Supporting Information for

BODIPY-Containing Porous Organic Polymers for Gas Adsorption

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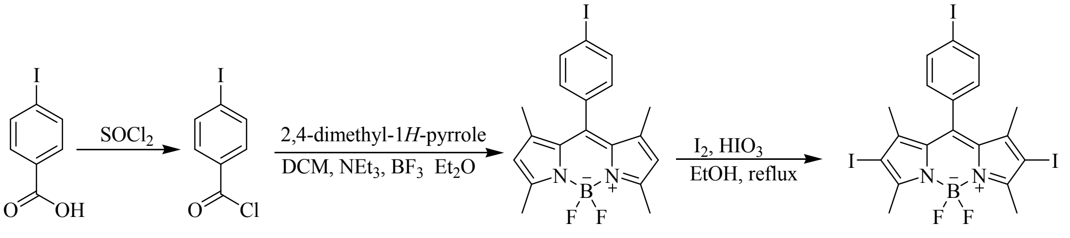
Experiment section

Synthesis of monomers

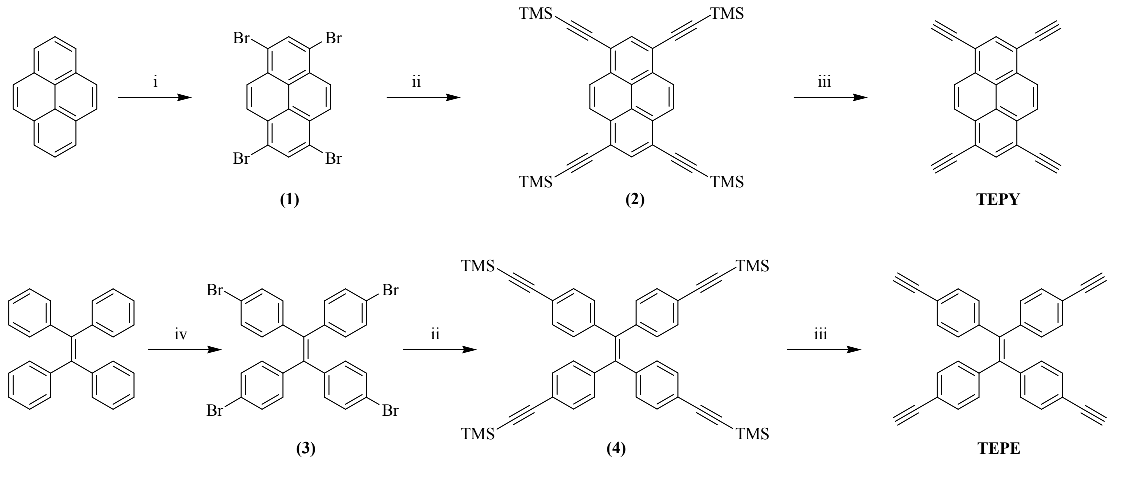


I-BDP **TI-BDP**

4-iodobenzoyl chloride: 4-iodobenzoic acid (4.96 g, 20 mmol) was dissolved in thionylchloride (20 mL), and the mixture was stirred and reflux for 3 hours, then removed thionylchloride in vacuum, the crude product was obtained as a white solid and used directly without further purification.

1,3,5,7-tetramethyl-8-(4-iodophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-S-indacene (I-BDP): To a solution of 2,4-dimethyl-1*H*-pyrrole (3.8 g, 40 mmol) in CH_2Cl_2 (250 mL), 4-iodobenzoyl chloride (20 mmol) in 50 mL CH_2Cl_2 was added under Ar atmosphere. Then the reaction mixture was stirred at room temperature overnight, triethylamine (TEA) (20 mL) and $BF_3 \cdot OEt_2$ (20 mL) were added dropwise into the mixture at 0 °C, then the mixture was stirred for 12 h. The solvent was removed under reduced pressure to obtain a residue which was dissolved in CH_2Cl_2 and washed with saturated Na_2CO_3 (100 mL) and water (100 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, CH_2Cl_2) to obtain a red powder (3.81 g), yield 42.0%. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.85 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 5.99 (s, 2H), 2.55 (s, 6H), 1.42 (s, 6H).

