

Supporting Information for

Nitrogen-Rich Conjugated Microporous Polymers: Impact of Building Block on Porosity and Gas Adsorption

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Synthesis of DA-CMP2: To a mixture of 2,2'-diamino-3,3',5,5'-tetrabromobiphenyl (250 mg, 0.5 mmol) and 1,4-diethynylbenzene (126 mg, 1.0 mmol) in anhydrous dimethylformamide (5 mL) and triethylamine (5 mL), tetrakis(triphenylphosphine)palladium(0) (15 mg, 13 μ mol) and CuI (5 mg, 0.0263 mmol) were added. The mixture was degassed and purged with N₂. The reaction mixture was stirred at 100 °C for 48 h, and cooled to room temperature. The brown precipitates were collected through filtration and washed with H₂O, CH₂Cl₂, THF and methanol, respectively. Further purification of the polymer was carried out by Soxhlet extraction with THF for 72 h. The polymer was dried in vacuum for 24 h at 70 °C and obtained as a brown powder (Yield: 163 mg, 76%). Elemental combustion analysis (%) Calcd for (C₂₂H₁₅N₂)_n: C 85.99, H 4.89, N 9.12; Found: C 82.63, H 4.35, N 7.86.

Synthesis of Azo-CMP1: To a mixture of 2,4,7,9-tetrabromobenzo[c]cinnoline (248 mg, 0.5 mmol) and 1,4-benzene diboronic acid (166 mg, 1.0 mmol) in dimethylformamide (15 mL), tetrakis(triphenylphosphine)palladium(0) (15 mg, 13 μ mol) and an aqueous solution of K₂CO₃ (2.0 M, 3 mL) were added. The mixture was

degassed and purged with N₂, and stirred at 150 °C for 48 h. Then the mixture was cooled to room temperature and poured into methanol, the precipitate was collected by filtration, and washed with H₂O, CH₂Cl₂, THF and methanol, respectively. Further purification of the polymer was carried out by Soxhlet extraction with THF for 72 h. The product was dried in vacuum for 24 h at 70 °C and obtained as a fine yellow solid powder (Yield: 154 mg, 95%). Elemental combustion analysis (%) Calcd for (C₁₈H₁₁N₂)_n: C 84.35, H 4.72, N 10.93; Found: C 79.16, H 4.46, N 7.21.

Synthesis of Azo-CMP2: To a mixture of 2,4,7,9-tetrabromobenzo[c]cinnoline (248 mg, 0.5 mmol) and 1,4-diethynylbenzene (126 mg, 1.0 mmol) in anhydrous dimethylformamide (5 mL) and triethylamine (5 mL), tetrakis(triphenylphosphine)palladium(0) (15 mg, 13 μmol) and CuI (5 mg, 0.0263 mmol) were added. The mixture was degassed and purged with N₂. The reaction mixture was stirred at 100 °C for 48 h and cooled to room temperature. The precipitate was collected through filtration and washed with H₂O, CH₂Cl₂, THF methanol, respectively. Further purification of the polymer was carried out by Soxhlet extraction with THF for 72 h. Then the polymer was dried in vacuum for 24 h at 70 °C and obtained as a burgundy powder (Yield: 186 mg, 88%). Elemental combustion analysis (%) Calcd for (C₂₂H₁₁N₂)_n: C 87.13, H 3.63, N 9.24; Found: C 82.16, H 3.46, N 7.07.

Table S1. Surface areas for the polymers from different batch

polymer	1 st batch	2 nd batch	3 rd batch	$SD_{\text{BET}}^{\text{b}}$
	$S_{\text{BET}}^{\text{a}}$ [m ² g ⁻¹]	$S_{\text{BET}}^{\text{a}}$ [m ² g ⁻¹]	$S_{\text{BET}}^{\text{a}}$ [m ² g ⁻¹]	n=3
DA-CMP1	662	678	653	14 (2.2%)
DA-CMP2	603	587	615	11 (1.9%)
Azo-CMP1	1146	1175	1086	37 (3.3%)
Azo-CMP2	898	904	862	18 (2.1%)

^a Surface area calculated from N₂ adsorption isotherm in the relative pressure (P/P_0) range from 0.05 to 0.20; ^b Standard deviation of surface area (the number in parentheses is relative standard deviation).

