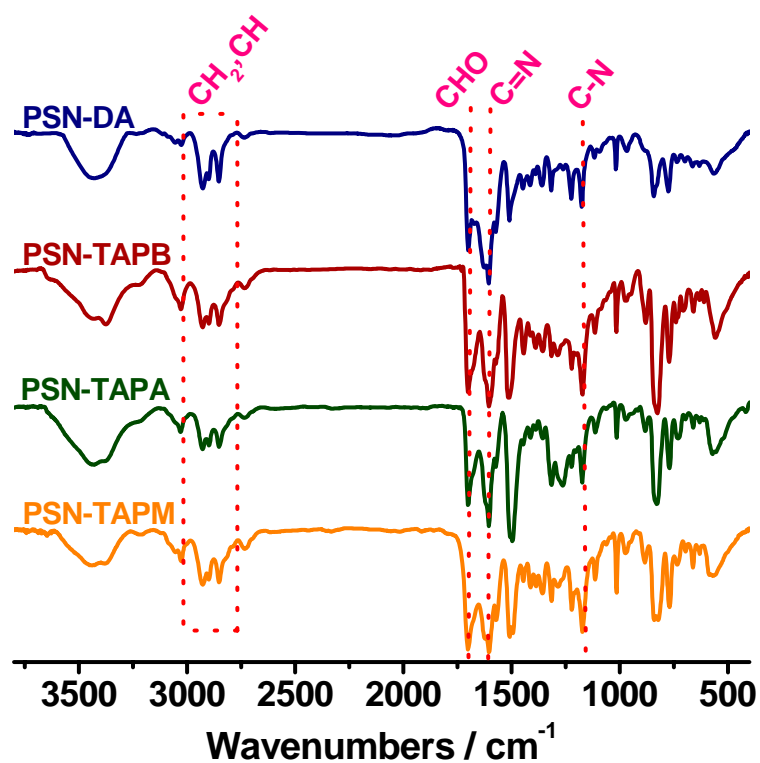


Fig. S1. FTIR spectra of the microporous poly(Schiff base) networks.

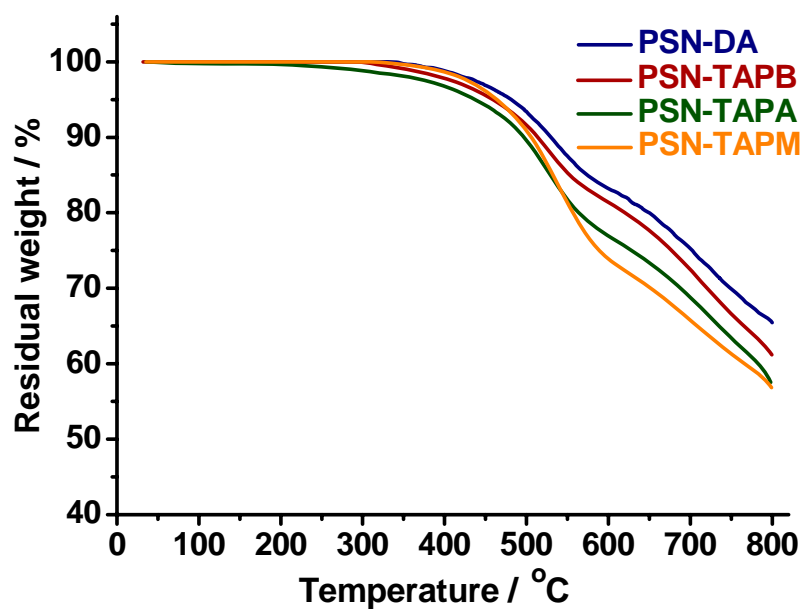


Fig. S2. TG curves of the four poly(Schiff base)s.

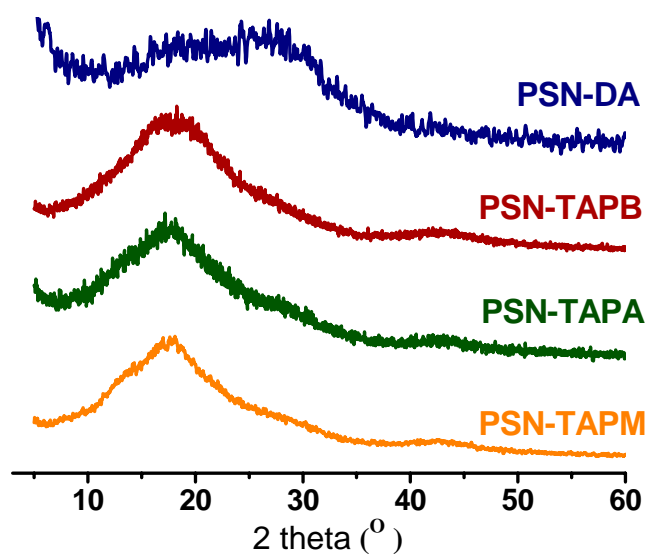


Fig. S3. Wide angle X-ray diffractions of the four microporous poly(Schiff base)s.

