Electronic Supplementary Information (ESI)

Triarylboron-based fluorescent conjugated microporous polymers

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Section A. Methods

^{1}H spectra were recorded on a Varian Mercury-300 NMR spectrometer, where chemical shifts (δ in ppm) were determined with a residual proton of the solvent as standard. Matrix-assisted laser desorption ionization time-of-flight mass (MALDI-TOF MS) spectra were performed on an Applied Biosystems BioSpectrometry model Voyager-DE-STR spectrometer in reflector or linear mode using 9-nitroanthracene or dithranol as a matrix. Solid-state ^{13}C CP/MAS NMR measurements were recorded on a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 5 kHz and a CP contact time of 2 ms. All ^{13}C CP MAS chemical shifts are referenced to the resonances of adamantane ($C_{10}H_{16}$) standard (δ CH_2 = 38.5). The ^{11}B MAS NMR spectra were also recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CP MAS probe head whose X channel was tuned to 128.39 MHz for ^{11}B, using a magnetic field of 9.39T at 297 K. The dried and finely powdered samples were packed in the ZrO_2 rotor closed with Kel-F cap which were spun at 5 kHz rate. A total of 1200 scans were recorded with 3s recycle delay for each sample. All ^{11}B MAS chemical shifts are referenced to the resonances of boron nitride (BN), 99.5% (metals basis) standard (δ=0.00). The diffuse reflectance spectra (Kubleka-Munk spectrum) were recorded on a JASCO model V-670 spectrometer equipped with integration sphere model IJN-727. Fluorescence measurements were carried out on a RF-5301PC. Infrared spectra were recorded on a JASCO model FT IR-6100 Fourier transform infrared spectrophotometer. Elemental analyses were carried out on an Elementar model vario EL cube analyzer. Field emission scanning electron microscopy was performed on a JEOL model JEM-6700 microscope operating at an accelerating voltage of 5.0 kV. Transmission electron microscopy was performed on a JEOL model JEM-2100 microscope. The sample was prepared by drop-casting a methanol suspension of BCMPs onto a copper grid. Powder X-ray diffraction data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from 2θ = 1.5° to 60° with 0.02° increment at 25 °C. Nitrogen sorption isotherms were measured at 77 K with a

Bel Japan Inc. model BELSORP-mini II analyzer. Before measurement, the samples were degassed in vacuum at 150 °C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume, the Saito-Foley (SF) method was applied for the estimation of pore size distribution.

Section B. Materials and Synthesis

$BF_3 \cdot Et_2O$, 1,4-diiodo-2,3,5,6-tetramethylbenzene, tris(4-bromophenyl)amine, tetrakis(triphenylphosphine)palladium(0), bis-(triphenylphosphine)palladium(II) dichloride and n-BuLi were purchased from Aldrich and used as received. Other organic solvents for reactions were distilled over appropriate drying reagents under nitrogen. Deuterated solvents for NMR measurement were obtained from Aldrich.

Synthesis of Tris(iododuryl)borane[1]

To a solution of 1,4-diiodo-2,3,5,6-tetramethylbenzene (2.0 g, 5.18 mmol) in Et_2O (40 mL) was added dropwise a hexane solution of n-BuLi (1.6 M, 3.2 mL, 5.18 mmol) at -78 °C. The reaction mixture was allowed to warm to 0 °C and stirred for 20 min, and then $BF_3 \cdot OEt_2$ (0.21 mL, 1.75 mmol) was added to the mixture at -78 °C. The reaction mixture was warmed up to room temperature over 1 h and stirred for 16 h. After addition of water, a part of white product can be obtained by filter, and the left mixture was extracted with Et_2O. The extract was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by washing with ether and methanol to afford target compound (1.09 g, 79%) as a colorless solid. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.04 (s, 18H, CH_3), 2.44 (s, 18, CH_3). Anal. Calcd for $C_{30}H_{36}BI_3$ (788.13): C, 45.72; H, 4.60. Found: C, 45.68; H, 4.76. FT-IR (KBr): ν 566, 655, 804, 936, 1002, 1091, 1276, 1389, 1443, 1527, 2917, 3448 cm^{-1}.

