

Supporting Information for

Isoindigo-Based Microporous Organic Polymers for Carbon Dioxide Capture

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2. Experimental section

Synthesis of the monomers

6,6'-dibromoisindigo: To a suspension of 6-bromooxindole (500 mg, 2.36 mmol) and 6-bromoisatin (533 mg, 2.36 mmol) in AcOH (15 mL), conc. HCl solution (0.1 mL) was added and heated under reflux for 24 h. Then the mixture was cooled to room temperature and the precipitate was filtered. The solid material was washed with water, EtOH and AcOEt, respectively, and dried in under vacuum for 24 h to obtain brown product (yield: 851 mg, 85%). ¹H NMR (300 MHz, d₆-DMSO) δ (ppm) 11.08 (s, 2H), 8.99 (d, 2H), 7.19 (m, 2H), 7.00 (s, 2H).

6,6'-dibromo-N,N'-(2-methyl)-isoindigo: To a suspension of 6,6'-dibromoisindigo (420 mg, 1 mmol) and potassium carbonate (829 mg, 5 mmol) in dimethylformaldehyde (DMF) (20 mL), iodomethane (310 mg, 2.2 mmol) was injected through a septum under nitrogen. The mixture was stirred for 15 h at 100 °C and then poured into water (200 mL). The organic phase was extracted by CH₂Cl₂, washed with brine and dried over MgSO₄. After removal of the solvent under reduced pressure, the red solids were purified by silica chromatography (CH₂Cl₂: hexane = 1:1)

to give 6,6'-dibromo-N,N'-(2-methyl)-isoindigo (yield: 300 mg, 68%). ¹H NMR (300 MHz, CDCl₃) δ(ppm) 9.11 (d, 2H), 7.20 (m, 2H), 6.96 (d, 2H), 3.27 (s, 6H).

6,6'-dibromo-N,N'-(2-ethyl)-isoindigo: To a suspension of 6,6'-dibromoisindigo (420 mg, 1 mmol) and potassium carbonate (829 mg, 5 mmol) in dimethylformaldehyde (DMF) (20 mL), bromoethane (240 mg, 2.2 mmol) was injected through a septum under nitrogen. The mixture was stirred for 15 h at 100 °C and then poured into water (200 mL). The organic phase was extracted by CH₂Cl₂, washed with brine and dried over MgSO₄. After removal of the solvent under reduced pressure, the deep-red solids were purified by silica chromatography (CH₂Cl₂: hexane = 1:1) to give 6,6'-dibromo-N,N'-(2-ethyl)-isoindigo (yield: 320 mg, 67%). ¹H NMR (300 MHz, CDCl₃) δ(ppm) 9.03 (d, 2H), 7.11 (m, 2H), 6.89 (s, 2H), 3.74 (m, 4H), 1.23 (t, 6H).

Synthesis of tetra(4-ethynylphenyl)methane: To a three necked round bottom flask containing bromine (3.2 mL, 62.5 mmol), tetraphenylmethane (2.0 g, 6.24 mmol) was added in small portions under vigorous stirring at room temperature. After the addition was completed, the resulting solution was stirred for 20 min and then cooled to -78 °C. At this temperature, ethanol (20 mL) was added slowly and the reaction mixture was allowed to warm to room temperature overnight. The precipitate was filtered off and washed subsequently with saturated aqueous sodium hydrogensulfite solution (50 mL) and water (50 mL). After drying in vacuum, tetrakis(4-bromophenyl)methane was obtained as a white solid. To a solution of tetrakis(4-bromophenyl)methane (2.0 g, 3.2 mmol), copper(I) iodide (23 mg, 0.125 mmol),

triphenylphosphine (100 mg, 0.38 mmol) and dichlorobis(triphenylphosphine)palladium (II) (130 mg, 0.19 mmol) in triethylamine (25 mL) and THF(15 mL), trimethylsilylacetylene (1.488 g, 15.18 mmol) was added under a nitrogen atmosphere. The mixture was heated to 100 °C and stirred for 24 h. After cooling to room temperature, the precipitate was filtered and washed with ether. The combined filtrates were evaporated under reduced pressure and the crude product was purified by column chromatography (silica gel, light petroleum) to give tetrakis(4-(2-(trimethylsilyl)ethynyl)phenyl)methane as an intermediate. Hydrolysis of this compound was carried out by treatment with a mixture of MeOH /NaOH (50 mL, 1 M) with stirring at room temperature for 12 h. Standard workup involved evaporation of the organic solvent, extraction of the residue with ether, drying with Mg₂SO₄ overnight, and removal of the solvent under reduced pressure. The crude product was purified by column chromatography (silica gel, light petroleum) to give tetra(4-ethynylphenyl)methane as a white solid (yield: 0.93 g, 70%). ¹H NMR (600 MHz, CDCl₃) δ (ppm) 7.39 (d, 8H), 7.12 (d, 8H), 3.06 (s, 4H).

