

SUPPORTING INFORMATION

A new supramolecular sulfonated polyimide for use in proton exchange membranes for fuel cells

Yun-Sheng Ye, Yao-Jheng Huang, Chih-Chia Cheng, Feng-Chih Chang*

Institute of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan

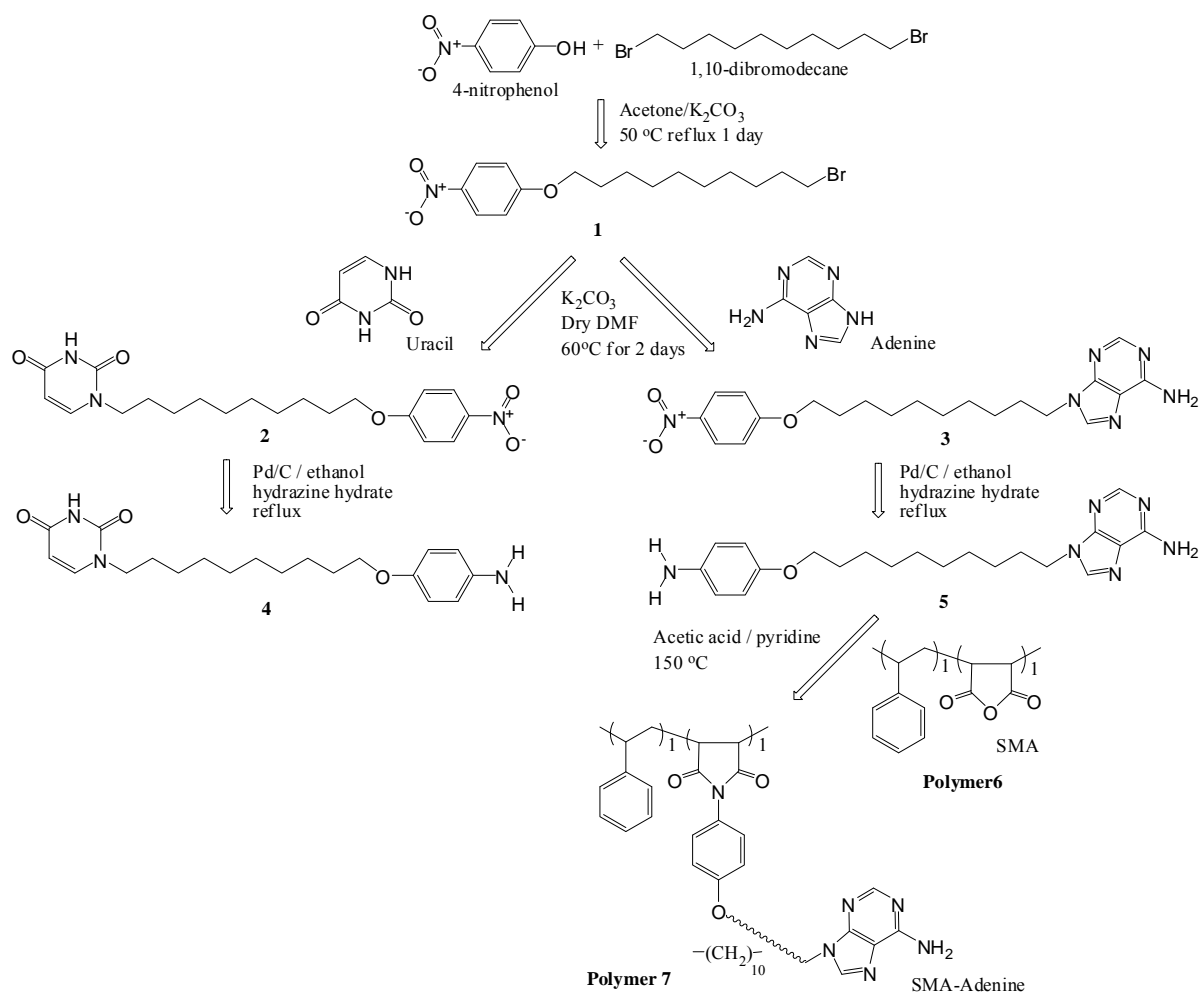
E-mail: changfc@mail.nctu.edu.tw; Tel: +886 03 57131512

