

Electronic Supplementary information (ESI) for  
**Highly sulfonated co-polyimides containing cross-linkable  
hydrophobic tetrafluorostyrol side-groups for proton exchange  
membranes**

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## A. Supplementary Method

### 1. Materials

1,3-bis(2-trifluoromethyl-4-aminophenoxy)-5-(2,3,5,6-tetrafluoro-4-vinylphenoxy)benzene (6FTFPB) and 1,4-bis(4-amino-2-trifluoromethylphenoxy)benzene (6FAPB) were synthesized in our laboratory according to the literature.<sup>1,2</sup> 4,4'-Diaminodiphenylether-2,2'-disulfonic acid (ODADS) was synthesized according to synthesis routines reported by Okamoto et al.<sup>3</sup> 1,4,5,8-Naphthalenetetracarboxylicdianhydride (NTDA) was purchased from TCI chemical company. Triethylamine (TEA), m-cresol, dimethyl sulfoxide (DMSO) and benzoic acid were purchased from Aladdin Reagents Co., Ltd. (China). Fuming sulfuric acid (SO<sub>3</sub> 30%), hydrochloric acid and acetone were purchased from Tianjin Chemical Reagent (China) and were used as received.

### 2. Synthesis of sulfonated co-polyimides

A typical polycondensation procedure, illustrated by preparation of the SPI-20-60 (where 20 and 60 is the molar percentage of monomer 6FTFPB and ODADS in the total diamine monomers, respectively), can be described as follows (Scheme 1). To a 50 mL completely dried three-necked round-bottomed flask, 0.4324 g (1.2 mmol) of ODADS, 10 mL of m-cresol and 0.29 g (2.9 mmol) of triethylamine were added successively under nitrogen flow with stirring. After ODADS was completely dissolved, 0.2474 g (0.4 mmol) of 6FTFPB, 0.1713 g (0.4 mmol) of 6FAPB, 0.5364 g (2 mmol) of NTDA and 0.34 g (2.8 mmol) of benzoic acid were added. The mixture was stirred at room temperature for 30 minutes, and then heated at 80 °C for 4 h and 180 °C for 20 h. After cooling to 100 °C, an additional 15 mL of m-cresol was added to dilute the viscous solution. And then the solution was poured into 300 mL of acetone. The precipitate was collected by filtration, and extracted with acetone in a Soxhlet extractor for 48 h. The resulting yellow copolymer was dried in vacuum at 120 °C for 48 h.

### **3. Preparation of membranes**

The polymer membranes were prepared by solution casting from DMSO. A solution of dried sulfonated copolyimide (in the triethylammonium salt form) in DMSO with a concentration of ~8 wt% was filtered and then cast onto a clean glass plate, and dried at 80 °C for 10 h and under vacuum at 120 °C for 24 h. The cross-linked membranes were obtained by treating for 2 h in vacuum oven which was pre-heated to 260 °C, while the uncross-linked membrane was not thermal treated. After cooling down to room temperature, the membranes were soaked in deionized water and then peeled off. The membranes, in triethylammonium sulfonated salt form, were completely converted to the corresponding sulfonic acid-form membranes by immersing in 1 M HCl at room temperature for 24 h. The membranes were thoroughly washed with deionized water and then dried in vacuum at 120 °C for 24 h.

### **4. Measurements**

FTIR spectra were measured on a Nicolet Impact 410 Fourier-transform infrared spectrometer. <sup>1</sup>H NMR spectra of the copolymers were measured on a Bruker AVANCE NMR spectrometer (<sup>1</sup>H, 300 MHz) using DMSO-d<sub>6</sub> as solvent and tetramethylsilane (TMS) as internal reference. The viscosities of the copolymers were determined by an Ubbelohde viscometer in a thermo static container with a polymer concentration of 0.5 g dL<sup>-1</sup> in DMSO at 25 °C.

#### **Ion exchange capacity (IEC)**

The IEC values of the membranes were determined by acid–base titration. The dried membrane samples in the acid form were weighed and then immersed in 2.0 M NaCl solution for 48 h to replace the protons of sulfonic acid groups with sodium ions. The solution was titrated by 0.01 M NaOH solution with

phenolphthalein as an indicator. The IEC (meq. g<sup>-1</sup>) values were calculated from the amount of NaOH consumed in the titration and the weights of the dried membrane samples. The volumetric IEC (IEC<sub>v</sub>) values were calculated based on water uptake measurements according to the following equation:

$$IEC_v = \frac{IEC}{\frac{1}{\rho_p} + \frac{0.01WU}{\rho_w}}$$

where the IEC is determined by acid-base titration, WU (%) is the water uptake of the membranes,  $\rho_p$  (g cm<sup>-3</sup>) and  $\rho_w$  (g cm<sup>-3</sup>) is the density of polymers and water, respectively.