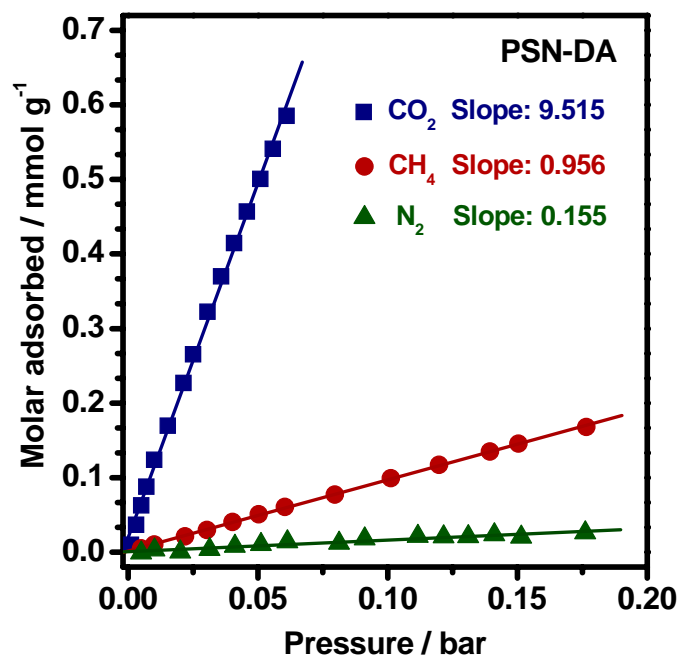


Fig. S4. Adsorption selectivities of CO₂ over CH₄ and N₂ for PSN-DA from initial slope calculations according to CO₂ (blue), CH₄ (red) and N₂ (green) isotherms collected at 273 K.

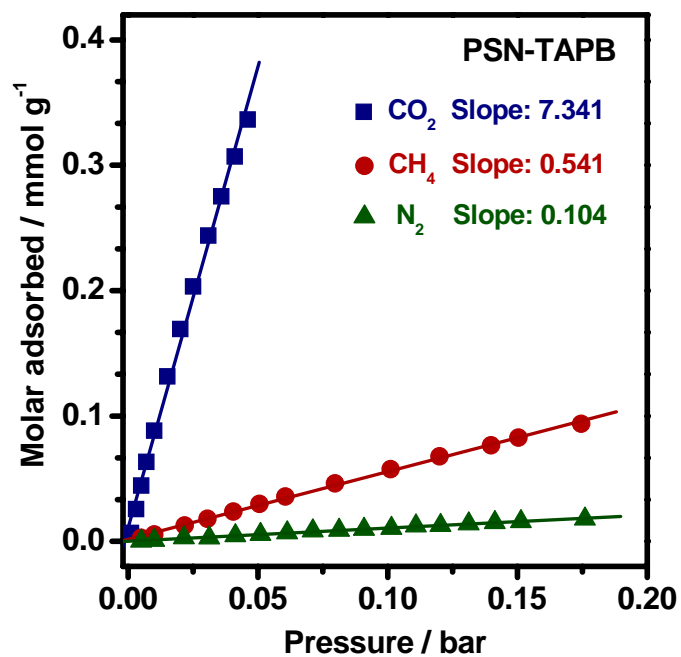


Fig. S5. Adsorption selectivity of CO₂ over CH₄ and N₂ for PSN-TAPB from initial slope calculations according to CO₂ (blue), CH₄ (red) and N₂ (green) isotherms collected at 273 K.