Synthesis of Tris[(trimethylsilylethynyl)duryl]borane[1]

To a solution of tris(iododuryl)borane (1.16 g, 1.48 mmol), $PdCl_2(PPh_3)_2$ (155 mg, 0.22 mmol), CuI (80 mg, 0.44 mmol) in dry Et_3N (50 mL) and THF (20 mL) was added a solution of trimethylsiliylacetylene (0.93 mL, 6.5 mmol) in Et_3N (10 mL) at room temperature. The mixture was refluxed with stirring for 10 h. After addition of water, the mixture was extracted with Et_2O. The extract was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting mixture was subjected to column chromatography on silica gel to give white crystals (0.92 g, 1.30 mmol) in 90% yield. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.25 (s, 27H, $SiCH_3$), 1.87 (s, 18H, CH_3), 2.31 (s, 18H, CH_3). Anal. Calcd for $C_{45}H_{63}BSi_3$ (699.05): C, 77.32; H, 9.08. Found: C, 77.28; H, 9.17.

Synthesis of Tris(ethynylduryl)borane[1]

A solution of tris[(trimethylsilylethynyl)duryl]borane (0.5 g, 0.72 mmol) and KOH (0.5 g, 9.04 mmol) in MeOH (30 mL) and THF (15 mL) was stirred for 5 h. The mixture was concentrated under reduced pressure. After addition of water, the mixture was extracted with Et_2O. The extract was over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting mixture was suspended with hexane. The insoluble part was collected by filtration and washed with hexane to give a white solid (0.32 g, 6.65 mmol) in 93% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.91 (s, 18H, CH_3), 2.33 (s, 18H, CH_3), 3.51 (s, 3H, C≡C*H*). Anal. Calcd for $C_{36}H_{39}B$ (482.51): C, 89.61; H, 8.15. Found: C, 89.70; H, 8.27. FT-IR (KBr): *ν* 625, 822, 858, 1008, 1033, 1100, 1194, 1250, 1286, 1400, 1452, 1560, 1622, 1741, 2092, 2924 and 3291 cm^{-1}.

Synthesis of tris-(4-trimethylsilylethynyl)phenylamine[2]

To a solution of tris(4-bromophenyl)amine (1.0 g, 2.07 mmol), copper(I) iodide (11.0 mg, 0.058 mmol), triphenylphosphine (16.0 mg, 0.061 mmol) and dichlorobis(triphenylphosphine)palladium(II) (84.0 mg, 0.12 mmol) in triethylamine (40 mL) was added trimethylsilylacetylene (1.3 mL, 9.32 mmol) dropwise under a nitrogen atmosphere. The mixture was heated to 50 °C and stirred for 8 h. After cooling to room temperature, the precipitate that was formed was filtered and washed with ether. The combined filtrates were evaporated under reduced pressure and the crude product was purified by column chromatography to give tris-(4-trimethylsilylethynyl)phenylamine as a light yellow solid (yield: 95%). ^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 0.23 (s, 27H, SiCH_3), 6.95 (d, 6H, *J* = 6, Ph-*H*), 7.34 (d, 6H, *J* = 6, Ph-*H*). Anal. Calcd for $C_{33}H_{39}NSi_3$ (505.26): C, 78.36; H, 7.77; N, 2.77. Found: C, 78.31; H, 7.80; N, 2.73.

Synthesis of Tri(4-ethynylphenyl)amine[2]

Desilylation of tris-(4-trimethylsilylethynyl)phenylamine (0.9 g, 1.68 mmol) was achieved by stirring the compound in 90 mL methanol with K_2CO_3 (0. 78 g, 5.043 mmol) at room temperature under nitrogen atmosphere for 48 h. The solvent was evaporated and the residue was extracted with diethyl ether. The organic layer was dried over $MgSO_4$, and the solvent was removed again. The residue was purified by silica gel column chromatography to a pure white solid ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.06 (s, 3H, C≡C*H*), 7.01 (d, 6H, J = 8.0 Hz, Ph-*H*), 7.38 (d, 6H, J = 8.0 Hz, Ph-*H*). Anal. Calcd for $C_{24}H_{15}N$ (317.38): C, 90.82; H, 4.76; N, 4.41. Found: C, 90.71; H, 4.80; N, 4.35. FT-IR (KBr): ν 426, 537, 555, 641, 672, 722, 765, 839, 1110, 1171, 1276, 1319, 1504, 1603, 2108, 3278 cm^{-1}.