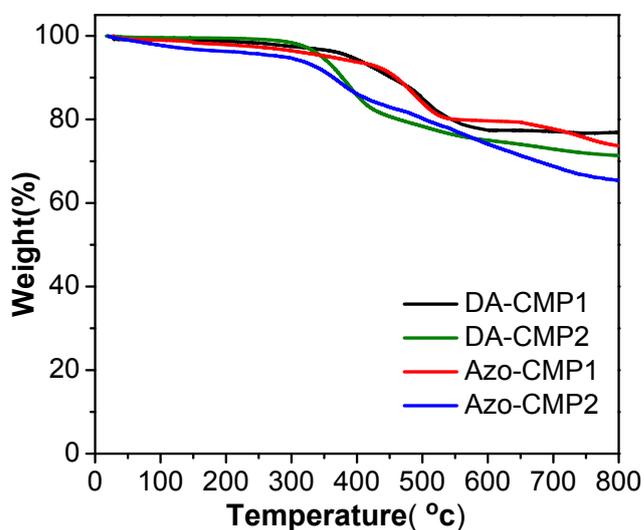


Figure S1. Thermogravimetric analysis trace of the polymer networks under a nitrogen atmosphere with a heating rate of 10 °C/min.

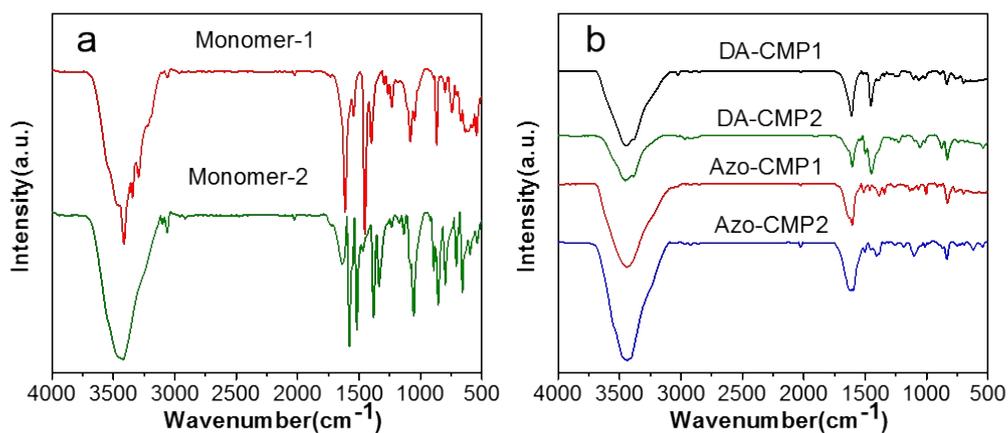


Figure S2. FT-IR spectra of the (a) monomers and (b) polymer networks.

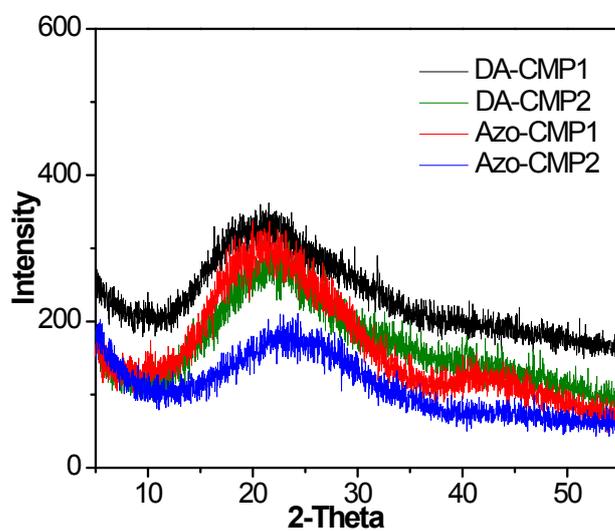


Figure S3. Powder XRD for the microporous polymer.

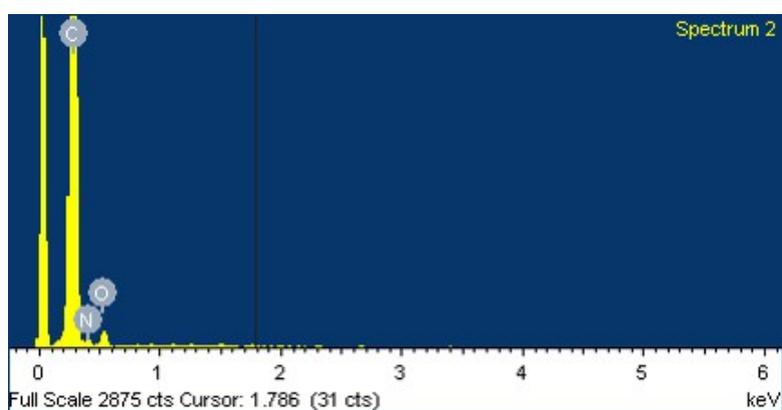


Figure S4. Energy dispersive X-ray spectroscopy spectrum of DA-CMP1. The signal for oxygen might be from the water adsorbed in the porous material because of its high porosity.