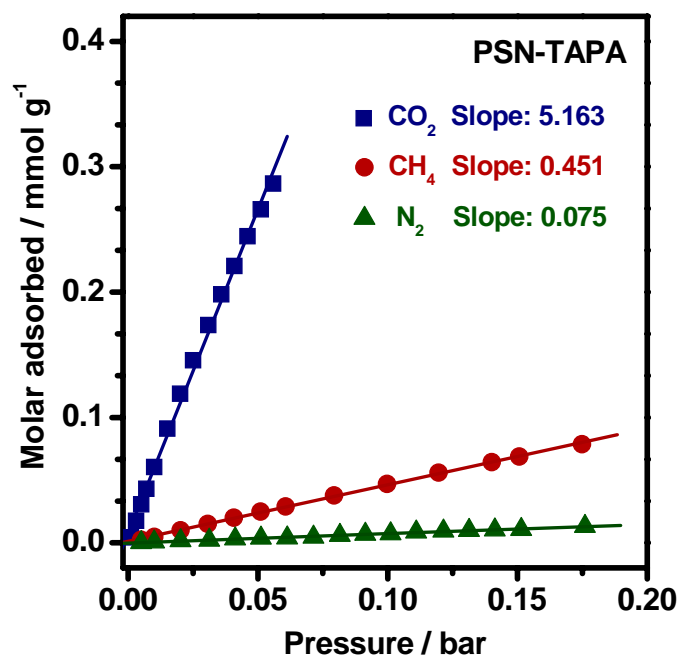


Fig. S6. Adsorption selectivities of CO₂ over CH₄ and N₂ for PSN-TAPA from initial slope calculations according to CO₂ (blue), CH₄ (red) and N₂ (green) isotherms collected at 273 K.

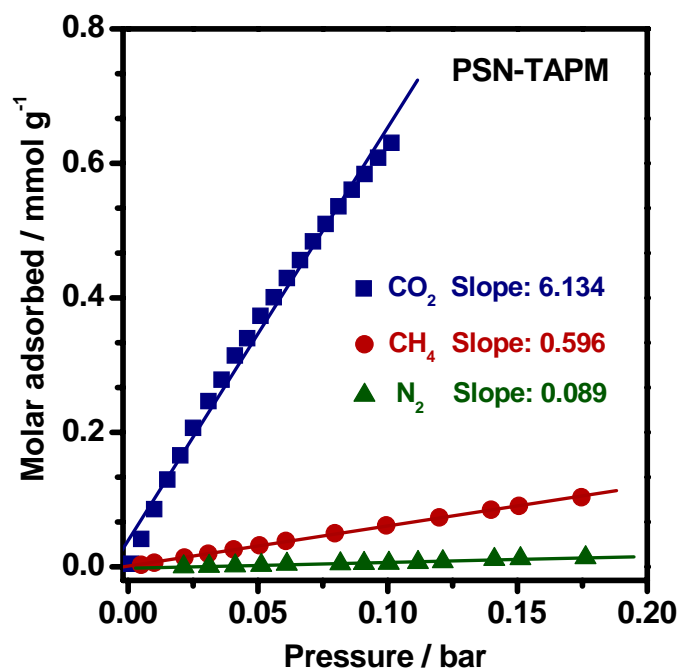


Fig. S7. Adsorption selectivities of CO₂ over CH₄ and N₂ for PSN-TAPM from initial slope calculations according to CO₂ (blue), CH₄ (red) and N₂ (green) isotherms were collected at 273 K.

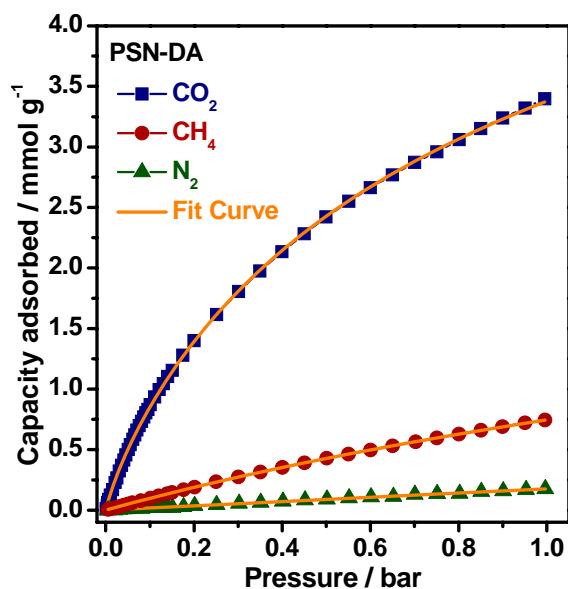


Fig. S8. PSN-DA Experimental pure component curves for CO₂, CH₄ and N₂ at 273K, and the corresponding solid curves are the single-site Langmuir-Freundlich fits for CO₂, CH₄ and N₂.