Synthesis of BCMP-1

Tris(ethynyldduryl)borane (400.0 mg, 0.83 mmole), copper iodide (15.8 mg, 0.083 mmo) and bis-(triphenylphosphine)palladium(II) dichloride (59.0 mg, 0.083 mmol) were dissolved in the mixture of THF (8.0 mL) and Et_3N (8.0 mL). The reaction mixture was heated to 80 °C and stirred for 72 h under a dry nitrogen atmosphere. The mixture was cooled to room temperature and the precipitated homocoupled polymer was filtered and washed four times with chloroform, water, methanol, and acetone to remove any unreacted monomer or catalyst residues. Further purification of the polymer was achieved by Soxhlet extraction with methanol and THF for 48 h. The product was dried in vacuum for 24 h at 70 °C. BCMP-1 was isolated in 96.9% yield.

Synthesis of BCMP-2

Tris(iododuryl)borane (100 mg, 0.127 mmole), tri(4-ethynylphenyl)amine (40.3 mg, 0.127 mmole), tetrakis(triphenylphosphine)palladium(0) (14.7 mg, 0.0127 mmol) and copper iodide (2.42 mg, 0.0127 mmol) were dissolved in the mixture of THF (5.0 mL) and Et_3N (5.0 mL). The reaction mixture was heated to 80 °C and stirred for 72 h under a dry nitrogen atmosphere. The mixture was cooled to room temperature and the precipitated homocoupled polymer was filtered and washed four times with chloroform, water, methanol, and acetone to remove any unreacted monomer or catalyst residues. Further purification of the polymer was achieved by Soxhlet extraction with methanol and THF for 48 h. The product was dried in vacuum for 24 h at 70 °C. BCMP-2 was isolated in 84.3% yield.

