

**Electronic supplementary information (ESI)**

**Multiblock-copolymerisation-derived sulfonated-poly(*p*-phenylene)-  
based polymer electrolyte membranes with simultaneously enhanced  
proton conductivity and mechanical strength**

Miru Yoshida-Hirahara,<sup>ab</sup> Masahiro Yoshizawa-Fujita,<sup>a</sup> Yuko Takeoka<sup>a</sup> and Masahiro  
Rikukawa<sup>\*a</sup>

<sup>a</sup> *Department of Materials and Life Sciences, Sophia University, 7-1 Kioi-cho, Chiyoda-  
ku, Tokyo 102-8554, Japan*

<sup>b</sup> *Research and Development Bureau, Saitama University, Shimo-Okubo 255, Sakura-  
ku, Saitama-shi 338-8570, Japan*

\* Corresponding author. E-mail: m-rikuka@sophia.ac.jp

### ■ Synthesis of S-6H (14) 3:1

NS-6H (14) 3:1 was prepared using NS-DPBP (2.500 g, 5.067 mmol), PAEK6H-Cl (14) (0.717 g, 1.69 mmol), PPh<sub>3</sub> (0.555 g, 2.11 mmol), NaI (0.103 g, 0.684 mmol), Zn (0.830 g, 12.7 mmol), NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.104 g, 0.159 mmol), and NMP (13.0 mL) following the general procedure described in the Experimental section. Yield: 72% (1.84 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 6.84–7.98 (m), 3.69 (s), 1.71 (s), 0.90 (s) ppm. IR (KBr): 3043, 2966, 1658, 1592, 1496, 1415, 1363, 1240, 1186, 1164, 871–676 cm<sup>-1</sup>. Elemental analysis: Calcd. for (CHN)<sub>n</sub> C, 71.53%; H, 5.31%. Found C, 71.53%; H, 5.16%.

S-6H (14) 3:1 was prepared using NS-6H (14) 3:1 (2.212 g), (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH·HBr (3.039 g, 19.72 mmol), and NMP (25.0 mL) following the general procedure described in the Experimental section. Yield: 58% (1.12 g). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 6.68–7.83 (m, peaks at 7.66, 7.51, 7.39, 7.20, 6.96) ppm. IR (ATR): 3400, 3966, 1656, 1585, 1490, 1415, 1380, 1360, 12435, 1160, 1120, 1031, 1005, 872–690 cm<sup>-1</sup>. Elemental analysis: Calcd. for (CHNS)<sub>n</sub> C, 69.64%; H, 3.99%; S, 6.63%. Found C, 65.45%; H, 4.13%; S, 6.21%. Molecular weight (GPC):  $M_n = 70,600 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w = 176,000 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w/M_n = 2.50$ .

### ■ Synthesis of S-6H (14) 2:1

NS-6H (14) 2:1 was prepared using NS-DPBP (2.000 g, 4.054 mmol), PAEK6H-Cl (14) (0.717 g, 1.69 mmol), PPh<sub>3</sub> (0.555 g, 2.11 mmol), NaI (0.103 g, 0.684 mmol), Zn (0.830 g, 12.7 mmol), NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.104 g, 0.159 mmol), and NMP (13.0 mL). Yield: 90% (2.00 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 6.84–7.98 (m), 3.69 (s), 1.71 (s), 0.90 (s) ppm. IR (KBr): 3043, 2966, 1658, 1592, 1496, 1415, 1363, 1240, 1186, 1164, 871–676 cm<sup>-1</sup>. Elemental analysis: Calcd. for (CHN)<sub>n</sub> C, 72.75%; H, 5.32%. Found C, 72.75%; H, 5.35%.

S-6H (14) 2:1 was prepared using NS-6H (14) 2:1 (1.708 g), (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH·HBr (21.42 g, 13.90 mmol), and NMP (20.0 mL). Yield: 49% (0.74 g). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 6.68–7.83 (m, peaks at 7.66, 7.51, 7.39, 7.20, 6.96) ppm. IR (ATR): 3400, 3966, 1656, 1585, 1490, 1415, 1380, 1360, 12435, 1160, 1120, 1031, 1005, 872–690 cm<sup>-1</sup>. Elemental analysis: Calcd. for (CHNS)<sub>n</sub> C, 71.25%; H, 4.17%; S, 5.81%. Found C, 67.92%; H, 4.25%; S, 6.09%. Molecular weight (GPC): *M*<sub>n</sub> = 58,000 g·mol<sup>-1</sup>, *M*<sub>w</sub> = 124,000 g·mol<sup>-1</sup>, *M*<sub>w</sub>/*M*<sub>n</sub> = 2.13.

#### ■ Synthesis of S-6H (14) 1:1

NS-6H (14) 1:1 was prepared using NS-DPBP (1.630 g, 3.304 mmol), PAEK6H-Cl (14) (1.402 g, 3.304 mmol), PPh<sub>3</sub> (0.555 g, 2.11 mmol), NaI (0.103 g, 0.684 mmol), Zn (0.830 g, 12.7 mmol), NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.104 g, 0.159 mmol), and NMP (12.0 mL). Yield: 92% (2.53 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 6.84–7.98 (m), 3.69 (s), 1.71 (s), 0.90 (s) ppm. IR (KBr): 3043, 2966, 1658, 1592, 1496,

1415, 1363, 1240, 1186, 1164, 871–676  $\text{cm}^{-1}$ . Elemental analysis: Calcd. for  $(\text{CHN})_n$  C, 74.53%; H, 5.35%. Found C, 74.52%; H, 5.13%.

S-6H (14) 1:1 was prepared using NS-6H (14) 1:1 (2.300 g),  $(\text{C}_2\text{H}_5)_2\text{NH}\cdot\text{HBr}$  (2.105 g, 13.7 mmol), and NMP (25.0 mL). Yield: 96% (2.024 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): 3400, 3966, 1656, 1585, 1490, 1415, 1380, 1360, 12435, 1160, 1120, 1031, 1005, 872–690  $\text{cm}^{-1}$ . Elemental analysis: Calcd. for  $(\text{CHNS})_n$  C, 74.66%; H, 4.56%; S, 4.09%. Found C, 72.94%; H, 4.64%; S, 4.63%. Molecular weight (GPC):  $M_n = 22,000 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w = 69,200 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w/M_n = 3.16$ .