Experimental Section

Materials. 1,10-Dibromodecane, 4-nitrophenol, uracil, adenine, potassium carbonate, palladium on activated carbon (unreduced, 10% Pd), styrene (St) and maleic anhydride (Mah) were purchased from Acros. 4,4'-(1,1'-biphenyl-4,4'-diyldioxy)dianiline (BAPB), ionic co-monomer 4,4'-bis(4-aminophenoxy)biphenyl-3,3'-disulfonic acid (BAPBDS) and 9-Hexadecyladenine (A-C16) were synthesized as previous reported.^{S1,S2} Hydrazine hydrate (80%), 2-propanol (IPA), triethylamine (TEA), isoquinoline, and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) were purchased from Sigma–Aldrich. *N,N*-Dimethylformamide (DMF; Sigma–Aldrich) was vacuum-distilled prior to use. All other chemicals were purchased in reagent grade from Sigma–Aldrich and used as received.

S1. (a) T. Watari, J. Fang, K. Tanaka, H. Kita, K. I. Okamoto, T. Hirano, *J. Membr. Sci.*, 2003, **219**, 137.;(b) C. C. Cheng, C. F. Huang, Y. C. Yen, F. C. Chang, *J Polym Sci Part A: Polym Chem*, 2008, **46**, 6416.

Scheme S1. Synthesis route for monomer 4 and polymer 7.



Synthesis and Characterization of Monomers

1-(10-Bromodecyloxy)-4-nitrobenzene (1). 1,10-Dibromodecane (6.00 g, 20.0 mmol) was added to a stirred mixture of 4-nitrophenol (1.39 g, 10.0 mmol) and potassium carbonate (1.66 g, 12.0 mmol) in acetone (50 mL) and then the suspension was stirred at 50 °C for 1 day. After cooling to room temperature, the mixture was filtered to remove most of the salts and then the solvent was evaporated under vacuum. The product was crystallized from petroleum ether. Yield: 83%. M.p. = 55.4 °C. 1H NMR ($CDCl_3$): δ = 1.26 (H6), 1.39 (H5), 1.77 (H4, H4'), 3.35 (H7), 3.99 (H3), 6.89 (H2, H2'), 8.1 (H1, H1') ppm. ^{13}C NMR ($CDCl_3$): δ = 29.09 (g), 28.35 (i), 29.16–29.54 (h, j), 29.62 (f), 33.04 (m), 34.27 (n), 68.96 (e), 114.64 (c, c'), 126.07 (b, b'), 141.55 (a), 164.4 (d) ppm.

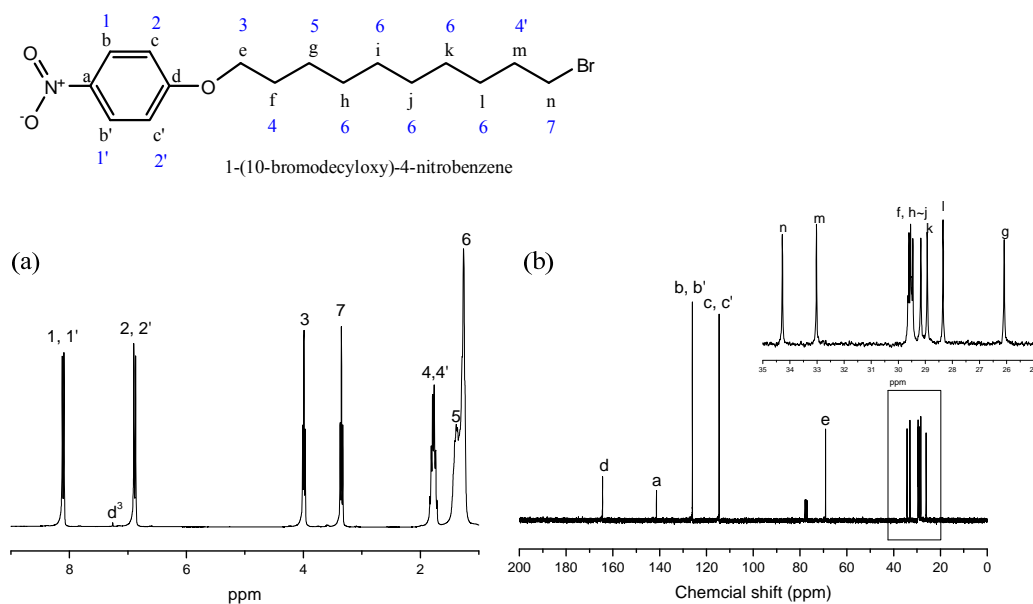


Fig. S1. (a) $^1\text{H-NMR}$ and (b) $^{13}\text{C-NMR}$ spectra of monomer 1.