Section C. The ^{13}C and ^{11}B CP/MAS NMR spectra

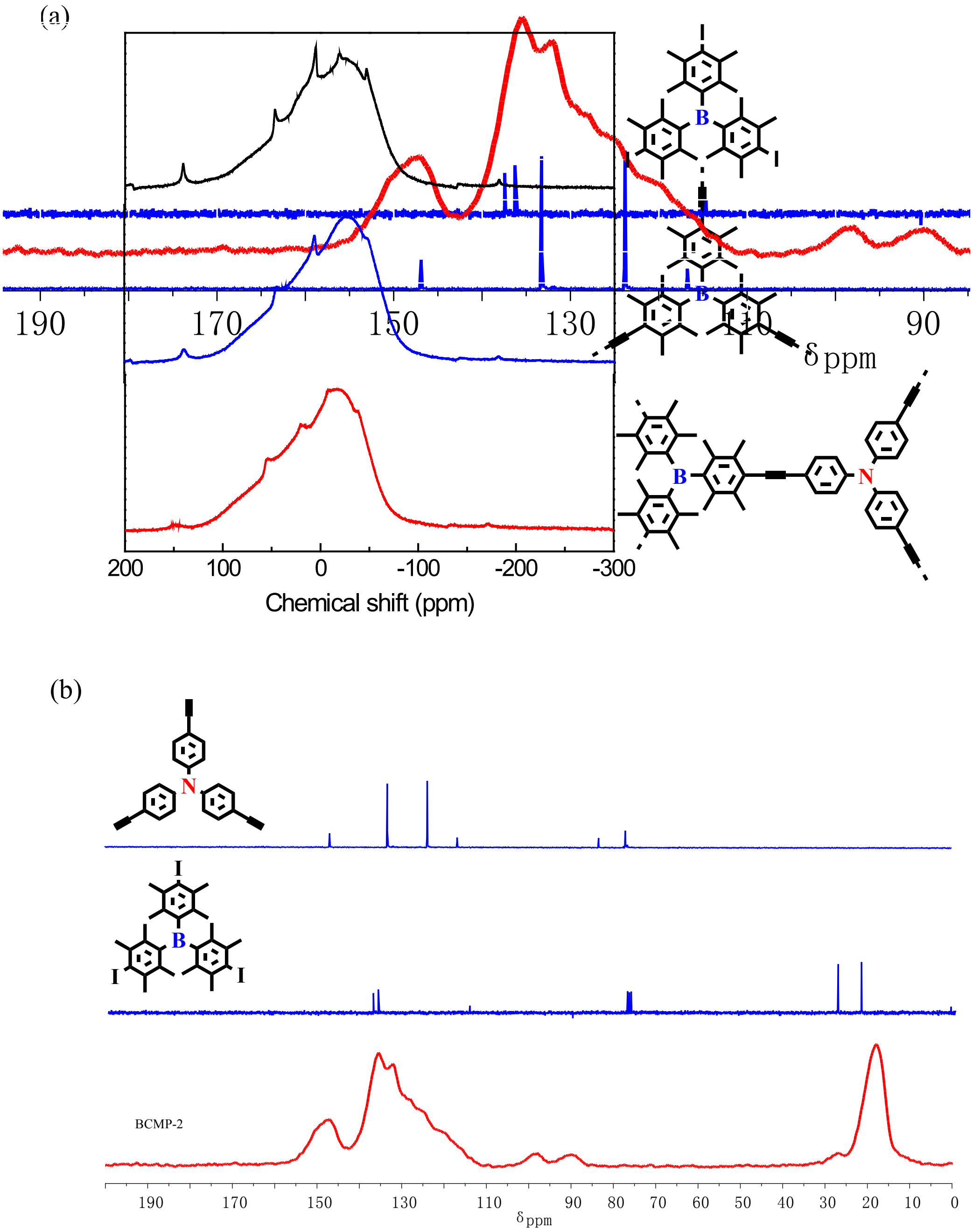

Figure S1. (a) ^{11}B CP/MAS NMR spectra of tris(iododuryl)borane (black line), BCMP-1 (blue line) and BCMP-2 (red line) (b) ^{13}C CP/MAS NMR of BCMP-2 and ^{13}C NMR spectra of tris(iododuryl)borane and tri(4-ethynylphenyl)amine.