#### ■ Synthesis of S-6F (10) 3:1

NS-6F (10) 3:1 was prepared using NS-DPBP (3.000 g, 6.080 mmol), PAEK6F-Cl (10) (1.093 g, 2.027 mmol),  $\text{PPh}_3$  (0.985 g, 3.75 mmol), NaI (0.182 g, 1.22 mmol), Zn (1.000 g, 15.29 mmol),  $\text{NiCl}_2(\text{PPh}_3)_2$  (0.184 g, 0.281 mmol), and NMP (14.0 mL) following the general procedure described in the Experimental section. Yield: 72% (1.84g).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.83–7.96 (m), 3.67 (s), 0.87 (s) ppm. IR (KBr): 3068, 2966, 1660, 1591, 1490, 1415, 1363, 1240, 1207, 1186, 1164, 875–690  $\text{cm}^{-1}$ . Elemental analysis: Calcd. for  $(\text{CHNS})_n$  C, 67.26%; H, 4.55%; S, 5.05%. Found C, 67.05%; H, 4.48%; S, 5.05%.

S-6F (10) 3:1 was prepared using NS-6F (10) 3:1 (2.510 g),  $(\text{C}_2\text{H}_5)_2\text{NH}\cdot\text{HBr}$  (3.270 g, 21.22 mmol), and NMP (30.0 mL) following the general procedure described in the Experimental section. Yield: 48% (1.06 g). IR (ATR): 3400, 3067, 1660, 1585, 1490, 1415, 1235, 1205, 1120, 1031, 1005, 872–690  $\text{cm}^{-1}$ . Elemental analysis: Calcd. for  $(\text{CHNS})_n$  C, 64.99%; H, 3.33%; S, 5.68%. Found C, 60.06%; H, 3.84%; S, 5.93%. Molecular weight (GPC):  $M_n = 50,800 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w = 118,000 \text{ g}\cdot\text{mol}^{-1}$ ,  $M_w/M_n = 2.31$ .

#### ■ Synthesis of S-6F (10) 2:1

NS-6F (10) 2:1 was prepared using NS-DPBP (3.000 g, 6.080 mmol), PAEK6F-Cl (10) (1.640 g, 3.040 mmol),  $\text{PPh}_3$  (0.957 g, 3.65 mmol), NaI (0.177 g, 1.18 mmol), Zn (1.432 g, 21.90 mmol),  $\text{NiCl}_2(\text{PPh}_3)_2$  (0.179 g, 0.274 mmol), and NMP (14.0 mL). Yield: 86% (3.57 g).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.83–7.96 (m), 3.67 (s), 0.87 (s) ppm. IR (KBr): 3068, 2966, 1660, 1591, 1490, 1415, 1363, 1240, 1207, 1186, 1164, 875–690  $\text{cm}^{-1}$ . Elemental analysis: Calcd. for  $(\text{CHNS})_n$  C, 67.13%; H, 4.45%; S, 4.68%. Found C, 67.29%; H, 4.34%; S, 4.68%.

S-6F (10) 2:1 was prepared using NS-6F (10) 2:1 (3.571 g),  $(\text{C}_2\text{H}_5)_2\text{NH}\cdot\text{HBr}$  (4.051 g, 26.29 mmol), and NMP (30.0 mL). Yield: 81% (1.83 g). IR (ATR): 3400, 3067, 1660, 1585, 1490, 1415, 1235, 1205, 1120, 1031, 1005, 872–690  $\text{cm}^{-1}$ . Elemental analysis: Calcd. for  $(\text{CHNS})_n$  C, 65.02%; H,

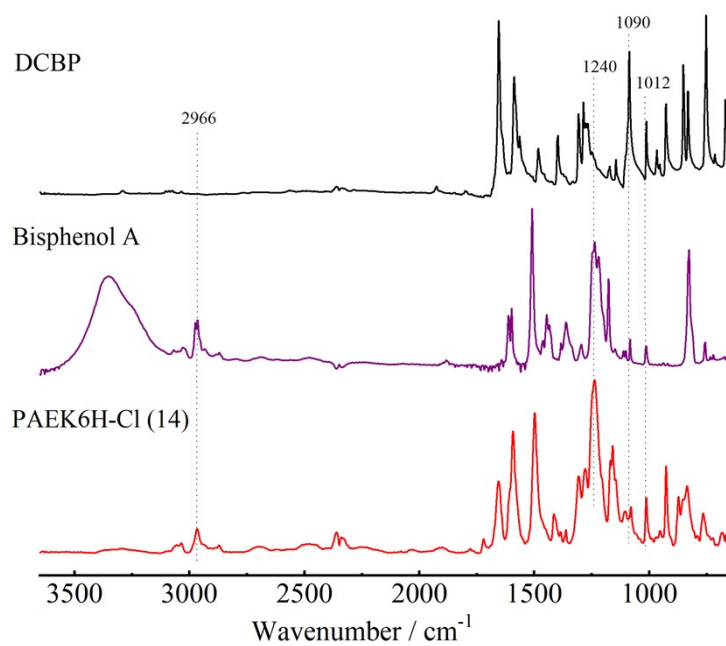
3.31%; S, 5.22%. Found C, 56.00%; H, 6.30%; S, 4.86%. Molecular weight (GPC):  $M_n = 61,400$   $\text{g}\cdot\text{mol}^{-1}$ ,  $M_w = 239,000$   $\text{g}\cdot\text{mol}^{-1}$ ,  $M_w/M_n = 3.89$ .