1,3,5,7-tetramethyl-2,6-diiodo-8-(4-iodophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-S-indacene (TI-BDP): A mixture of **I-BDP** (1.13g, 2.5 mmol), I_2 (1.6 g, 6.25 mmol) and HIO_3 (0.88 g, 5.0 mmol) in 100 mL EtOH was refluxed for 3 h. The mixture was then cooled to room temperature. The precipitate was filtered and washed thoroughly with MeOH to yield 1.38 mg (88 %) of product as an orange powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.88 (d, *J* = 8.3 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 2.64 (s, 6H), 1.43 (s, 6H).



i) Br_2, nitrobenzene, 160ºC, 3h; ii) trimethylsilylethyne, $Pd(PPh_3)_4$, CuI, toluene/triethylamine, 80ºC; iii) K_2CO_3, MeOH; iv) Br_2, CH_2Cl_2/HAc.

1,3,6,8-tetrabromopyrene (1): To a solution of pyrene (2.02 g, 10.0 mmol) in nitrobenzene (150 mL), bromine (2.2 mL, 44.0 mmol) was added under vigorous stirring. Then, the mixture was heated to 160 ºC and stirred for 3 h. The cooled reaction suspension was poured into acetone and the precipitate was filtered. Further drying of the precipitate in high vacuum gave the crude product, which was used without further purification (5.04 g, 9.73 mmol, 97%).

1,3,6,8-tetrakis(trimethylsilanylethynyl)pyrene (2): Compound 1 (2.07 g, 4.0 mmol) was suspended in triethylamine (30 mL) and toluene (10 mL), and tetrakis(triphenylphosphine)palladium(0) (185 mg, 0.16 mmol), and copper(I) iodide (61.2 mg, 0.32 mmol) were added. The flask was evacuated and flushed with nitrogen. The reaction mixture was heated to 60 ºC, and trimethylsilylethyne (2.35 g, 24.0 mmol) was injected into the solution through a septum. Then, the reaction mixture was heated to 80 ºC and stirred overnight under argon atmosphere. The cooled reaction mixture was diluted with water and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, petroleum ether) to afford compound 2 as an orange solid (2.06 g, 3.5 mmol, 88%).

1,3,6,8-tetraethynylpyrene (**TEPY**): Compound 2 (1 g, 1.7 mmol) was suspended in methanol (100 mL). K_2CO_3 (1.9 g, 13.6 mmol) was added and the reaction mixture was stirred overnight and then poured into water (500 mL) and filtered. The filtrate was washed with water and to afford **TEPY** as a slightly brown solid (480 mg, 1.61 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 4H), 8.38 (s, 2H), 3.67 (s, 4H).

1,1,2,2-tetrakis(4-bromophenyl)ethane (3): Bromine (4.0 mL, 80.0 mmol) was added to a solution of tetraphenylethylene (3.32 g, 10.0 mmol) in 10 mL glacial acetic acid and 20 mL dichloromethane at 0 ^{o}C. Then the resulting mixture was stirred at room temperature for 3 h, and then poured into 100 mL ice water, and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by recrystallization with methanol and obtained a white solid (6.15 g, 95%). ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 8.4 Hz, 8H), 6.84 (d, J = 8.4 Hz, 8H).

1,1,2,2-tetrakis(4-(2-(trimethylsilyl)ethynyl)phenyl)ethane (4): Compound 3 (3.24 g, 5.0 mmol) was suspended in triethylamine (30 mL) and THF (10 mL), and tetrakis(triphenylphosphine)palladium(0) (231 mg, 0.20 mmol) and copper(I) iodide (77 mg, 0.40 mmol) were added. The flask was evacuated and flushed with nitrogen. The reaction mixture was heated to 60 ºC and trimethylsilylethyne (2.94 g, 30.0 mmol) was injected through a septum. The mixture was heated to 80 ºC and stirred overnight under argon atmosphere. The cooled reaction mixture was diluted with water and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, petroleum ether) to afford 4 as a white solid (2.97 g, 4.14 mmol, 83%).