### **Water uptake (WU) and swelling ratio measurements**

Water uptake and dimensional change were obtained by measuring the weight, length of membranes in the acid form. Before the initial measurements, the membranes were dried in vacuum at 120 °C for 24 h. Then the membranes were immersed in deionized water to reach equilibrium at the desired temperature. Before weight and length measurements of hydrated membranes, the water on surfaces of membrane was removed. The water uptake (WU) content (%) was calculated by

$$WU = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$

where  $W_{dry}$  and  $W_{wet}$  are the weights of dried and wet membranes, respectively. The water volume fraction ( $X_v$ ) was the volumetric water uptake according to reference:<sup>4</sup>

$$X_v = \frac{0.01WU}{0.01WU + \frac{\rho_w}{\rho_p}}$$

The swelling ratio was calculated from the change of film length by:

$$Swelling\ ratio = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\%$$

where  $L_{\text{wet}}$  (mm) and  $L_{\text{dry}}$  (mm) are the lengths of the wet and dry membranes, respectively.

### **Proton conductivity**

Proton conductivity of fully hydrated membranes (4 cm×1 cm) was measured by a four-electrode AC impedance method from 0.1 Hz to 100 kHz with 10 mV AC perturbation and 0.0V DC rest voltage using a Princeton Applied Research Model 273A potentiostat (Model 5210 frequency response detector, EG&G PARC, Princeton, NJ). The measurements were carried out with the cells immersed in the constant-temperature water. The humidity dependence of the proton conductivity from 50 to 95% RH was investigated at 80°C in the frequency range 10<sup>1</sup>-10<sup>6</sup> Hz. The humidity was equilibrated by saturated salt solution in a closed system. The proton conductivity ( $\sigma$ ) was calculated from the following equation:

$$\sigma = \frac{L}{RA}$$

where  $L$  (cm) is the distance between the counter electrodes and the working electrode,  $R$  ( $\Omega$ ) is the resistance of the membrane and  $A$  (cm<sup>2</sup>) is the membrane area. The activation energy ( $E_a$ ) of conductivity was calculated by fitting the Arrhenius equation:

$$\sigma = \sigma^0 \exp\left(-\frac{E_a}{RT}\right)$$

where  $R$  is the gas constant. The effective proton mobility  $\mu$  (cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) was determined as follows:

$$\mu = \frac{\sigma}{Fc(H^+)}$$

where  $F$  is the Faraday constant.

### **Methanol permeability**

The methanol permeability of membrane was determined using a diffusion cell consisting of two compartments, each with a capacity of approximately 150 mL,

separated by a membrane. Prior to the test, the membranes were equilibrated in deionized water for at least 24 h. The membrane was placed between two compartments. Then one compartment was filled with deionized water and the other filled with a 10 M methanol solution. The solutions in two compartments were stirred continuously during the permeability measurement. Methanol permeated across the membrane by the concentration difference between the two compartments. The concentration of the methanol in the water reservoir was measured by a SHIMADZU GC-8A chromatograph. The methanol permeability was calculated as follows:

$$C_B(t) = \frac{A DK}{V_B L} C_A (t - t_0)$$

where  $A$  (cm<sup>2</sup>) is the effective area,  $L$  (cm) is the thickness of membrane,  $V_B$  (mL) is the volume of the permeated reservoirs.  $C_A$  and  $C_B$  (mol L<sup>-1</sup>) are the methanol concentration in the feed and in the permeate, respectively.  $t$  and  $t_0$  (s) represent time and the time lag, respectively. The  $DK$  (cm<sup>2</sup> s<sup>-1</sup>) value is the methanol permeability.

### **Thermal properties**

Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC821e instrument at a heating rate of 10 °C min<sup>-1</sup> from 100°C to 300°C under nitrogen.

The dynamic mechanic analysis (DMA) was performed on TA Q800 at a heating rate of 5 °C min<sup>-1</sup> from 100 to 400 °C and a frequency of 1 Hz. The tests were carried out with a fixed frequency of 1 Hz, 1 N applied pre-force and oscillation amplitude of 25 μm. The membranes were cut into 6 mm × 40 mm .