#### ■ Synthesis of S-6F (10) 1:1

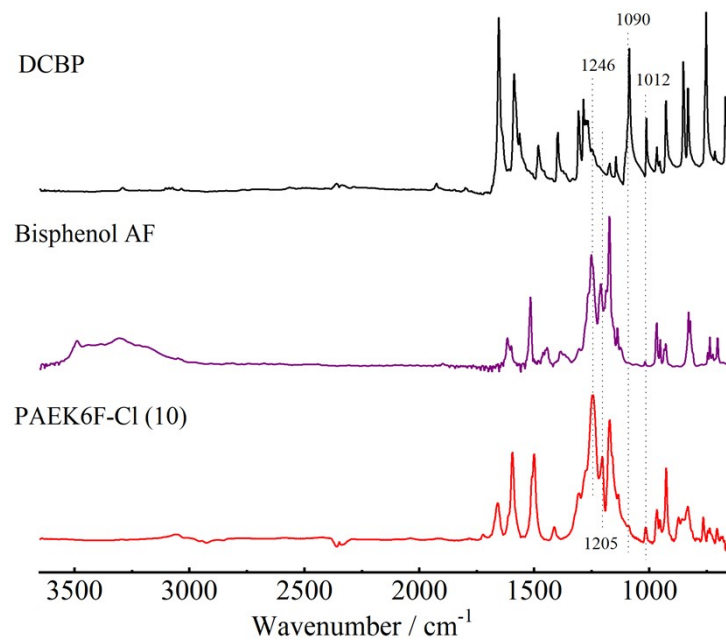
NS-6F (10) 1:1 was prepared using NS-DPBP (2.200 g, 4.459 mmol), PAEK6F-Cl (10) (2.406 g, 4.458 mmol),  $\text{PPh}_3$  (0.957 g, 3.65 mmol), NaI (0.177 g, 1.18 mmol), Zn (1.432 g, 21.90 mmol),  $\text{NiCl}_2(\text{PPh}_3)_2$  (0.179 g, 0.274 mmol), and NMP (14.0 mL). Yield: 91% (3.80 g).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.83–7.96 (m), 3.67 (s), 0.87 (s) ppm. IR (KBr): 3068, 2966, 1660, 1591, 1490, 1415, 1363, 1240, 1207, 1186, 1164, 875–690  $\text{cm}^{-1}$ . Elemental analysis: Calcd. for  $(\text{CHNS})_n$  C, 66.59%; H, 4.05%; S, 3.27%. Found C, 66.38%; H, 4.00%; S, 3.26%.

S-6F (10) 1:1 was prepared using NS-6F (10) 1:1 (3.798 g),  $(\text{C}_2\text{H}_5)_2\text{NH}\cdot\text{HBr}$  (3.123 g, 20.27 mmol), and NMP (30.0 mL). Yield: 39% (0.90 g). IR (ATR): 3400, 3067, 1660, 1585, 1490, 1415, 1235, 1205, 1120, 1031, 1005, 872–690  $\text{cm}^{-1}$ . Elemental analysis: Calcd. for  $(\text{CHNS})_n$  C, 65.13%; H, 3.26%; S, 3.52%. Found C, 60.70%; H, 3.67%; S, 3.91%. Molecular weight (GPC):  $M_n = 29,900$   $\text{g}\cdot\text{mol}^{-1}$ ,  $M_w = 47,300$   $\text{g}\cdot\text{mol}^{-1}$ ,  $M_w/M_n = 2.02$ .