1,1,2,2-tetrakis(4-ethynylphenyl)ethane (**TEPE**): Compound 4 (0.72 g, 1.0 mmol) was suspended in methanol (40 mL). K_2CO_3 (1.1 g, 8.0 mmol) was added and the reaction mixture was stirred overnight and then poured into water (500 mL) and the mixture extracted with dichlormethane. The organic phases were combined and washed with water and brine and then dried over $MgSO_4$. After filtration and solvent evaporation, the crude product was purified by recrystallization with methanol and dichlormethane. **TEPE** was obtained as a yellow solid (0.4 g, 0.93 mmol, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.2 Hz, 8H), 6.93 (d, J = 8.2 Hz, 8H), δ 3.07 (s, 4H).

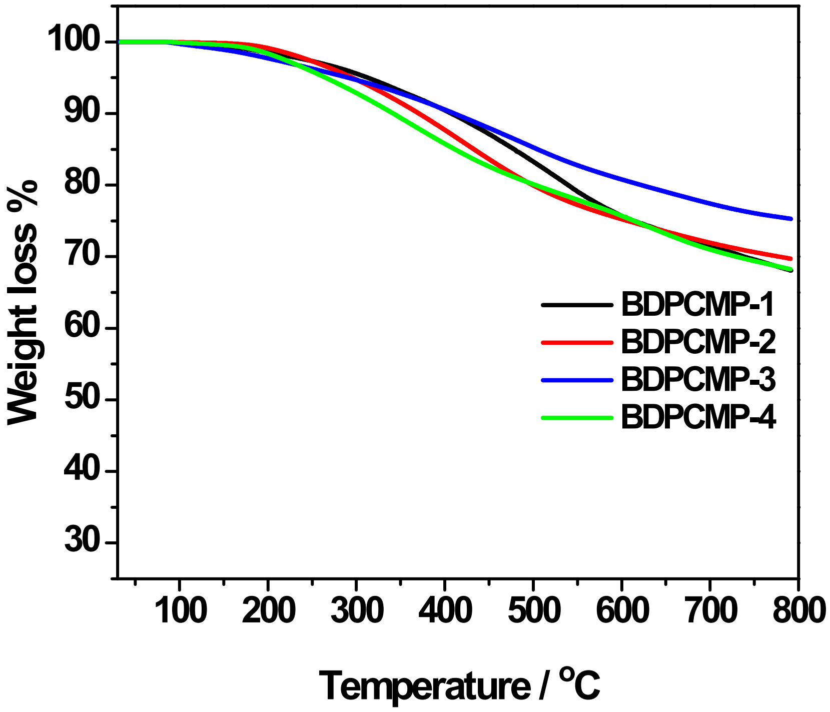


Fig. S1. Thermogravimetric analysis trace of the polymer networks under a nitrogen atmosphere with a heating rate of 10 °C/min.