The thermal gravimetric analyses (TGA) of the membranes were performed by a Perkin-Elmer TGA-1 thermo-gravimetric analyzer. Before test, all the membranes were dried and kept in the TGA furnace at 120 °C under nitrogen atmosphere for 30 min to remove water. The samples were evaluated in the range of 100-800 °C

at a heating rate of 10 °C min<sup>-1</sup> under nitrogen.

### **Gel fraction**

The gel fractions of the cross-linked polymer membranes were measured by solvent extraction. A piece of membrane sample was extracted with DMSO as extraction solvent at 80 °C for 24 h. The gel fractions were calculated as follows:

$$Gel\ fraction = \frac{W_2}{W_1} \times 100\%$$

where  $W_1$  are the initial weights of the membranes,  $W_2$  are the weights of the membranes after extraction in DMSO at 80 °C for 24 h.

### **Oxidative stability**

A small piece of the membrane sample was immersed in Fenton's reagent (3 wt% H<sub>2</sub>O<sub>2</sub>, 2 ppm Fe<sup>2+</sup>) at 80 °C. The oxidative stability was evaluated by the dissolution time of the membranes and the retained weight of membranes after treating in Fenton's reagent for 1h.

### **Hydrolytic stability**

The hydrolytic stability was investigated by measuring the elapsed time. The time that the membranes dissolved completely in water at 80 °C was considered as the elapsed time. The longer the elapsed time was, the better hydrolytic stability membrane had.

### **Mechanical property**

The tensile properties of dry membranes were measured at room temperature on SHIMADIU AG-I 1KN at a strain rate of 2 mm min<sup>-1</sup>. The size of samples was 20 mm × 4 mm.

### **Morphology**

Morphological information was gathered from Small-angle X-ray scattering

(SAXS) and atomic force microscope (AFM) measurements.

The SAXS were measured on membranes where the acidic protons were ion-exchanged for  $\text{Pb}^{2+}$  using a 1 wt% aqueous solution of  $\text{Pb}(\text{OAc})_2$ . The scattering experiments were performed on a SAXS system with sealed tube X-ray generator (SAXSess mc<sup>2</sup>). Hydrated membranes were analyzed in a solid sample holder at 25 °C. The scattering vector  $q$  ( $\text{nm}^{-1}$ ) was calculated according to following equation:

$$q = \frac{4\pi \sin \theta}{\lambda}$$

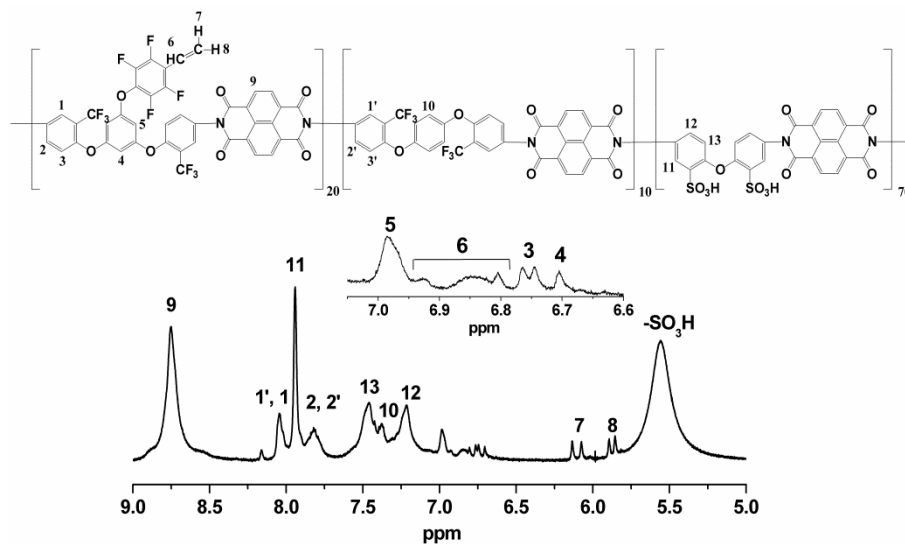
where the wavelength  $\lambda$  is 0.1542 nm and  $\theta$  is the scattering angle. The characteristic separation length  $d$ (nm), i.e. the Bragg spacing, was calculated from following equation:

