

Supplementary Information

**Synthesis and investigation of sulfonated poly(*p*-phenylene)-based ionomers with precisely controlled ion exchange capacity for use as polymer electrolyte membranes**

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#### ■ Synthesis of NS-PPBP

All reactants, catalyst reagents, and solvents were handled in a glove box under an argon atmosphere. NS-DPBP (5.000 g, 10.13 mmol), PPh<sub>3</sub> (1.039 g, 3.962 mmol), NaI (0.203 g, 1.36 mmol), Zn (0.890 g, 13.6 mmol), and NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.216 g, 0.330 mmol) were placed in a previously dried three-neck round-bottom flask. A mechanical stirring shaft and an addition funnel containing NMP (12.7 mL) was attached to the flask, and the flask was heated to 65 °C under a flow of argon. After NMP was added to the flask dropwise, the resulting mixture was stirred at 65 °C for 24 h with continuous and vigorous stirring. The resulting mixture was then quenched with 550 mL of HCl/acetone (1:10, v/v) solution. The crude product was purified by reprecipitation at least twice from chloroform into HCl/methanol (1:10, v/v) in order to remove the residual catalyst, and then washed by Soxhlet extraction with methanol for three days. The precipitate was then dried in vacuo at 50 °C for 12 h to obtain NS-PPBP as a white solid in 69% yield (2.95 g).

<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 6.84-7.97 (m, peaks at 7.84, 7.76, 7.59, 7.48, 7.38, 7.20, 7.13, 7.04, 6.95), 3.67 (s), 0.88 (s) ppm. IR (KBr): 3097, 3070, 2960, 2868, 1668, 1585, 1491, 1417, 1409, 1360, 1305, 1244, 1186, 1164, 1100, 1012, 960, 934, 873, 778, 757, 692, 682 cm<sup>-1</sup>.

#### ■ Synthesis of S-PPBP

The neopentyl protecting group of NS-PPBP was cleaved by acidolysis with (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH·HBr. NS-PPBP (1.14 g) was placed in a three-neck round-bottom flask filled with nitrogen, and a mechanical stirring shaft was attached to the flask. NMP (10.0 mL) was added to the flask, and the mixture was stirred at 80 °C. After NS-PPBP was completely dissolved in NMP, a solution of (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH·HBr (2.08 g, 13.5 mmol) in NMP (5.0 mL) was added to the flask, and the resulting mixture was stirred at 120 °C for 24 h. After cooling to room temperature, the mixture was poured into 550 mL of HCl/methanol (1:10, v/v) solution, and the solution was stirred for an additional 24 h at room temperature. The precipitate was immersed in 1 mol·dm<sup>-3</sup> HCl (aq) for 48 h to exchange the diethylammonium ions with protons. After conversion to the acid form, the crude product was purified by reprecipitation twice from the NMP solution into methanol, and then dried in vacuo at 80 °C for 12 h. S-PPBP was obtained as a red-brown solid in 84% yield (0.80 g).

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 6.57-7.77 (m, peaks at 7.64, 7.52, 7.25, 6.94) ppm. <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>): δ 160.9, 155.4, 144.1, 137.0-140.3 (peak at 138.3), 125.3-133.2 (peak at 128.7, 127.8), 118.8, 117.5 ppm. IR (ATR): 3210, 3066, 1658, 1583, 1489, 1408, 1313, 1232, 1155, 1120, 1026, 1003, 947, 870, 822, 777, 698 cm<sup>-1</sup>. Elemental analysis: Calcd. for (CHNS)<sub>n</sub> C, 64.76%; H, 3.44%; S, 9.10%. Found C, 62.53%; H, 3.88%; S, 8.91%.