Section D. The FT-IR spectra of monomers and BCMPs

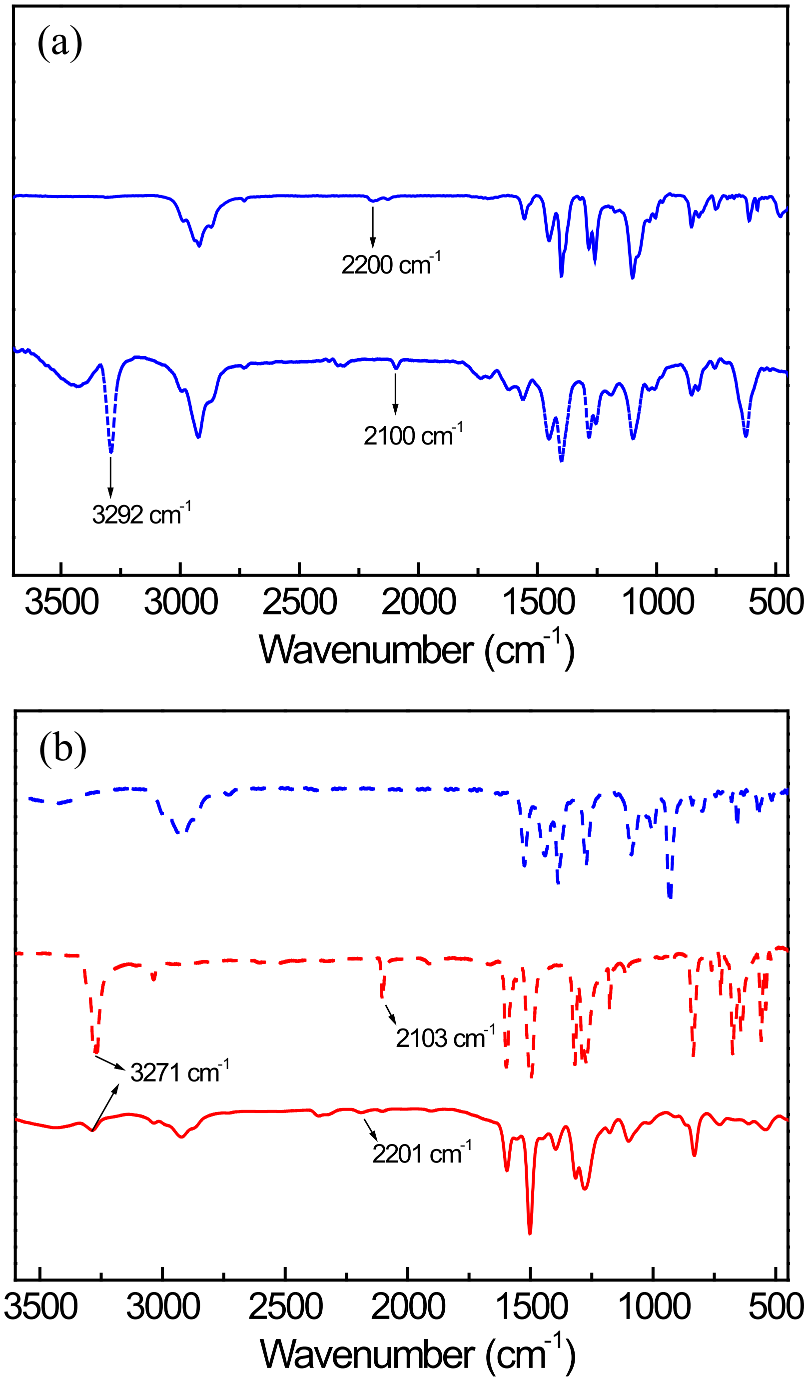

Figure S2. The IR spectra of BCMP-1 (solid blue line), its monomer (dash blue line) (a), and BCMP-2 (solid red line), tris-(4-trimethylsilylethynyl)phenylamine (dash red line) and tris(iododuryl)borane (dash blue line) (b).

Section E. The stability of BCMPs

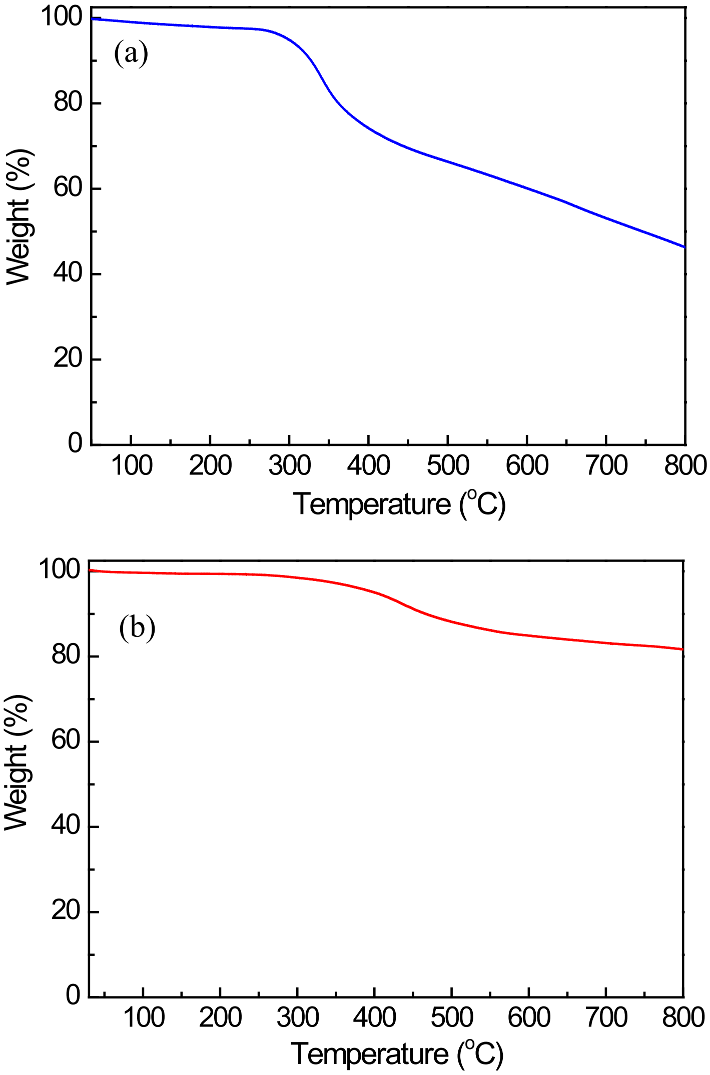

Figure S3. TGA curve of BCMP-1 (a) and BCMP-2 (b) under nitrogen.