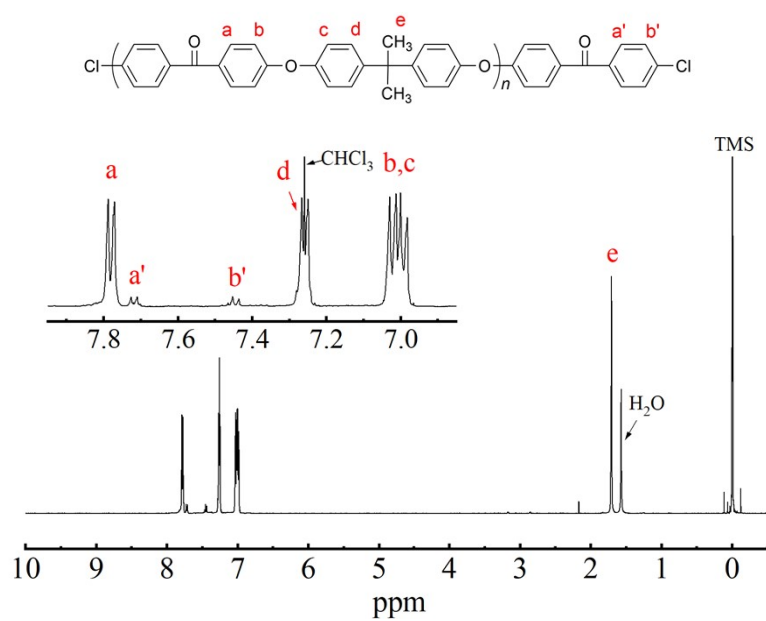


**Fig. S1** FT-IR spectra of DCBP, bisphenol A, and PAEK6H-Cl (14).

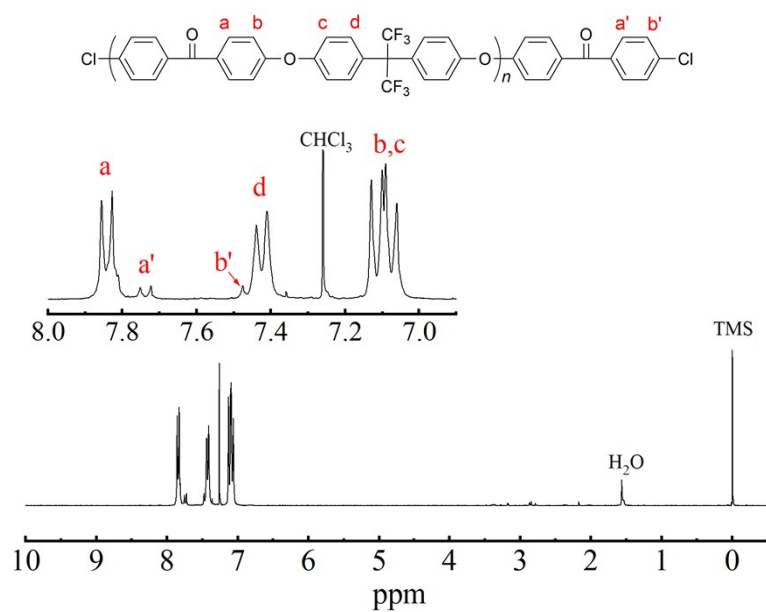


**Fig. S2** FT-IR spectra of DCBP, bisphenol AF, and PAEK6F-Cl (10).

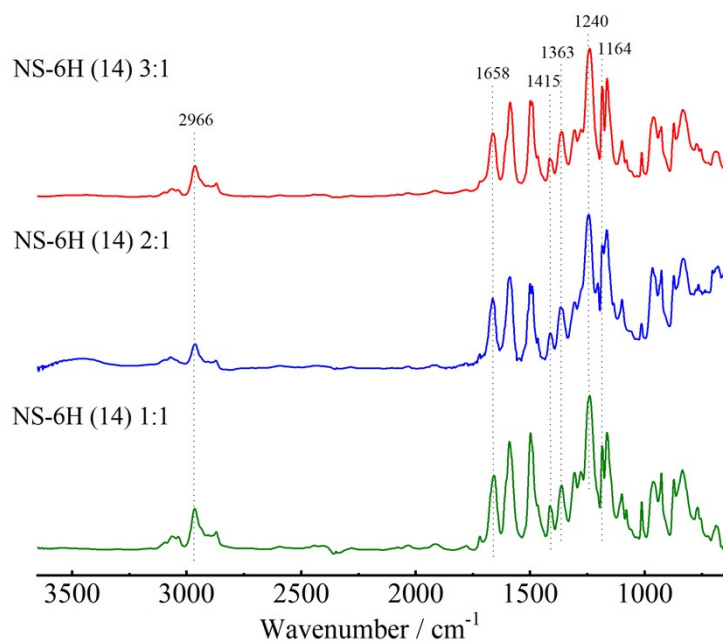




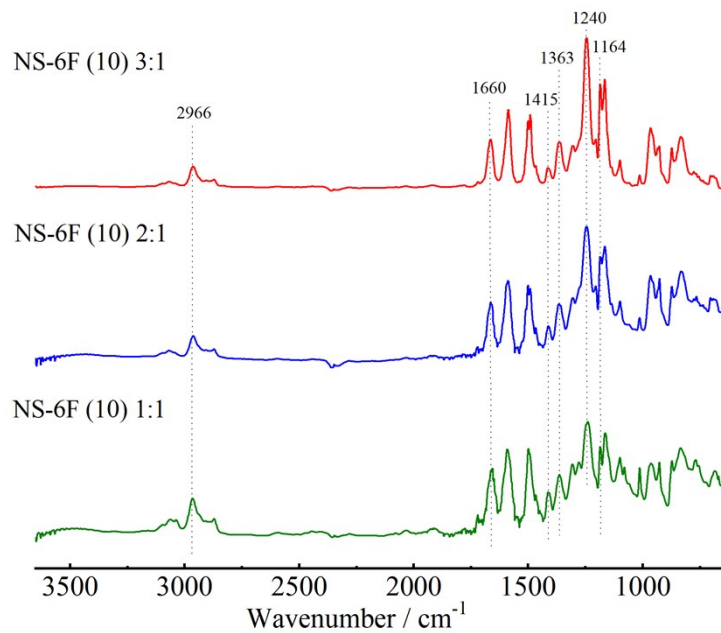
**Fig. S3**  $^1\text{H}$  NMR spectrum of PAEK6H-Cl (14) in  $\text{CDCl}_3$ .



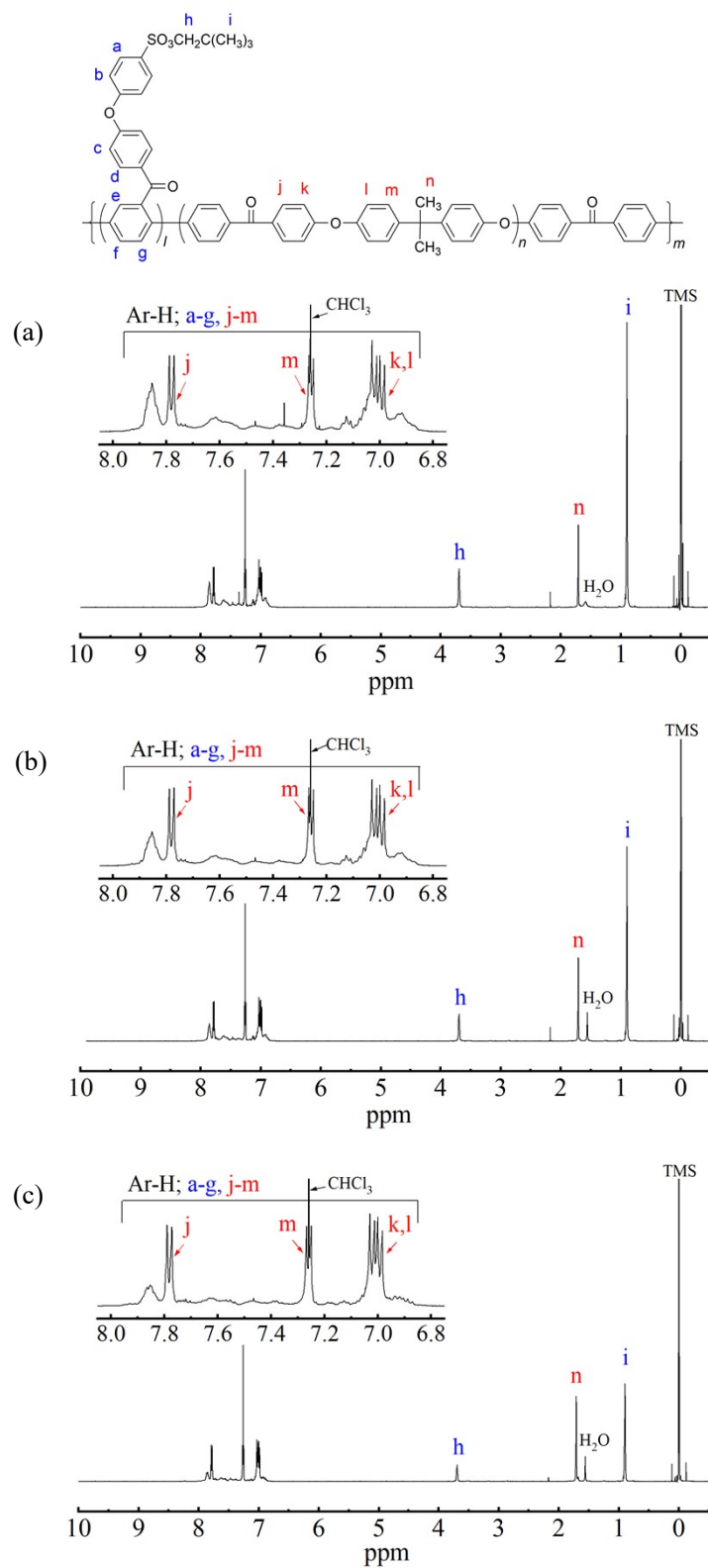
**Fig. S4**  $^1\text{H}$  NMR spectrum of PAEK6F-Cl (10) in  $\text{CDCl}_3$ .