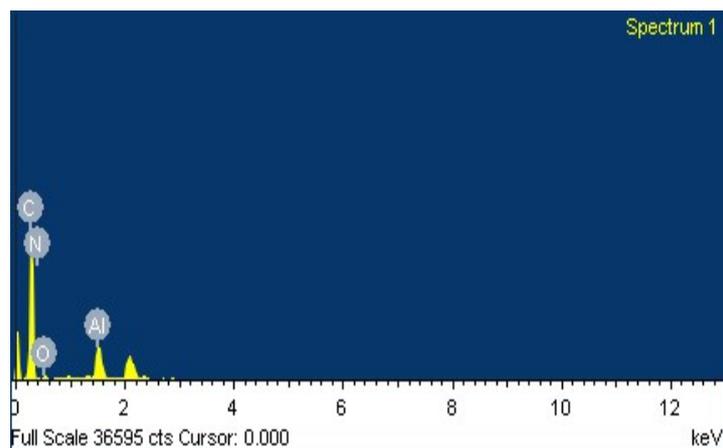


Figure S5. Energy dispersive X-ray spectroscopy spectrum of DA-CMP2. The signal for aluminum might be from the sample holder or substrate.

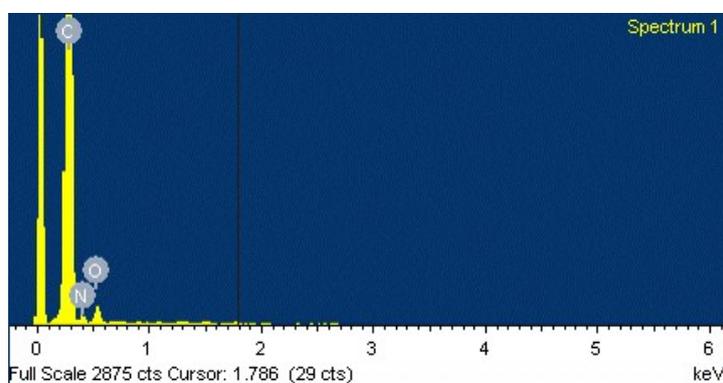


Figure S6. Energy dispersive X-ray spectroscopy spectrum of Azo-CMP1. The signal for aluminum might be from the sample holder or substrate.

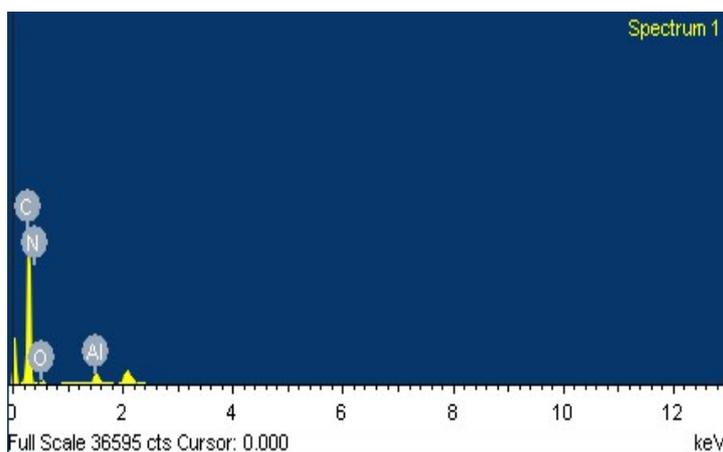


Figure S7. Energy dispersive X-ray spectroscopy spectrum of Azo-CMP2. The signal for aluminum might be from the sample holder or substrate.