#### ■ Synthesis of S-PPBP-co-PPBP (9:1)

Following the procedure for the synthesis of NS-PPBP, instead a reactant mixture of NS-DPBP (4.500 g, 9.120 mmol) and DPBP (0.348 g, 1.014 mmol) was added to the three-neck round-bottom flask with catalysts, and the resulting mixture was stirred at 65 °C for 24 h. NS-PPBP-co-PPBP (9:1) was obtained as a white solid in 70% yield (2.88 g).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.68-7.97 (m, peaks at 7.85, 7.78, 7.61, 7.47, 7.34, 7.18, 7.13, 7.04, 6.92, 6.80), 3.67 (s), 0.88 (s) ppm. IR (KBr): 3094, 3070, 2961, 2873, 1668, 1588, 1491, 1417, 1409, 1362, 1305, 1241, 1186, 1164, 1100, 1014, 964, 936, 875, 825, 775, 757, 692, 682  $\text{cm}^{-1}$ .

According to the same procedure for the synthesis of S-PPBP, NS-PPBP-co-PPBP (9:1) (2.30 g),  $(\text{C}_2\text{H}_5)_2\text{NH}\cdot\text{HBr}$  (3.61 g, 23.4 mmol), and NMP (20 mL) was stirred at 120 °C for 24 h. S-PPBP-co-PPBP (9:1) was obtained as a red-brown solid in 75% yield (1.45 g). Elemental analysis: Calcd. for  $(\text{CHNS})_n$  C, 66.26%; H, 3.52%; S, 8.38%. Found C, 64.51%; H, 3.80%; S, 8.08%.

#### ■ Synthesis of S-PPBP-co-PPBP (4:1)

NS-PPBP-co-PPBP (4:1) was prepared from NS-DPBP (4.000 g, 8.107 mmol) and DPBP (0.696 g, 2.028 mmol) following the general procedure described above. Yield: 59% (2.35 g). S-PPBP-co-PPBP (4:1) was prepared from NS-PPBP-co-PPBP (4:1) (2.00 g),  $(\text{C}_2\text{H}_5)_2\text{NH}\cdot\text{HBr}$  (2.75 g, 17.9 mmol), and NMP (20 mL). Yield: 72% (1.23 g).

$^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ) :  $\delta$  6.68-7.83 (m, peaks at 7.66, 7.51, 7.39, 7.20, 6.96) ppm. IR (ATR): 3066, 1655, 1583, 1489, 1415, 1313, 1232, 1155, 1120, 1026, 1003, 947, 870, 821, 777  $\text{cm}^{-1}$ . Elemental analysis: Calcd. for  $(\text{CHNS})_n$  C, 67.84%; H, 3.60%; S, 7.63%. Found C, 62.36%; H, 4.48%; S, 7.18%.

#### ■ Synthesis of S-PPBP-co-PPBP (7:3)

NS-PPBP-co-PPBP (7:3) was prepared from NS-DPBP (3.500 g, 7.094 mmol) and DPBP (1.043 g, 3.039 mmol). Yield: 84% (3.20 g). S-PPBP-co-PPBP (7:3) was prepared from NS-PPBP-co-PPBP (7:3) (2.10 g),  $(\text{C}_2\text{H}_5)_2\text{NH}\cdot\text{HBr}$  (3.57 g, 23.2 mmol), and NMP (20 mL). Yield: 72% (1.31 g).

$^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ) :  $\delta$  6.70-7.80 (m, peaks at 7.64, 7.39, 7.01 6.93) ppm. Elemental analysis: Calcd. for  $(\text{CHNS})_n$  C, 69.49%; H, 3.69%; S, 6.84%. Found C, 67.52%; H, 3.86%; S, 6.77%.

#### ■ Synthesis of S-PPBP-co-PPBP (10:9)

NS-PPBP-co-PPBP (10:9) was prepared from NS-DPBP (2.500 g, 5.067 mmol) and DPBP (1.525 g, 4.443 mmol). Yield: 90% (3.01 g). S-PPBP-co-PPBP (10:9) was prepared from S-PPBP-co-PPBP (10:9) (2.80 g),  $(\text{C}_2\text{H}_5)_2\text{NH}\cdot\text{HBr}$  (2.23 g, 14.5 mmol), and NMP (20 mL). Yield: 95% (2.40 g).