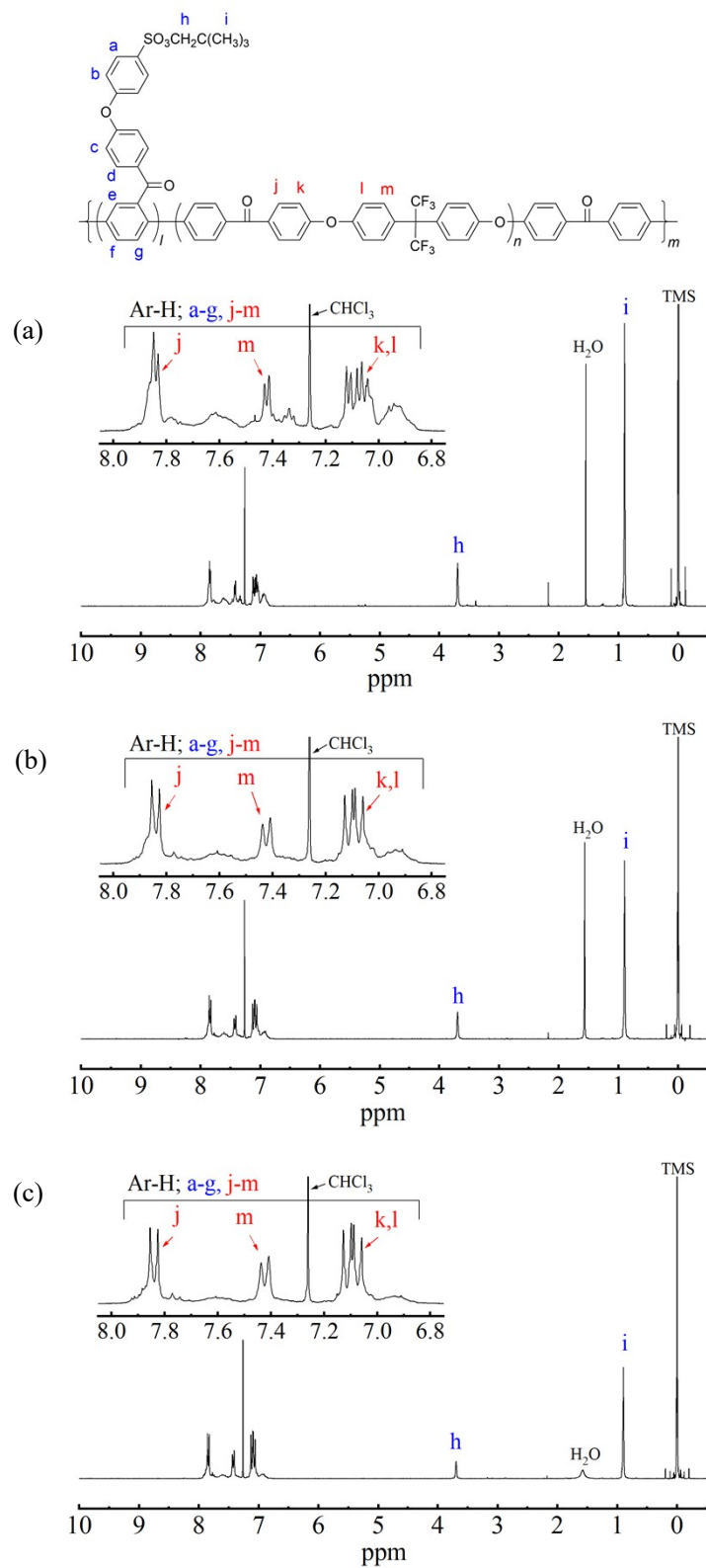
**Fig. S5** FT-IR spectra of NS-6H-series samples.



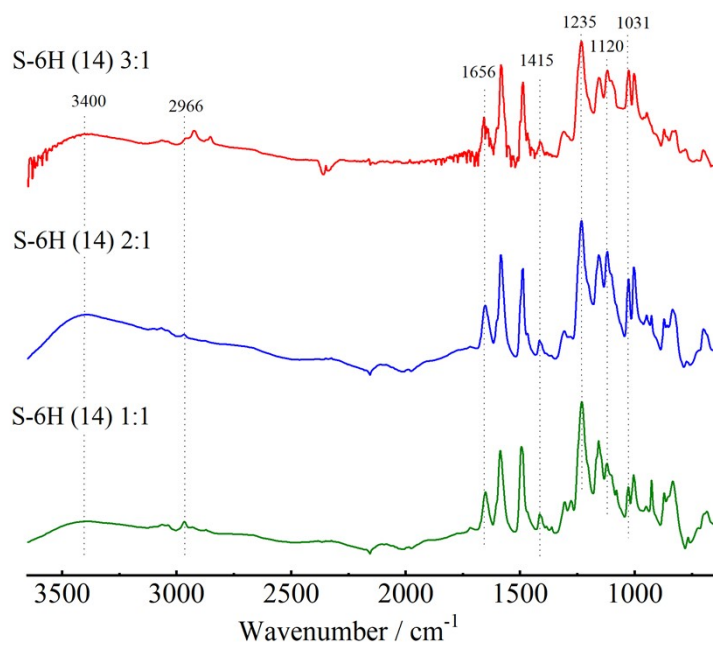
**Fig. S6** FT-IR spectra of NS-6F-series specimens.