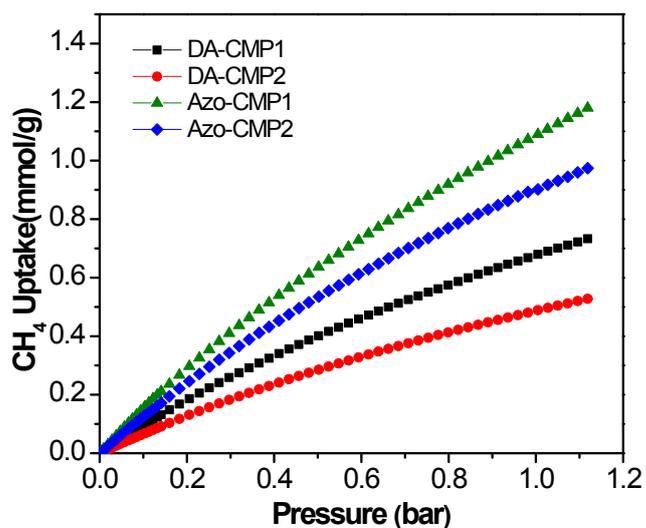


Figure S8. CH₄ adsorption isotherms of the polymer networks collected at 273 K.

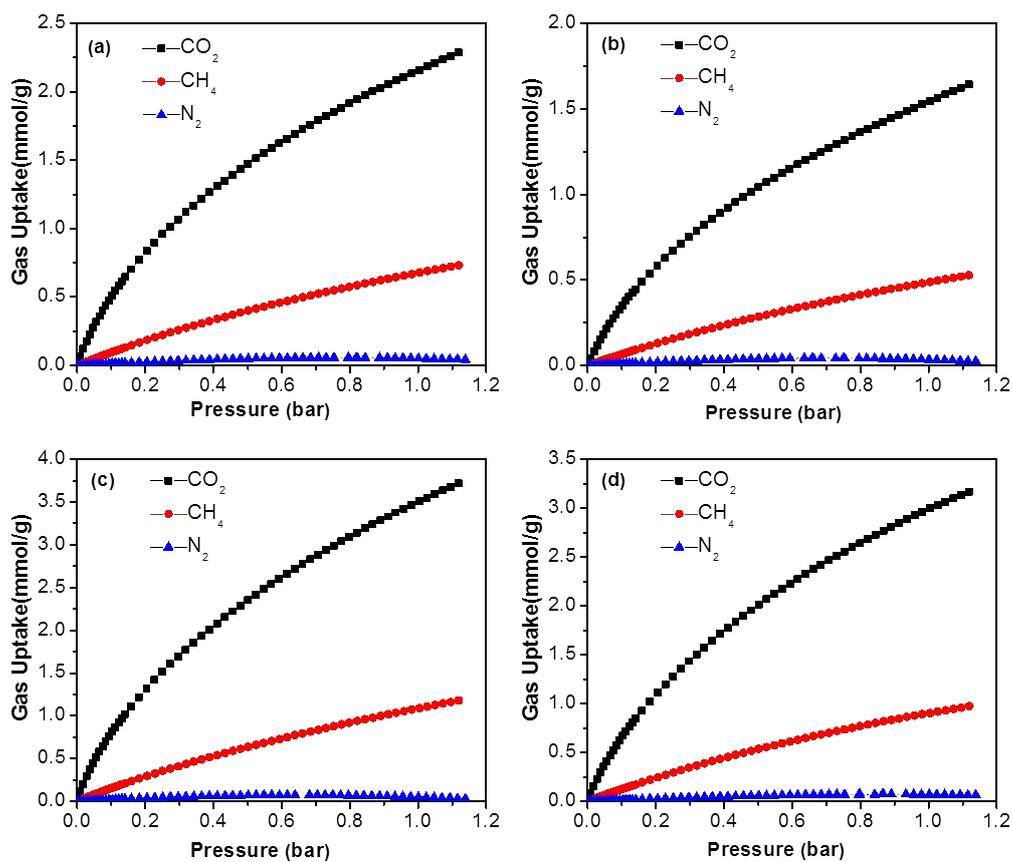


Figure S9. Adsorption isotherms of CO₂, CH₄ and N₂ gases at 273 K for (a) DA-CMP1, (b) DA-CMP2, (c) Azo-CMP1 and (d) Azo-CMP2.

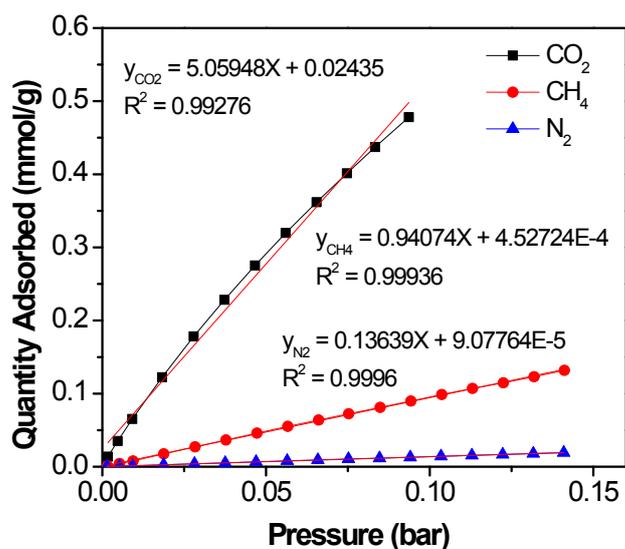


Figure S10. Gas adsorption selectivity for the DA-CMP1 using the ratios of the Henry's law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.15 bar) and 273 K.