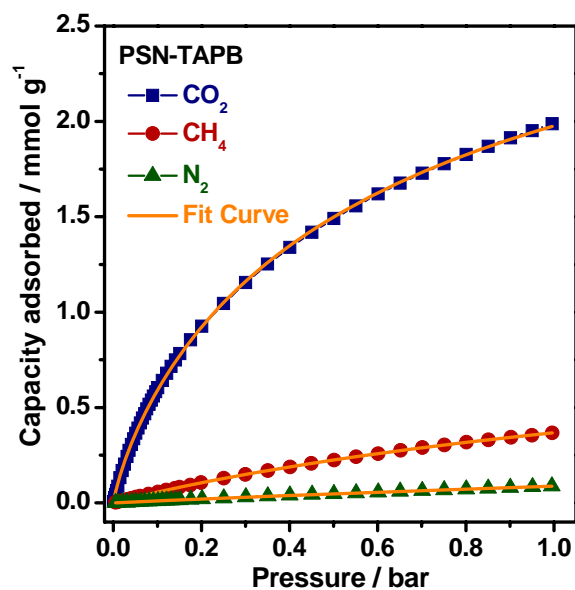


Fig. S9. PSN-TAPB Experimental pure component curves for CO₂, CH₄ and N₂ at 273K, and the corresponding solid curves are the single-site Langmuir-Freundlich fits for CO₂, CH₄ and N₂.

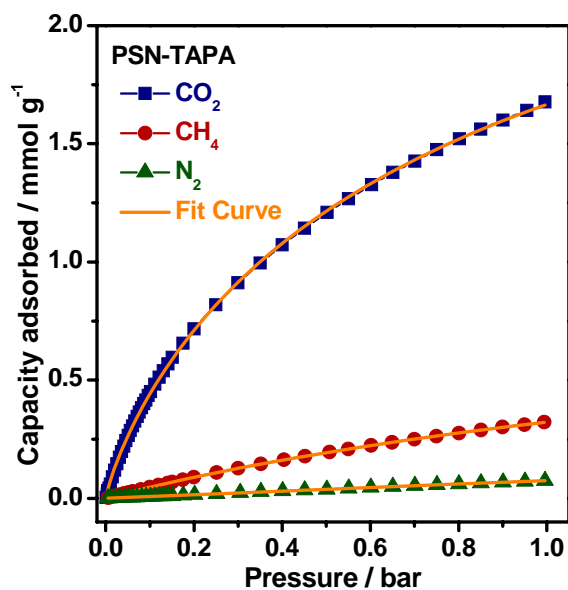


Fig. S10. PSN-TAPA Experimental pure component curves for CO₂, CH₄ and N₂ at 273K, and the corresponding solid curves are the single-site Langmuir-Freundlich fits for CO₂, CH₄ and N₂.

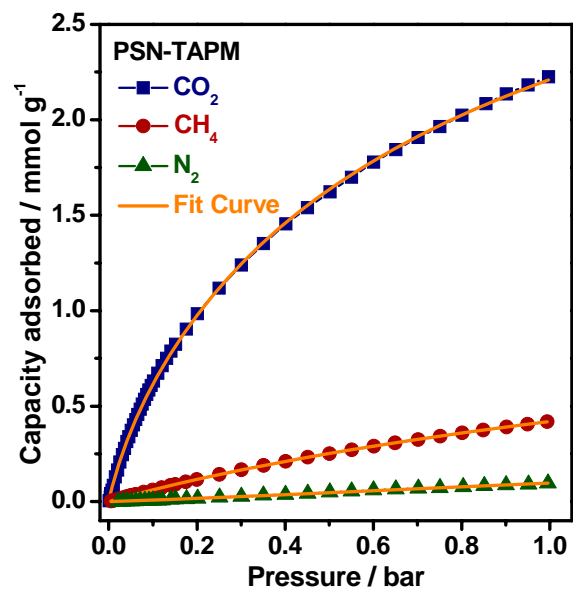


Fig. S11. PSN-TAPM Experimental pure component curves for CO₂, CH₄ and N₂ at 273K, and the corresponding solid curves are the single-site Langmuir-Freundlich fits for CO₂, CH₄ and N₂.