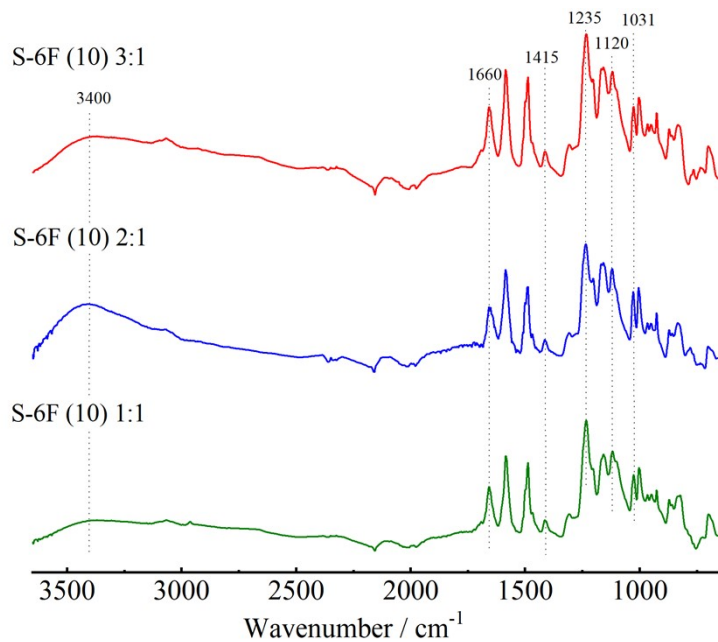
**Fig. S7**  $^1\text{H}$  NMR spectra of (a) NS-6H (14) 3:1, (b) NS-6H (14) 2:1, and (c) NS-6H (14) 1:1 in  $\text{CDCl}_3$ .



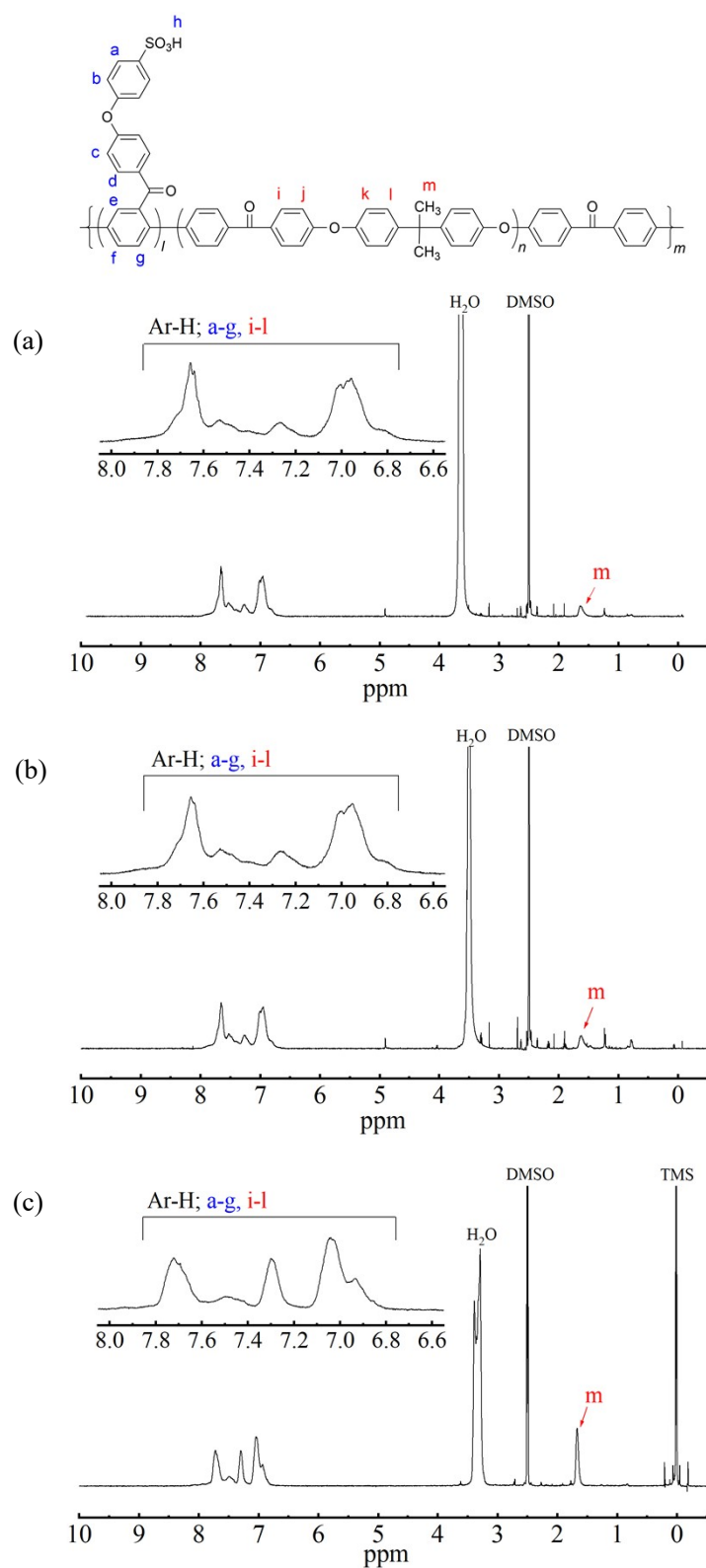
**Fig. S8**  $^1\text{H}$  NMR spectra of (a) NS-6F (10) 3:1, (b) NS-6F (10) 2:1, and (c) NS-6F (10) 1:1 in  $\text{CDCl}_3$ .