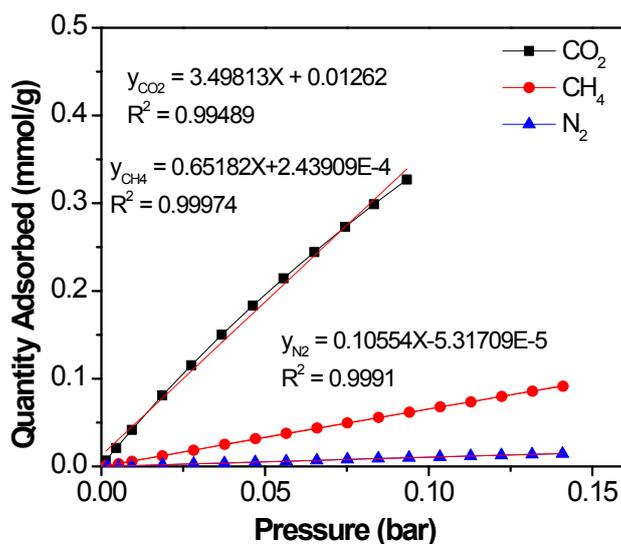


Figure S11. Gas adsorption selectivity for the DA-CMP2 using the ratios of the Henry's law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.15 bar) and 273 K.

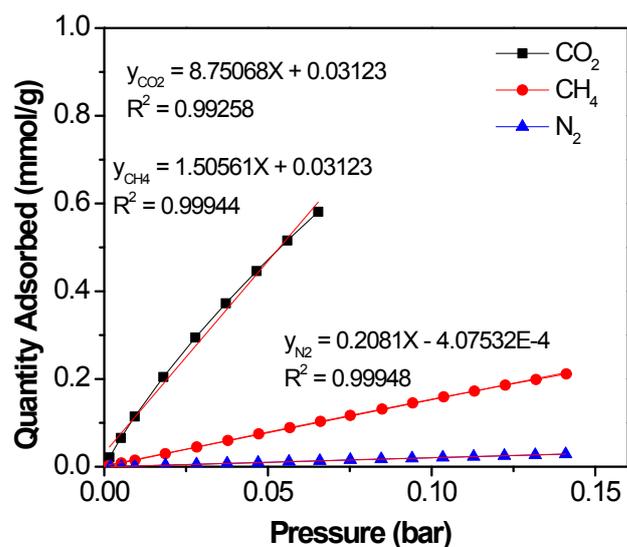


Figure S12. Gas adsorption selectivity for the Azo-CMP1 using the ratios of the Henry's law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.15 bar) and 273 K.

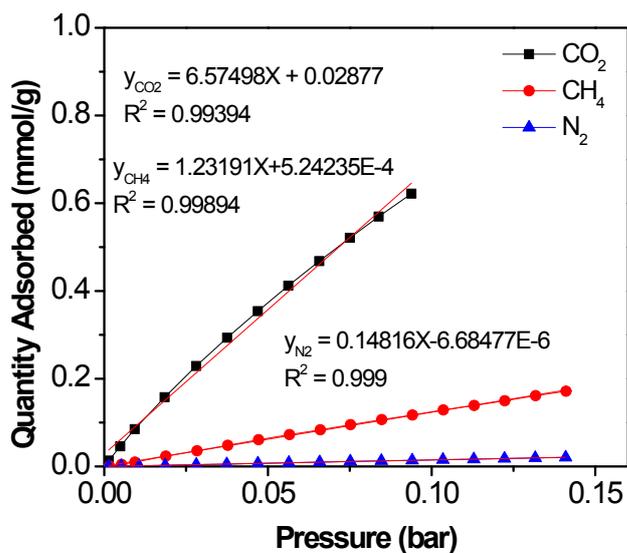


Figure S13. Gas adsorption selectivity for the Azo-CMP2 using the ratios of the Henry's law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.15 bar) and 273 K.