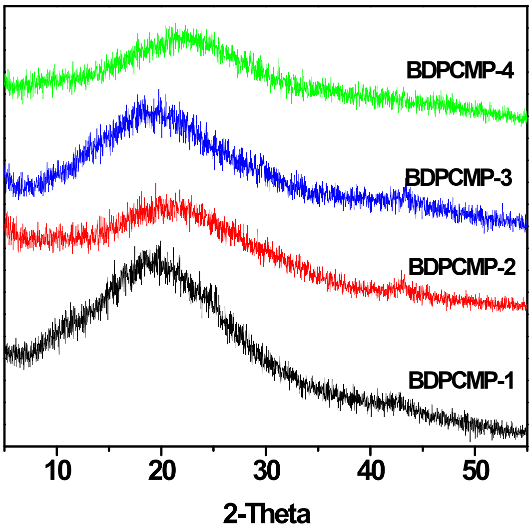


Fig. S2. Powder XRD patterns of the polymer networks

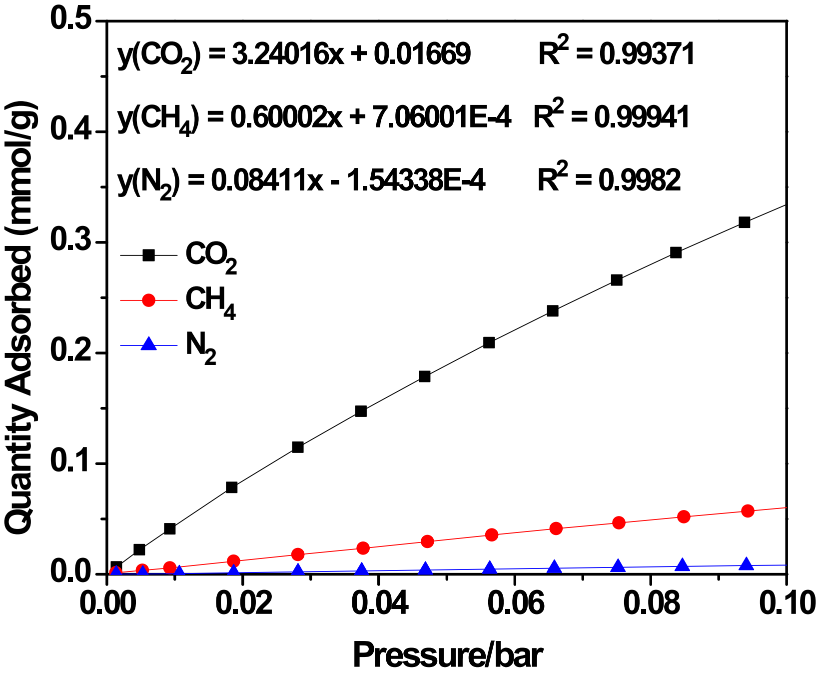


Fig. S3. Gas adsorption selectivity for BDPCMP-1 using the ratios of the Henry's law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.10 bar) and 273 K.

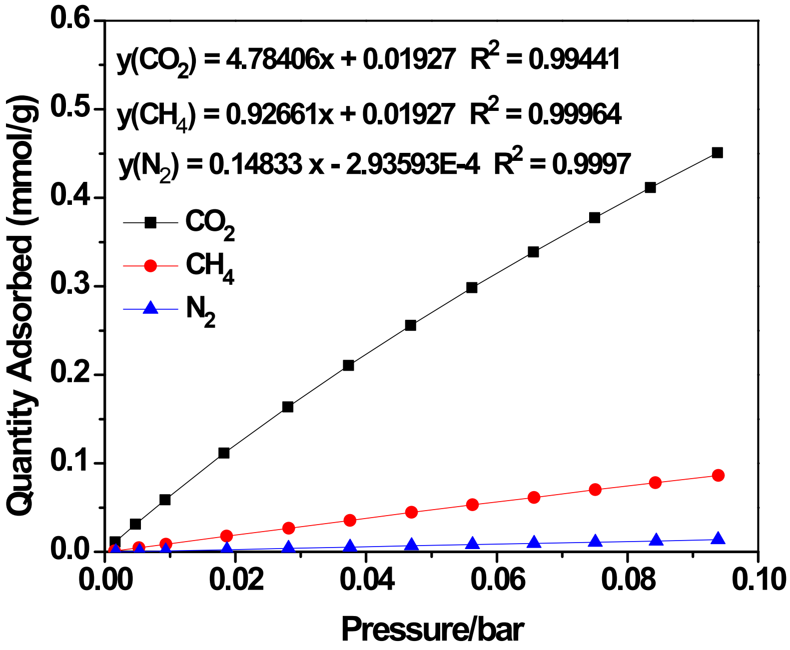


Fig. S4. Gas adsorption selectivity for BDPCMP-2 using the ratios of the Henry's law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.10 bar) and 273 K.