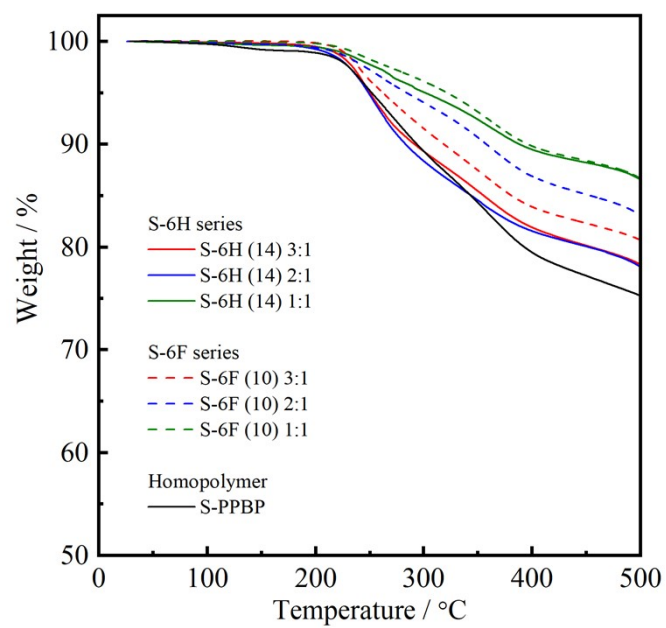
**Fig. S9** FT-IR spectra of S-6H-series samples.



**Fig. S10** FT-IR spectra of S-6F-series specimens.



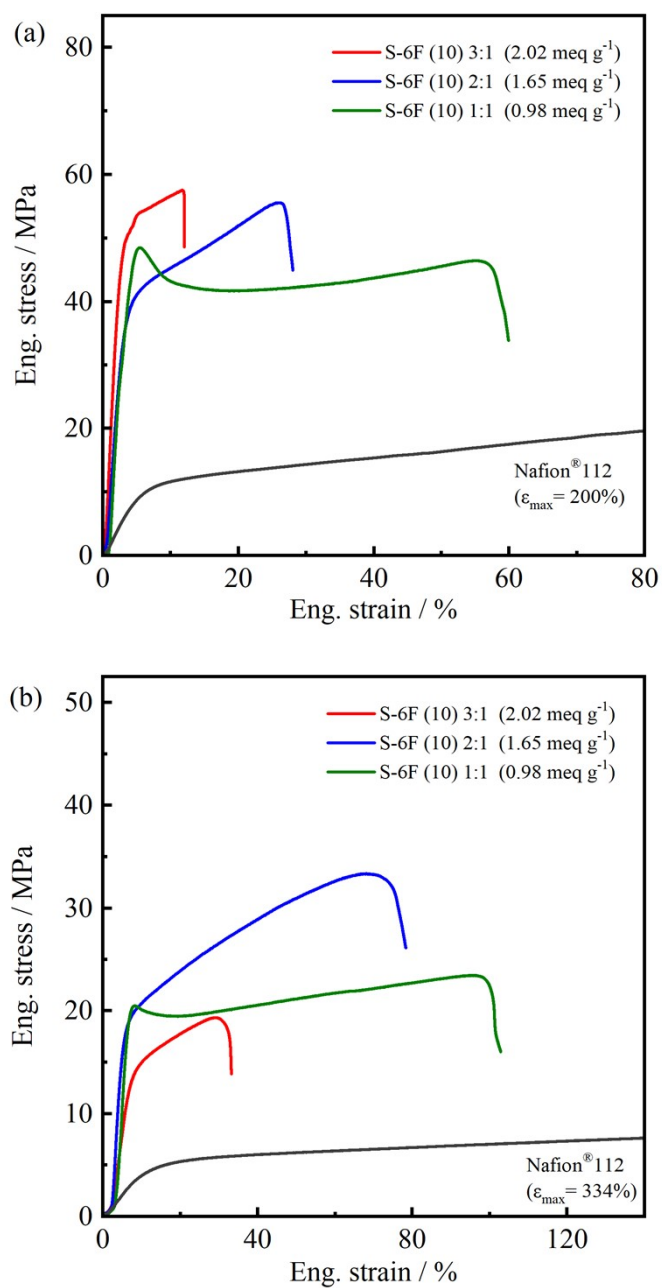
**Fig. S11**  $^1\text{H}$  NMR spectra of (a) S-6H (14) 3:1, (b) S-6H (14) 2:1, and (c) S-6H (14) 1:1 in  $\text{DMSO-}d_6$ .