Nitrophenoxy-alkane-uracil (2). Monomer 1 (7.79 g, 20.0 mmol), uracil (4.48 g, 40.0 mmol), and KOH (5.52 g, 40 mmol) were added to dry DMF (200 mL) under an Ar atmosphere and stirred at 60 °C for 1 day. The suspension was cooled to room temperature and filtered to remove most of the salt; the solvent was then evaporated under vacuum. The product was crystallized from CH_2Cl_2 . Yield: 63%. M.p. = 120.2 °C. $^1\text{H NMR}$ ($\text{DMSO-}d_6$): δ = 1.22 (H6), 1.35 (H5), 1.53, 1.68 (H4, H4'), 3.6 (g), 4.06 (H3), 5.51 (H9), 7.09 (H2, H2'), 7.62 (H8), 8.16 (H10, H10'), 11.19 (H7) ppm. $^{13}\text{C NMR}$ ($\text{DMSO-}d_6$): δ = 25.92 (l, g), 29.48 (f, h-k), 48.1 (n), 69.32 (e), 101.3 (q), 115.63 (c, c'), 126.39 (b, b'), 141.38 (a), 146.29 (p), 151.48 (o), 164.56 (d, r) ppm.

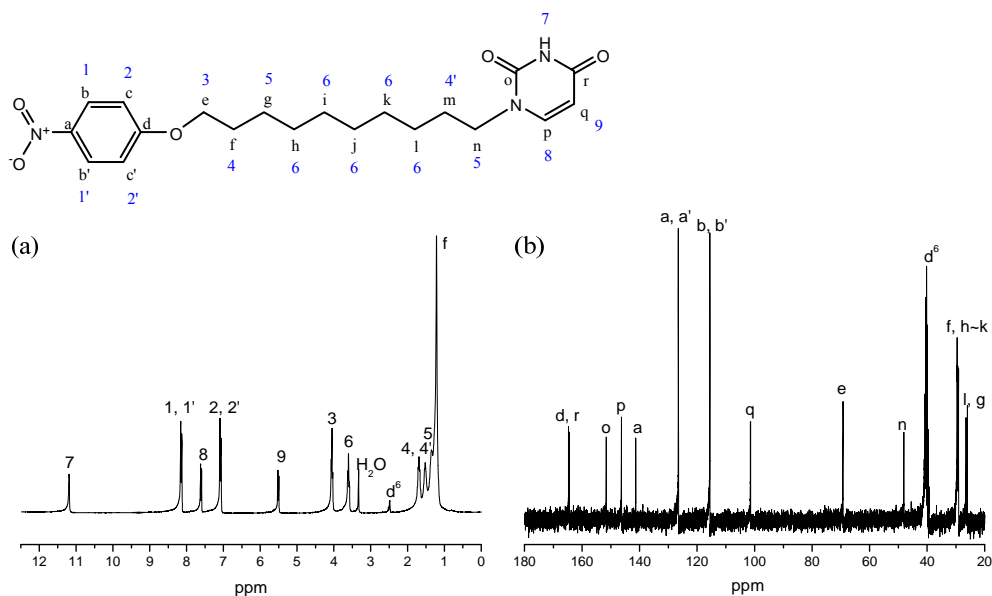


Fig. S2. (a) ^1H -NMR and (b) ^{13}C -NMR spectra of monomer 2.

Nitrophenoxy-alkane-adenine (3). Monomer 3 was synthesized and purified using the same procedure described above, except for the addition of adenine (rather than uracil). Yield: 69%. M.p. = 142.6 °C. ^1H NMR (DMSO- d_6): δ = 1.22 (H6), 1.35 (H5), 1.71, 1.78 (H4, H4'), 4.06 (H3, H7), 7.12 (H2, H2'), 7.17 (H10), 8.12 (H8, H9), 8.2 (H11, H11') ppm. ^{13}C NMR (DMSO- d_6): δ = 25.87 (l, g), 29.2 (f, h-k), 43.87 (n), 69.18 (e), 115.86 (c, c'), 119.19 (q), 126.5 (b, b'), 141.81 (a), 150.51 (p), 153.15 (s), 156.48 (r), 164.48 (d) ppm.