$$d = \frac{2\pi}{q}$$

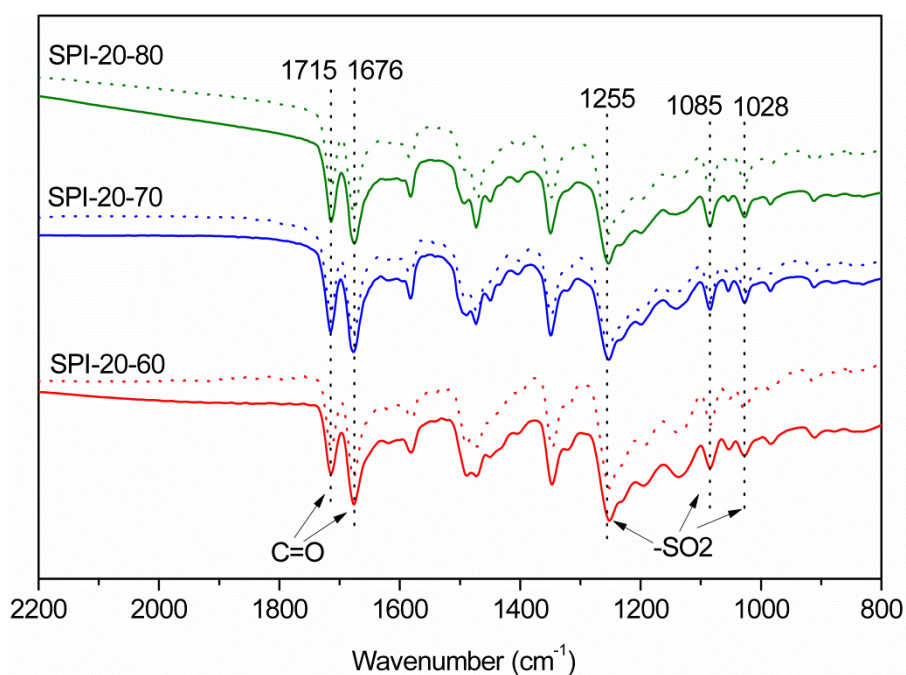
AFM images were taken on a commercial instrument (NSK Ltd. SPA300) by tapping mode under ambient conditions at room temperature. All treated samples were allowed to equilibrate by exposure to 100% relative humidity for at least 24 h before testing.