Section F. The crystalline of BCMPs

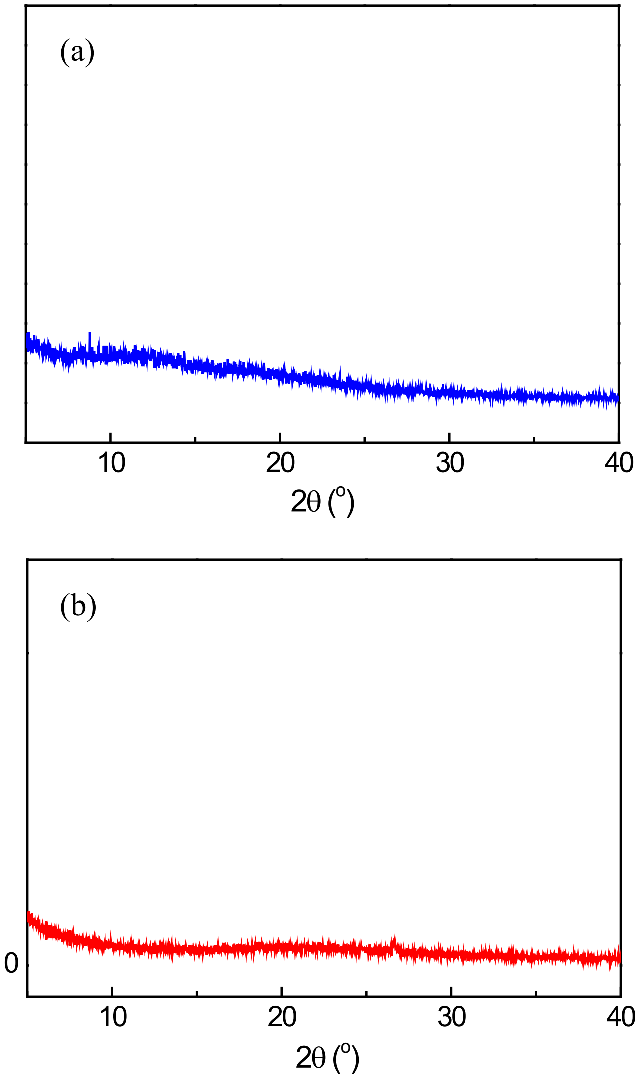

Figure S4. P-XRD curve of BCMP-1 (a) and BCMP-2 (b).