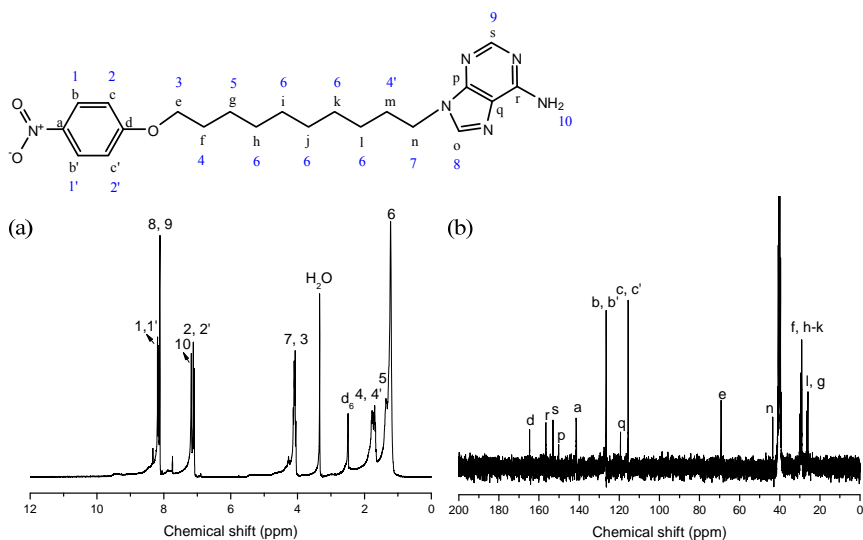


Fig. S3. (a) ^1H -NMR and (b) ^{13}C -NMR spectra of monomer 3.

Aminophenoxy-alkane-uracil (4). Monomer **3** (7.69 g, 20.0 mmol), 10% Pd/C (0.15 g), and hydrazine monhydrate (5 mL) were added to ethanol (200 mL) under an Ar atmosphere and then stirred at 80 °C for 3 h. The suspension was filtered to remove the Pd/C catalyst and then the filtrate was crystallized in ethanol. Yield: 89%. M.p. = 168.53 °C. ¹H NMR (DMSO-*d*₆): δ = 1.25 (H6), 1.35 (H5), 1.49-1.66 (H4, H4'), 3.59 (H7), 3.77 (H3), 4.55 (H11, H11'), 5.5 (H10), 6.46 (H2, H2'), 6.58 (H1, H1'), 7.61 (H9), 11.16 (H8) ppm. ¹³C NMR (DMSO-*d*₆): δ = 26.2 (l, g), 29.45 (f, h-k), 48.07 (n), 68.63 (e), 101.26 (q), 115.28–115.93 (a, a', b, b'), 143 (a), 146.29 (p), 150.51 (d), 151.48 (o), 164.56 (r) ppm.

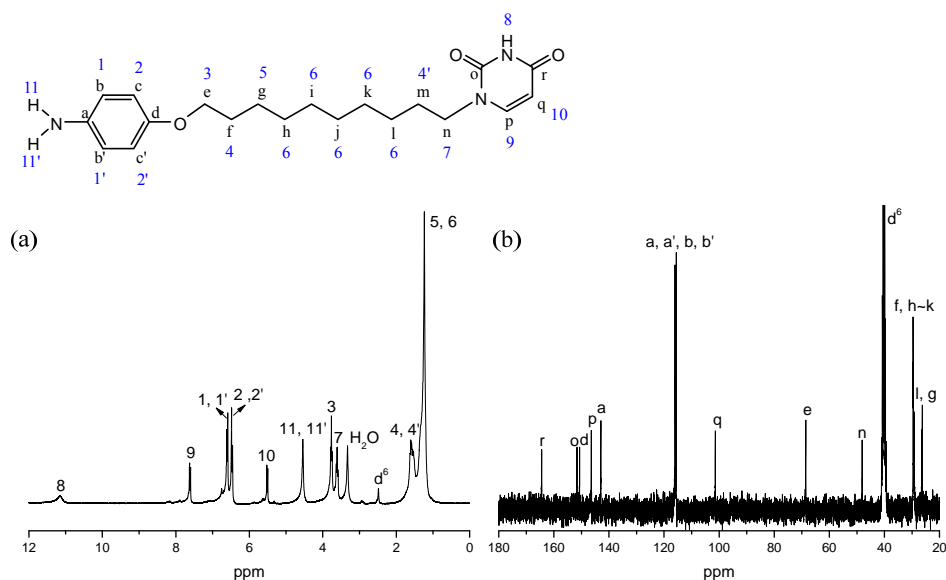


Fig. S4. (a) ¹H-NMR and (b) ¹³C-NMR spectra of monomer 4.