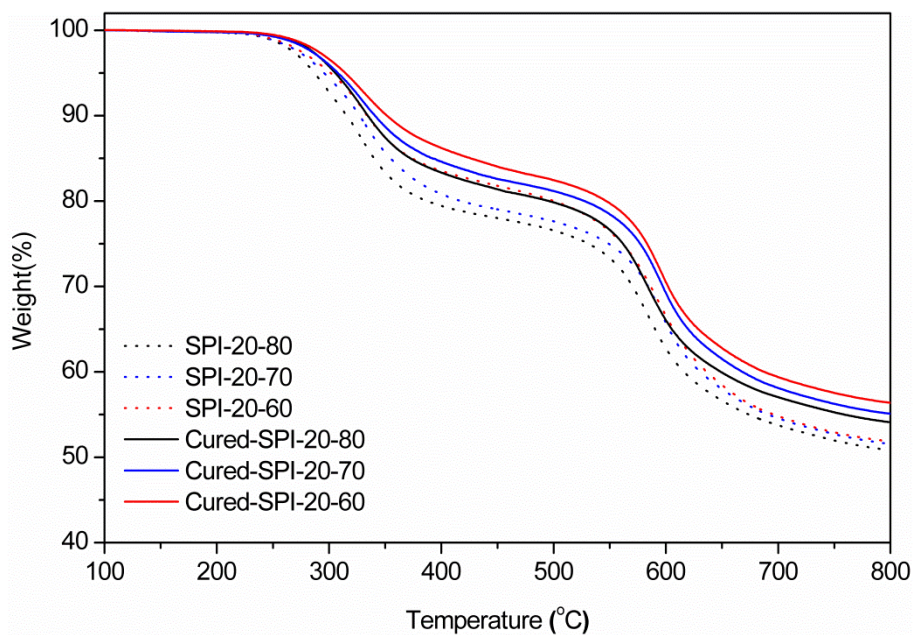
## B. Supplementary Figures



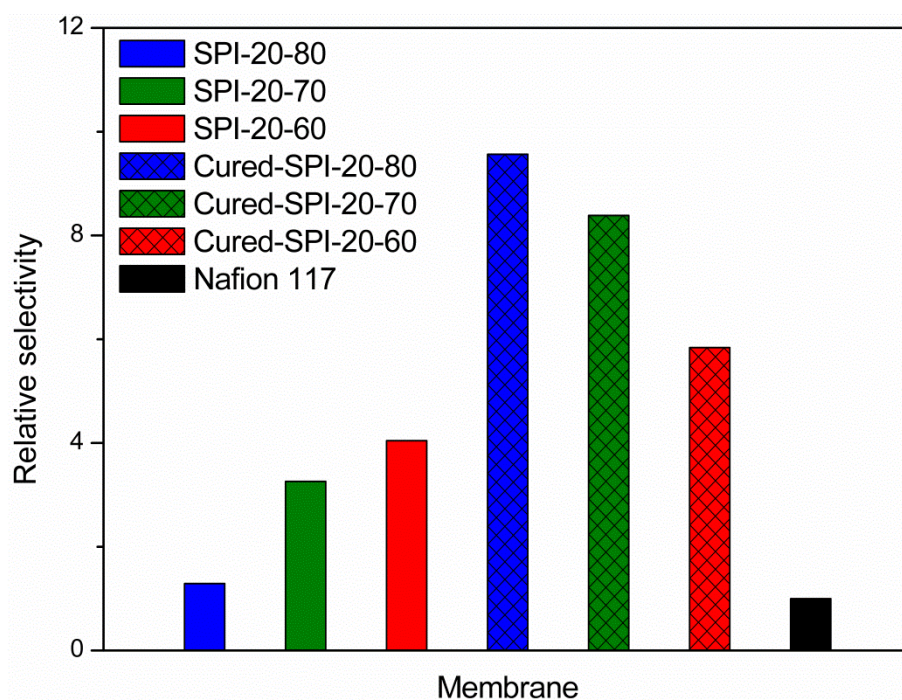
**Fig. S1**  $^1\text{H}$  NMR spectra of SPI-20-70.



**Fig. S2** FT-IR spectra of SPI-20s (dotted line) and Cured-SPI-20s (solid line).



**Fig. S3** TGA curves of SPI-20s and Cured-SPI-20s.



**Fig. S4** The relative selectivity of SPI-20s and Cured-SPI-20s membranes at room temperature. (Relative selectivity = selectivity of SPI-20s or Cured-SPI-20s membranes/ selectivity of Nafion 117 membrane, selectivity = proton conductivity/ methanol permeability).

## C. Supplementary Tables

Table S1 Intrinsic viscosity, Solubility, IEC<sub>w</sub> and IEC<sub>v</sub> of SPI-20s and Cured-SPI-20s.

Copolyimide	ODADS (mol%)	$\eta$ (dL g <sup>-1</sup> )	Solubility in DMSO	Gel fraction <sup>a</sup> (%)	IEC <sub>w</sub> <sup>b</sup> (meq.g <sup>-1</sup> )	IEC <sub>w</sub> <sup>c</sup> (meq.g <sup>-1</sup> )	IEC <sub>v(dry)</sub> (meq.cm <sup>-3</sup> )	IEC <sub>v(wet)</sub> (meq.cm <sup>-3</sup> )	
								RT <sup>d</sup>	80 °C <sup>e</sup>
SPI-20-80	80	0.80	Soluble	-	2.48	2.26	2.87	2.25	1.89
SPI-20-70	70	0.78	Soluble	-	2.15	1.96	2.47	2.10	1.82
SPI-20-60	60	0.90	Soluble	-	1.82	1.65	2.05	1.93	1.71
Cured-SPI-20-80	80	-	Swollen	84%	-	2.13	2.81	2.58	2.18
Cured-SPI-20-70	70	-	Swollen	81.4%	-	1.82	2.35	2.29	2.07
Cured-SPI-20-60	60	-	Swollen	84.8%	-	1.61	2.03	2.02	1.80

<sup>a</sup> Gel fraction was obtained from the ratio of the weight of the polymer after extraction in DMSO at 80 °C for 24 h and the initial weight. <sup>b</sup> Theoretical value. <sup>c</sup> Determined by titration. <sup>d</sup> Calculated according to WU data at room temperature. <sup>e</sup> Calculated according to WU data at 80 °C.

## D. Supplementary References

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