Synthesis of TBMIDM: This polymer was synthesized following the same method as TBMID. 6,6'-dibromo-N,N'-(2-methyl)-isoindigo (224 mg, 0.5 mmol), tetra(4-ethynylphenyl)methane (107 mg, 0.25 mmol), copper(I) iodide (10 mg) and tetrakis(triphenylphosphine)palladium(0) (15 mg) were used in this polymerization. After drying, a bright red powder was obtained (yield: 233 mg, 87%). Elemental combustion analysis (%) Calcd for (C₇₅H₅₂N₄O₄)_n: C 83.95, H 4.85, N 5.22; Found: C 78.88, H 4.28, N 3.59.

Synthesis of TBMIDE: 6,6'-dibromo-N,N'-(2-ethyl)-isoindigo (238 mg, 0.5 mmol),

tetra(4-ethynylphenyl)methane (107 mg, 0.25 mmol), copper(I) iodide (10 mg) and tetrakis(triphenylphosphine)palladium(0) (15 mg) were used in this polymerization. After drying, a deep-red powder was obtained (yield: 225 mg, 80%). Elemental combustion analysis (%) Calcd for $C_{79}H_{60}N_4O_4$: C 84.02, H 5.35, N 4.96; Found: C 77.95, H 4.80, N 4.05.

2. Characterization

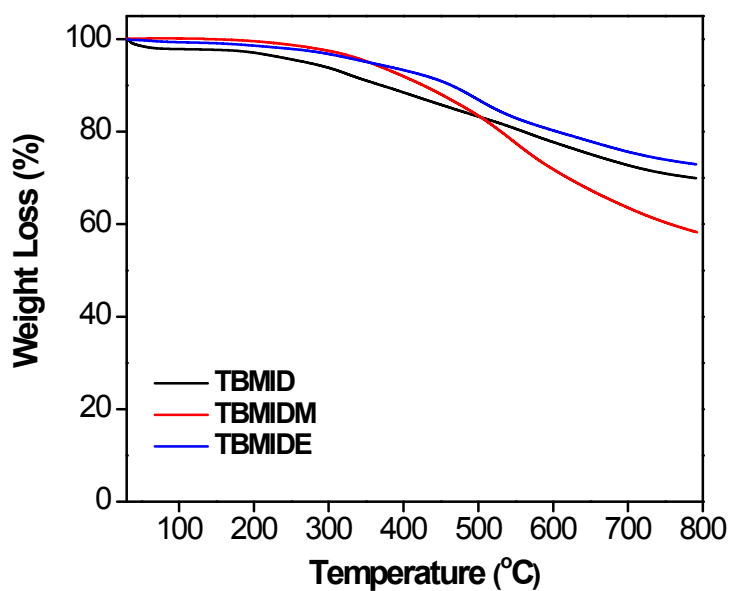


Figure S1. Thermogravimetric analysis trace of the polymer networks under a nitrogen atmosphere with a heating rate of 10 °C/min.

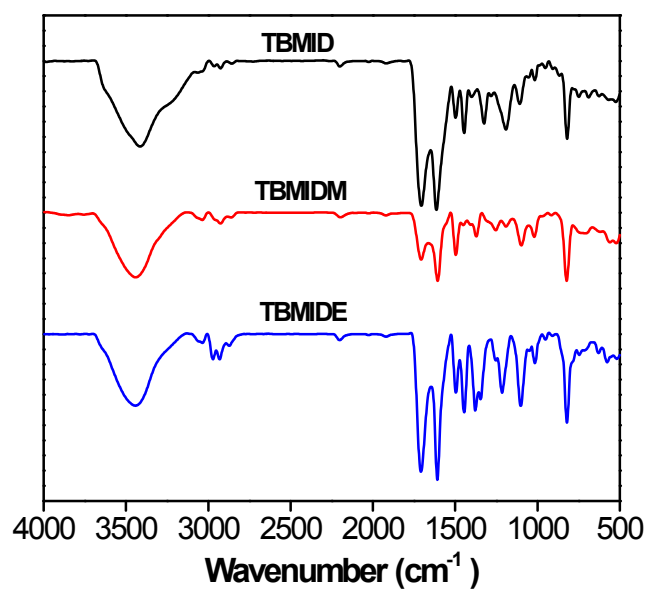


Figure S2. FT-IR spectra for the polymer networks.