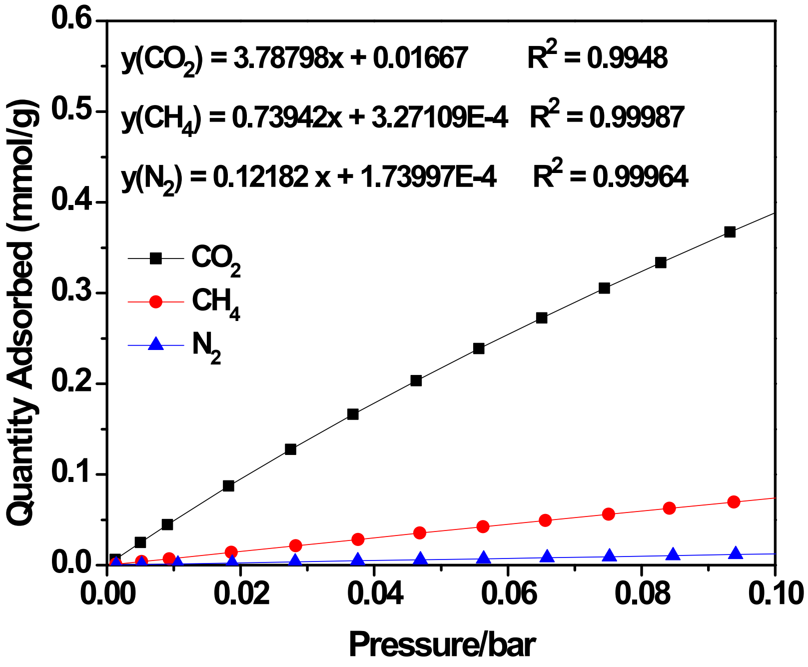


Fig. S5. Gas adsorption selectivity for BDPCMP-3 using the ratios of the Henry's law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.10 bar) and 273 K.

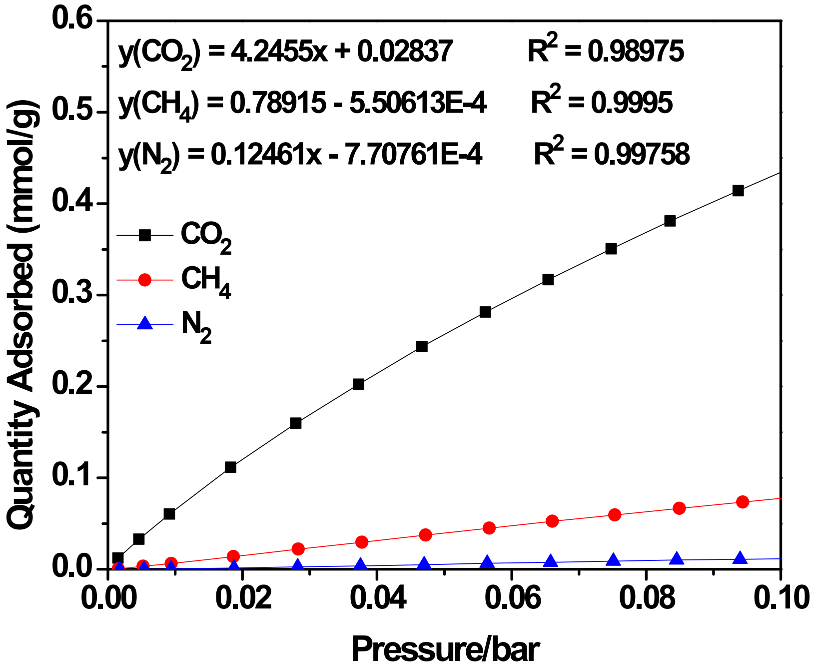


Fig. S6. Gas adsorption selectivity for BDPCMP-4 using the ratios of the Henry's law constant calculated from the initial slopes of the single-component gas adsorption isotherms collected at low pressure coverage (< 0.10 bar) and 273 K.