■ Synthesis of S-PPBP-*co*-PPBP (1:1)

NS-PPBP-*co*-PPBP (1:1) was prepared from NS-DPBP (2.500 g, 5.067 mmol) and DPBP (1.739 g, 5.067 mmol). Yield: 88% (3.10 g). S-PPBP-*co*-PPBP (1:1) was prepared from NS-PPBP-*co*-PPBP 1:1 (2.00 g), (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH·HBr (2.22 g, 14.4 mmol), and NMP (20 mL). Yield: 84% (1.50 g).

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) :  $\delta$  6.62-7.82 (m, peaks at 7.63, 7.38, 7.19, 7.13, 7.01, 6.89) ppm. IR (ATR): 3064, 1658, 1583, 1487, 1416, 1311, 1232, 1153, 1222, 1155, 1029, 1003, 947, 905, 870, 824, 776, 753 cm<sup>-1</sup>. Elemental analysis: Calcd. for (CHNS)<sub>n</sub> C, 73.06%; H, 3.88%; S, 5.13%. Found C, 70.37%; H, 4.21%; S, 4.58%.

■ Synthesis of S-PPBP-*co*-PPBP (1:3)

NS-PPBP-*co*-PPBP (1:3) was prepared from NS-DPBP (1.250 g, 2.533 mmol) and DPBP (2.608 g, 7.599 mmol). Yield: 87% (2.72 g). S-PPBP-*co*-PPBP (1:3) was prepared from NS-PPBP-*co*-PPBP 1:3 (1.94 g), (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH·HBr (1.57 g, 10.2 mmol), and NMP (20 mL). Yield: 82% (1.50 g).

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) :  $\delta$  6.69-7.82 (m, peaks at 7.64, 7.39, 7.20, 7.14, 7.03, 6.90) ppm. IR (ATR): 3037, 1658, 1581, 1487, 1416, 1311, 1230, 1151, 1069, 1022, 1003, 944, 905, 870, 823, 776, 753 cm<sup>-1</sup>. Elemental analysis: Calcd. for (CHNS)<sub>n</sub> C, 78.06%; H, 4.15%; S, 2.74%. Found C, 76.61%; H, 4.05%; S, 2.75%.

■ Synthesis of S-PPBP-*co*-PPBP (1:9)

NS-PPBP-*co*-PPBP (1:9) was prepared from NS-DPBP (0.500 g, 1.013 mmol) and DPBP (3.130 g, 9.120 mmol). Yield: 86% (2.50 g). S-PPBP-*co*-PPBP (1:9) was prepared from NS-PPBP-*co*-PPBP 1:9 (1.54 g), (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH·HBr (0.41 g, 2.7 mmol), and NMP (16 mL). Yield: 81% (1.22 g).

<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) :  $\delta$  6.61-7.77 (m, peaks at 7.62, 7.37, 7.19, 7.14, 7.02, 6.87) ppm. IR (ATR): 3060, 1658, 1581, 1487, 1417, 1311, 1232, 1153, 1022, 1002, 938, 870, 823, 772, 750 cm<sup>-1</sup>. Elemental analysis: Calcd. for (CHNS)<sub>n</sub> C, 81.40%; H, 4.32%; S, 1.14%. Found C, 80.69%; H, 4.36%; S, 1.30%.