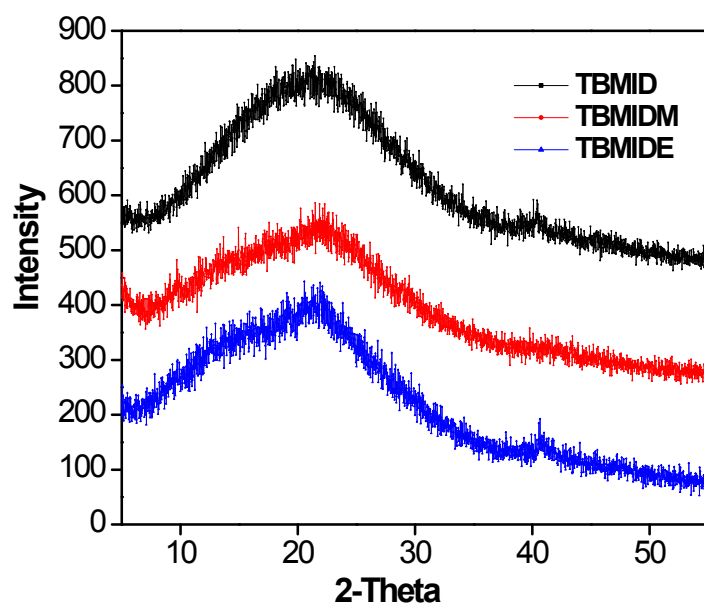


Figure S3. Powder XRD patterns for the polymer networks

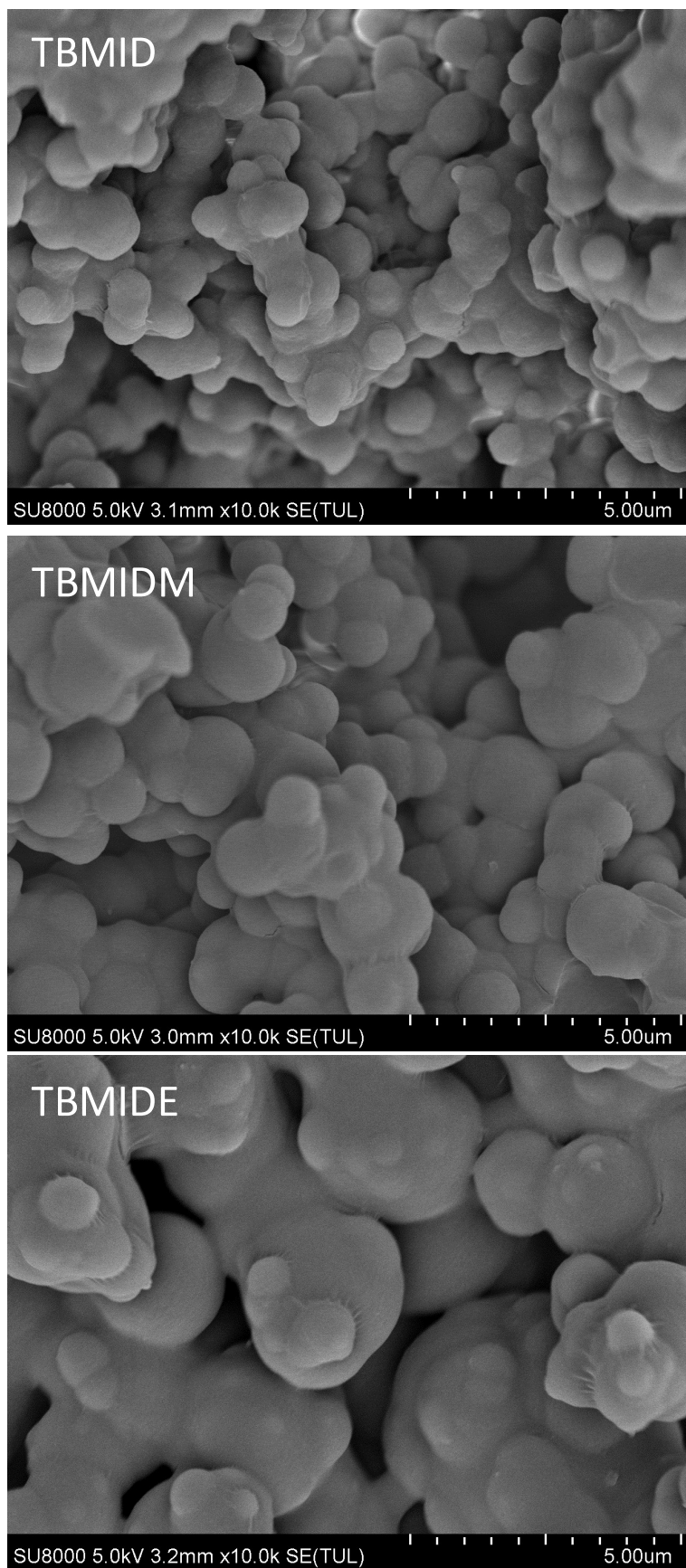


Figure S4. Scanning electron microscopy images for the polymer