Section G. The SEM and TEM images

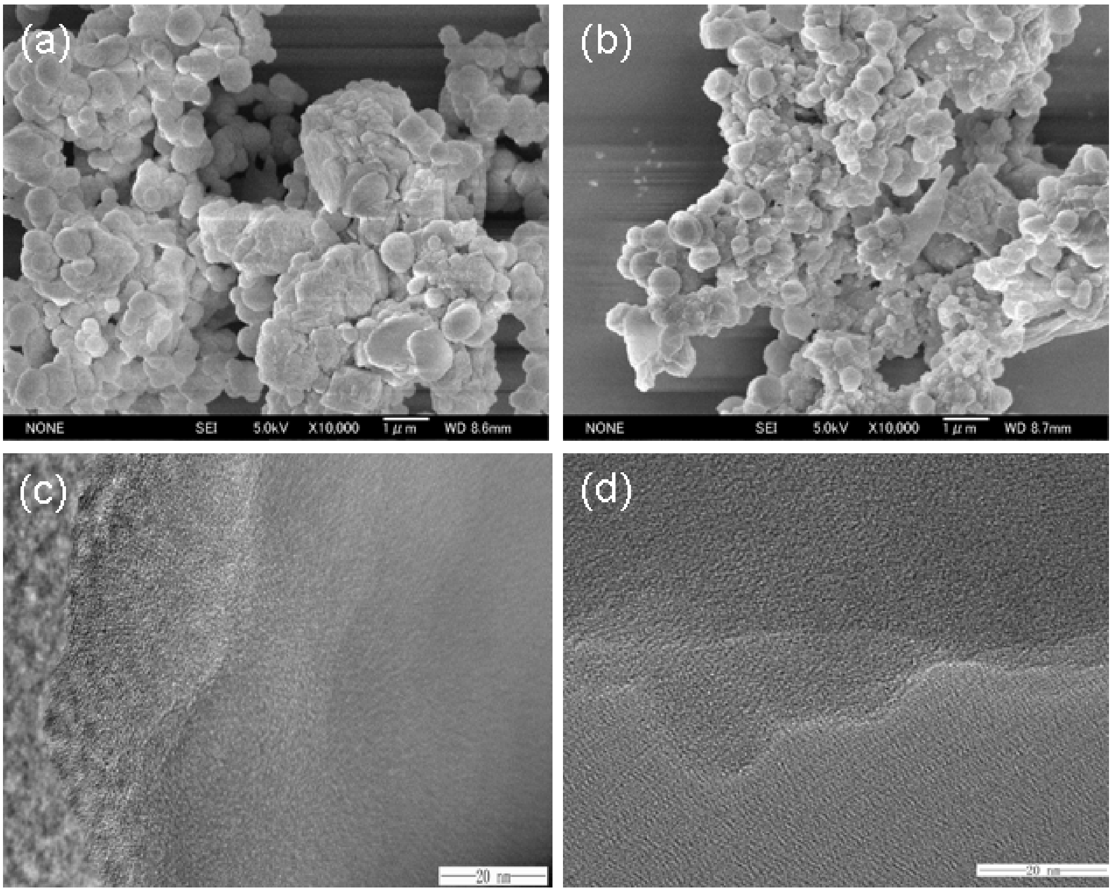

Figure S5. The SEM images of BCMP-1 (a), BCMP-2 (b) and TEM images of BCMP-1 (c) and BCMP-2 (d).

Section H. The UV spectra of monomers and BCMPs

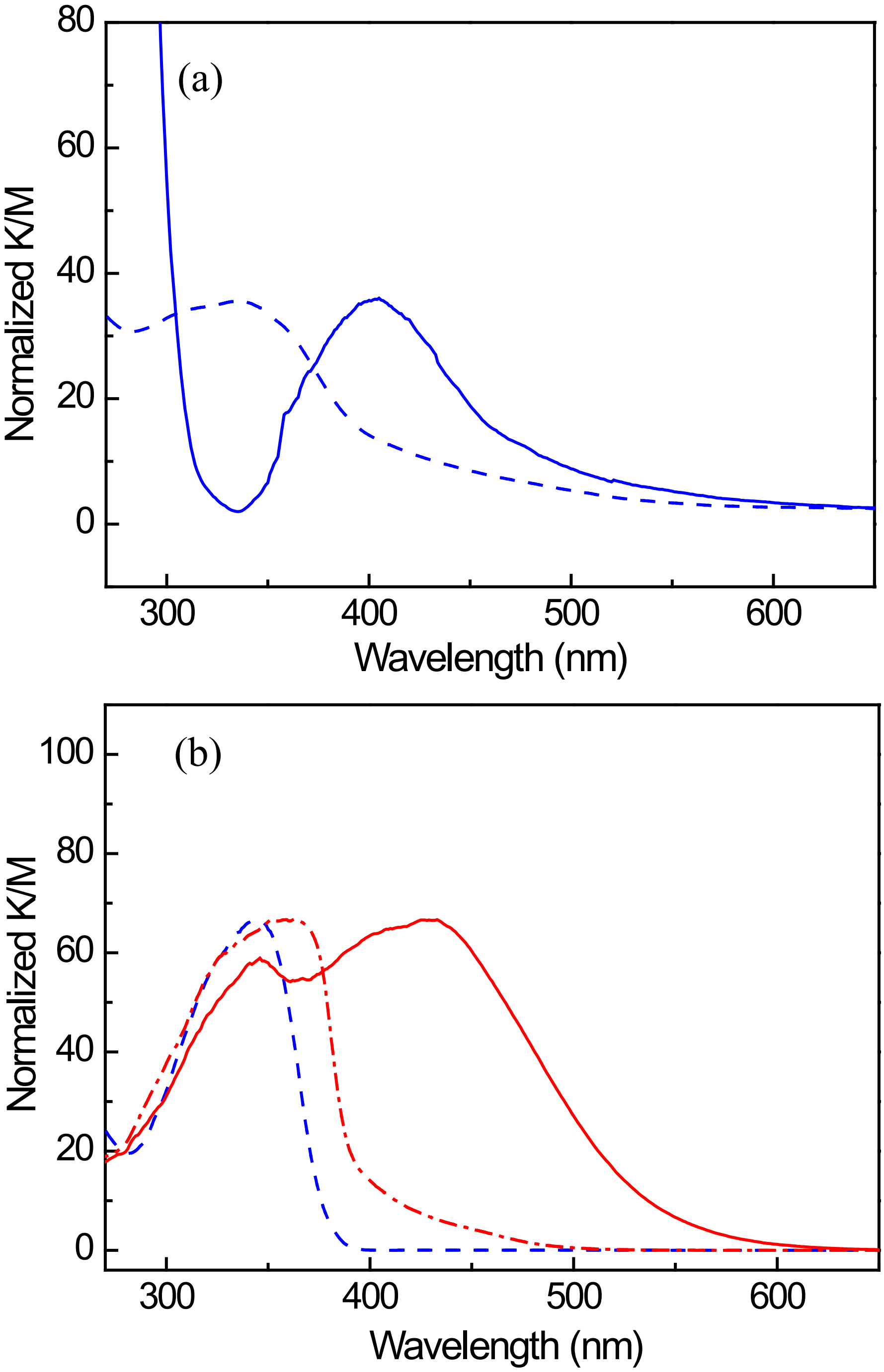

Figure S6. The UV spectra of BCMP-1 (solid blue line), its monomer (dash blue line) (a), and BCMP-2 (solid red line), its comonomers tris-(4-trimethylsilylethynyl)phenylamine (dash red line) and tris(iododuryl)borane (dash blue line) (b).