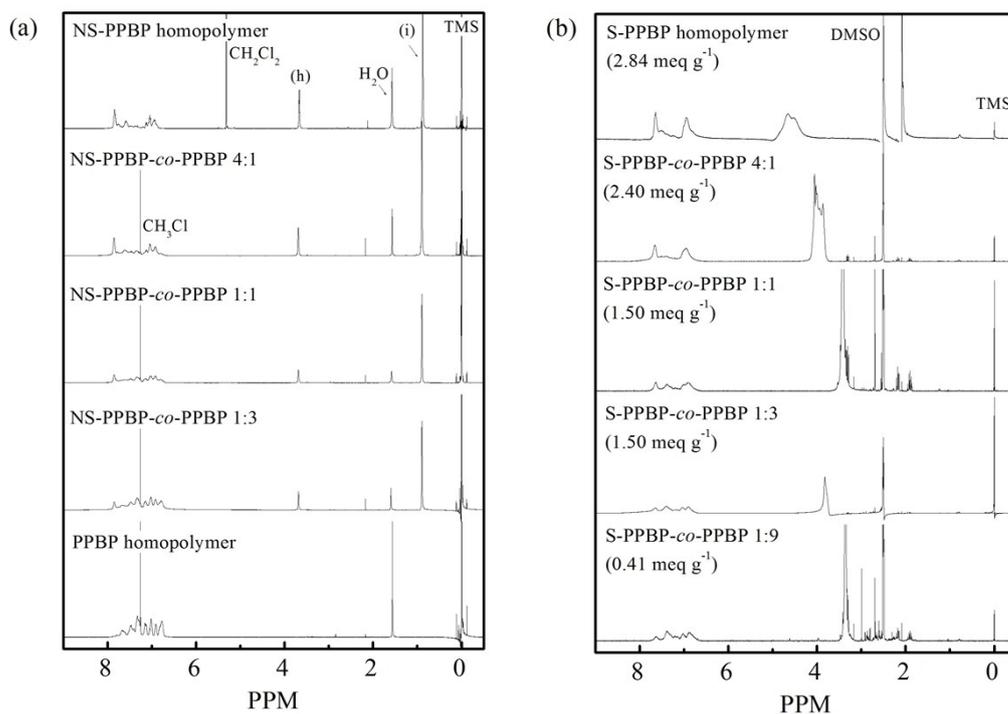


Figure S1. (a) <sup>1</sup>H NMR spectra of NS-PPBP, NS-PPBP-*co*-PPBPs, and PPBP in CD<sub>2</sub>Cl<sub>2</sub> or CDCl<sub>3</sub>. (b) <sup>1</sup>H NMR spectra of S-PPBP and S-PPBP-*co*-PPBPs in DMSO-*d*<sub>6</sub>.