networks with a scale bar of 5.0 μm .

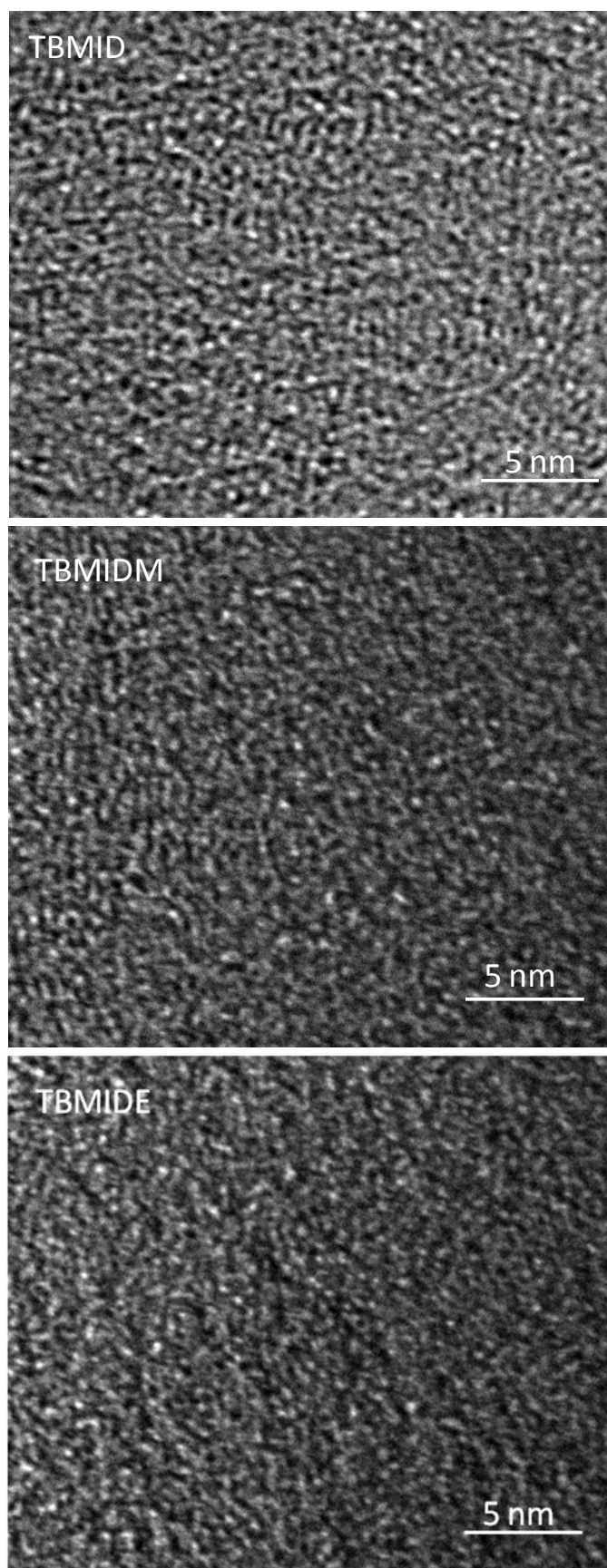


Figure S5. High resolution transmission electron microscopy images for the polymer networks with a scale bar of 5.0 nm.