**Fig. S12** TGA curves of S-6H- and S-6F-series specimens.

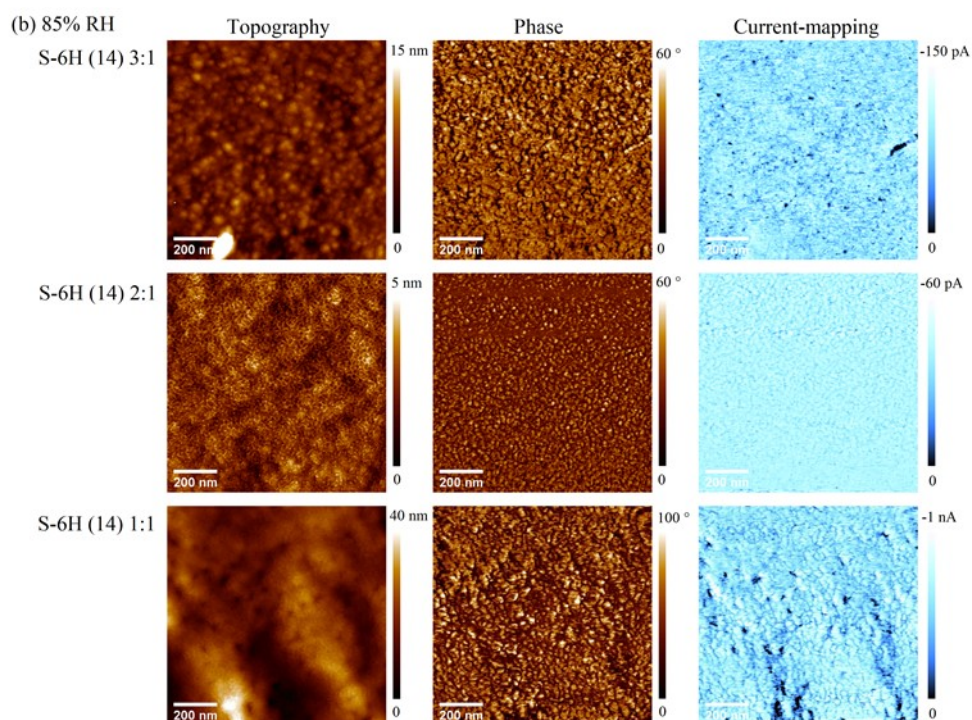




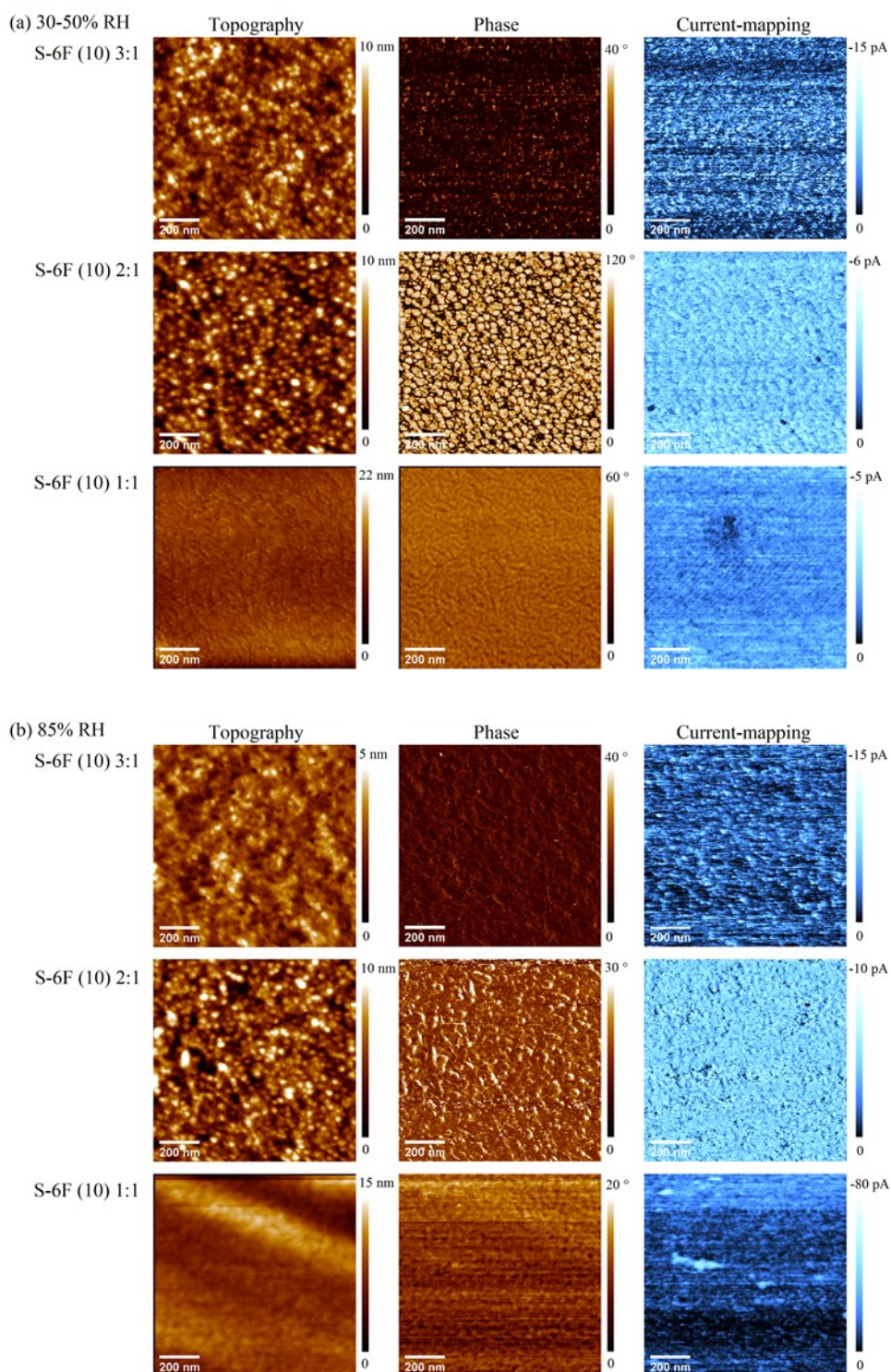


**Fig. S13** Stress–strain curves of S-6F membranes under (a) ambient conditions (RT, no extra humidification) and (b) at an elevated temperature and humidity (80 °C, 90% RH).

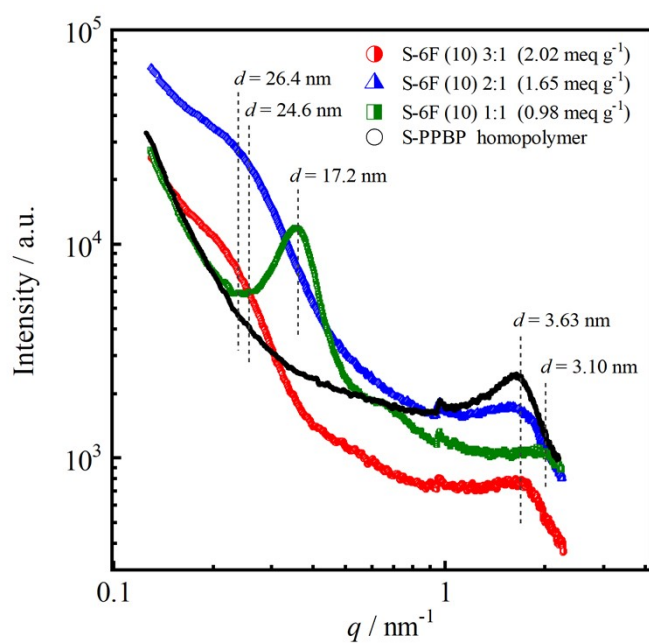




**Fig. S14** AFM images of S-6H membranes under (a) ambient (RT, 30%–50% RH) and (b) humid conditions (RT, 85% RH). Left, middle, and right columns: topography, phase, and current mapping, respectively; scan size,  $1000 \times 1000 \text{ nm}^2$ .



**Fig. S15** AFM images of S-6F membranes under (a) ambient (RT, 30%–50% RH) and (b) humid conditions (RT, 85% RH). Left, middle, and right columns: topography, phase, and current mapping, respectively; scan size,  $1000 \times 1000 \text{ nm}^2$ .



**Fig. S16** SAXS profiles of S-6F and S-PPBP membranes. Dotted lines indicate the interdomain spacing calculated using Bragg's law.