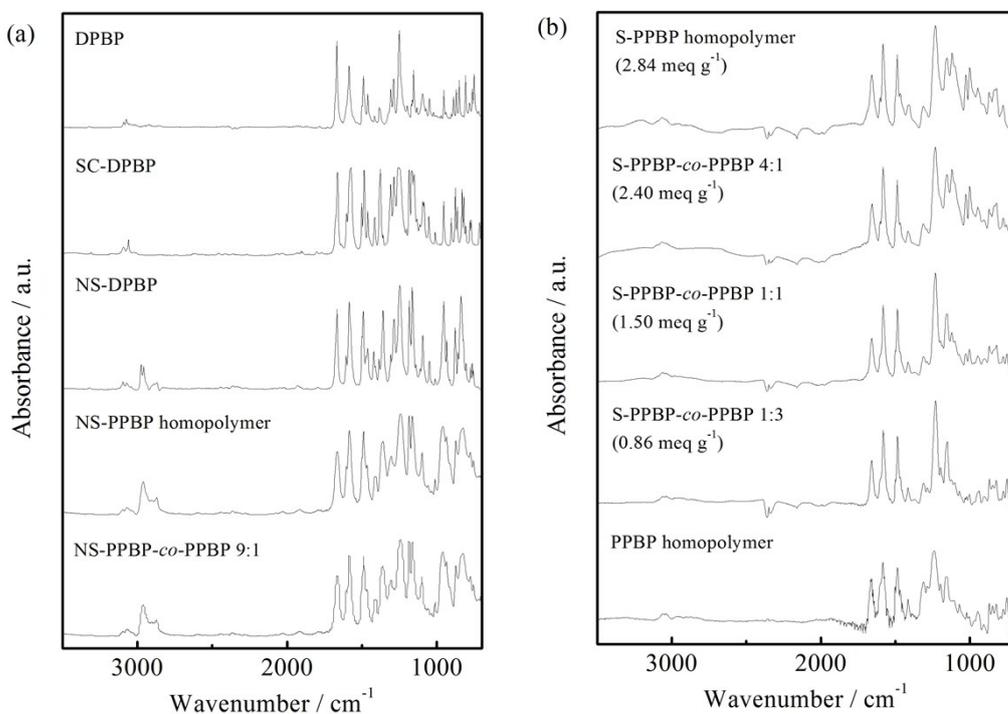


Figure S2. (a) FT-IR spectra of monomers, NS-PPBP, and NS-PPBP-*co*-PPBP. (b) FT-IR spectra of S-PPBP, S-PPBP-*co*-PPBPs, and PPBP.

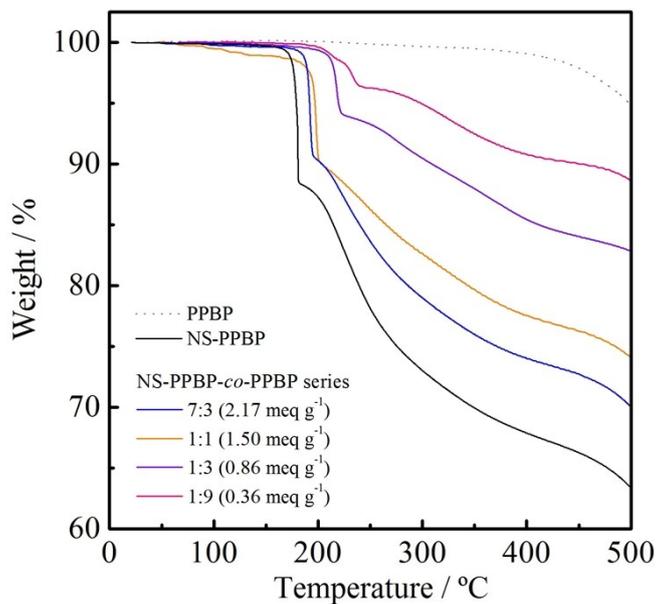


Figure S3. TGA curves of NS-PPBP, NS-PPBP-co-PPBPs, and PPBP.

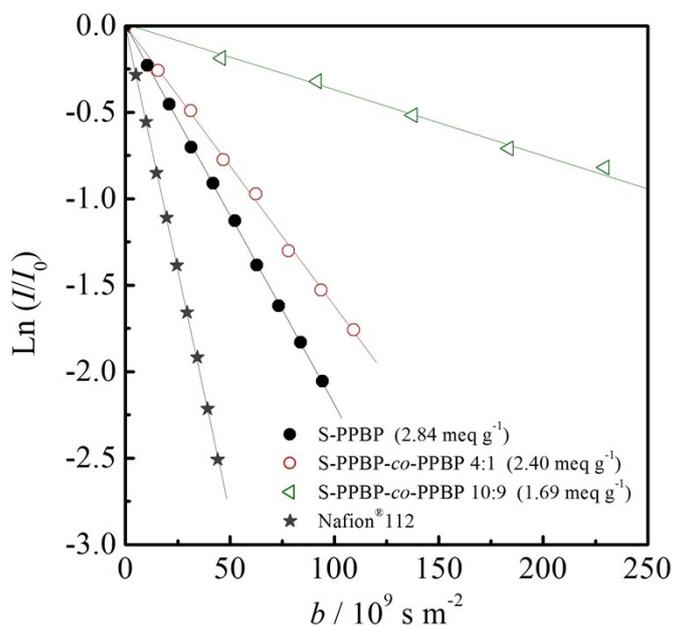


Figure S4. PFG-NMR signal amplitudes ( $I/I_0$ ) of stimulated echo decays as a function of parameter  $b$  ( $=16\gamma^2g^2\delta^2(\Delta\tau/2-\delta/8)/\pi^2$ ) for S-PPBP, S-PPBP-co-PPBPs, and Nafion<sup>®</sup>112 at 30 °C and 40% RH.