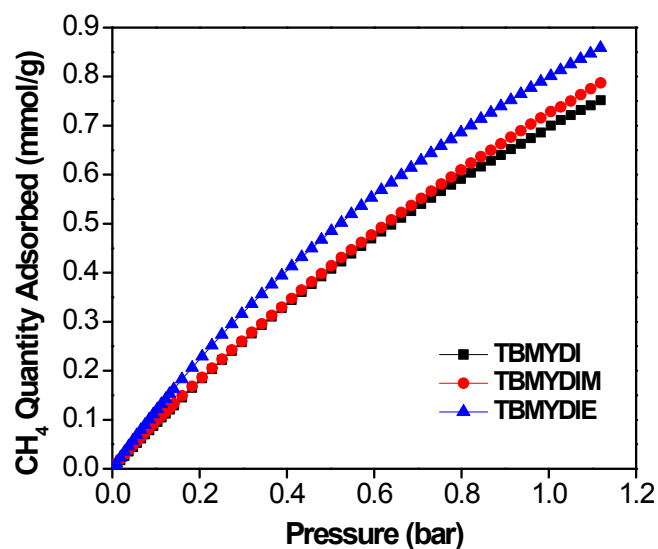


Figure S6. CH₄ adsorption isotherms collected at 273 K.

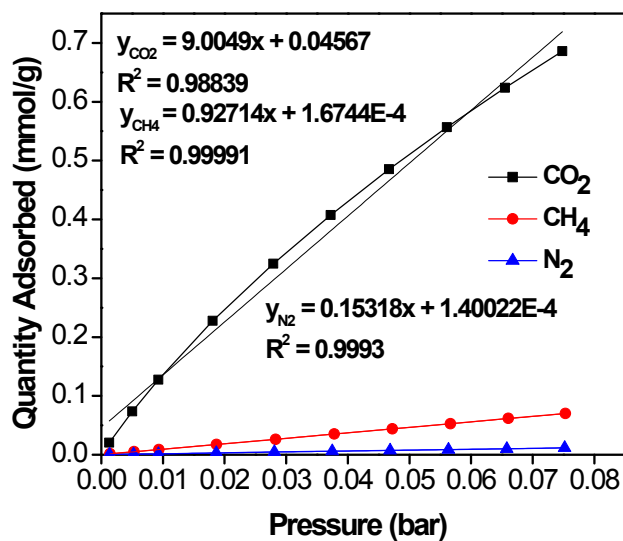


Figure S7. Gas adsorption selectivity for the TBMID using the ratios of the Henry law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.1 bar) and 273 K.

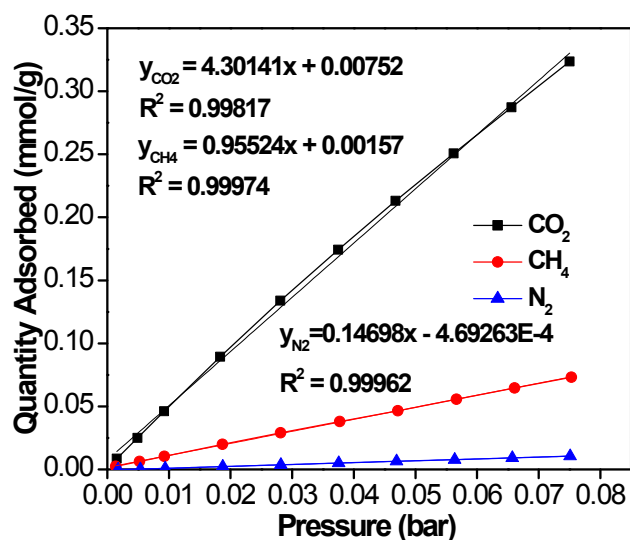


Figure S8. Gas adsorption selectivity for the TBMIDM using the ratios of the Henry law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.1 bar) and 273 K.

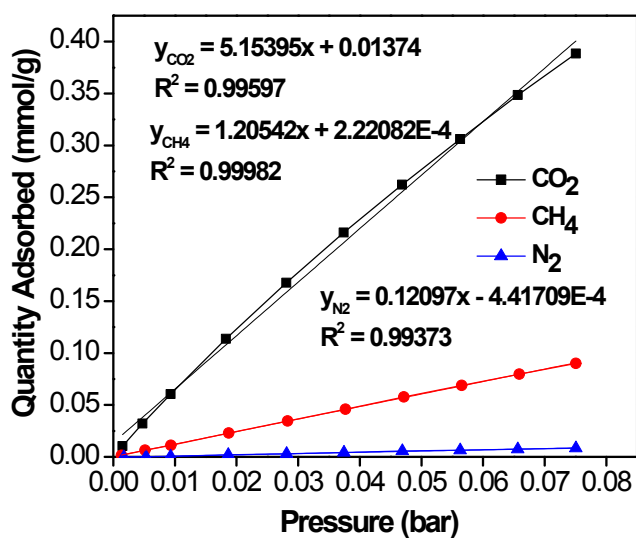


Figure S9. Gas adsorption selectivity for the TBMIDE using the ratios of the Henry law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.1 bar) and 273 K.