Section I. The PL spectra of BCMP-1

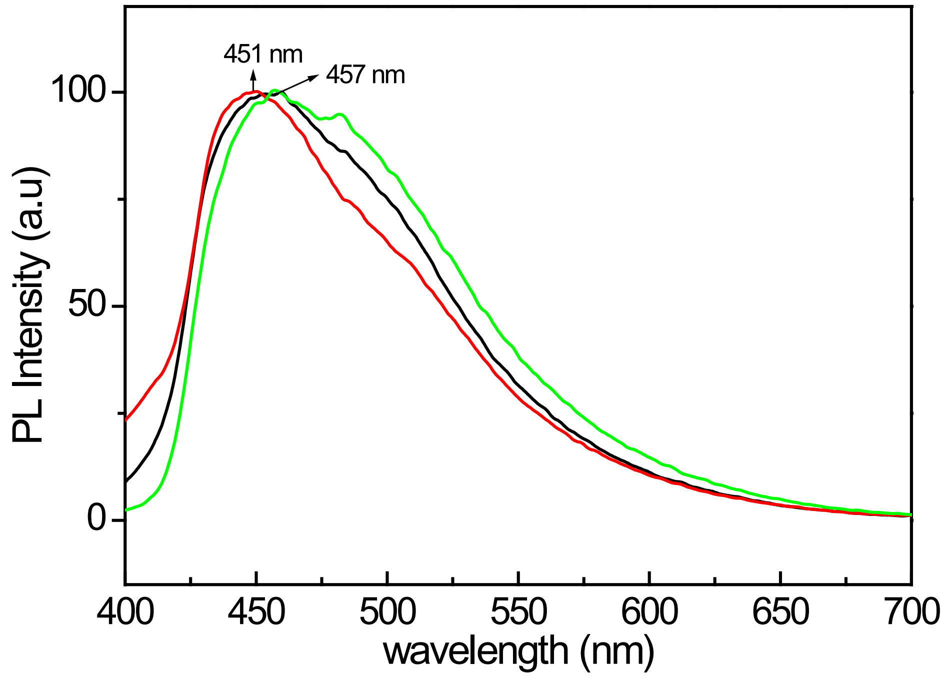

Figure S7. PL spectra of BCMP-1 in toluene (red line), chloroform (black line) and nitrobenzene (green line).

Table S1. Porosity properties and carbon dioxide uptake for BCMPs

Entry	BET Surface Area (m^2 g^{-1})	Mirco. Surface Area (m^2 g^{-1})	Total Pore Volume (cm^3 g^{-1})[a]	Mirco. Pore Volume (cm^3 g^{-1})[b]	CO_2 Uptake (mg g^{-1})[c]	CO_2 Uptake (mg g^{-1})[d]
BCMP-1	815	711	0.587	0.463	40.6	55.2
BCMP-2	911	557	0.611	0.487	50.7	74.5

[a] Total pore volume determined from the nitrogen isotherm at $P/P_o = 0.99$.
[b] Micropore volume determined from the nitrogen isotherm at $P/P_o = 0.01$.
[c] at 298 K
[d] at 273 K

Table S2. Elemental analysis of BCMP2.

Entry	C (wt %)	H (wt %)	N (wt %)
BCMP-1 (calculated)	90.18	7.57	
BCMP-1 (found)	87.94	9.02	
BCMP-2 (calculated)	89.69	6.82	1.97
BCMP-2 (found)	84.57	8.96	2.50

References

(1) S. Yamaguchi, T. Shirasaka, K. Tamao, *Org. Lett.*, 2000, **2**, 4129.

(2) J. X. Jiang, A. Trewin, F. B. Su, C. D. Wood, H. J. Niu, J. T. A. Joes, Y. Z. Khimyak, and A. I. Cooper, *Macromolecules* 2009, **42**, 2658.