Aminophenoxy-alkane-adenine (5). Monomer **5** was synthesized and purified using the procedure described above, except for the addition of monomer **3** (rather than monomer **2**). Yield: 85%. M.p. = 199.0 °C. ¹H NMR (DMSO-*d*₆): δ = 1.22 (H6), 1.35 (H5), 1.59, 1.76 (H4, H4'), 3.76 (H7), 4.09 (H3), 5.56 (H11, H11'), 6.49 (H2, H2'), 6.59 (H1, H1'), 7.19 (H10), 8.16 (H8, H9) ppm. ¹³C NMR (DMSO-*d*₆): δ = 26.43 (l, g), 29.35 (f, h-k), 44.03 (n), 68.64 (e), 115.24–115.98 (b, b', c, c'), 141.34 (o), 142.78 (a), 150.23 (s), 150.63 (d), 153.06 (p), 156.76 (r) ppm.

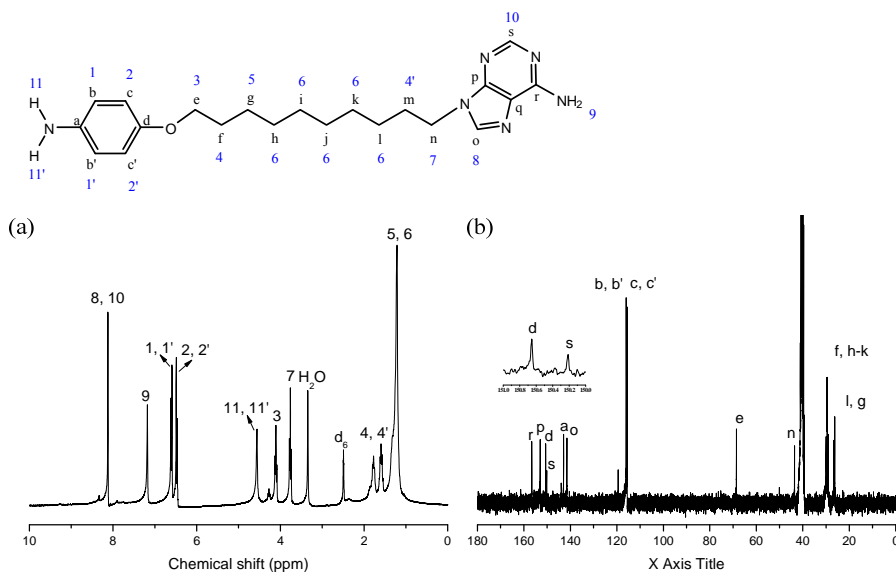


Fig. S5. (a) ^1H -NMR and (b) ^{13}C -NMR spectra of monomer 5.

Alternating poly(styrene-co-maleic anhydride) copolymer (SMA, Polymer 6). Mah (4.9 g, 50 mmol) was dissolved with heating (75 °C, 30 min) in toluene (100 mL) in a three-neck round-bottom flask. A solution of St in toluene (5.4 g, 50 mmol) was then added dropwise. The polymerization proceeded under Ar at 80 °C for another 30 min, during which time a white precipitate appeared. The SMA product was filtered off, washed thoroughly with toluene, and then dried at 50 °C in a vacuum oven for 10 h. Yield: 75%. ^1H NMR (DMSO- d_6): δ = 6.0–7.6 (ArH), 1.2–3.8 (aliphatic CH_2 and CH) ppm. IR: ν = 1853, 1779 (C=O), 696 (C=C phenyl) cm^{-1} .

SMA-alkane-adenine (SMA-A, Polymer 7). A solution of polymer 6 (1 g), monomer 5 (3 g), isoquinoline (1 mmol), and acetic acid (10 mL) in a 100-mL round-bottom flask was heated under reflux for 24 h before being cooled and poured into methanol (250 mL). The precipitate was filtered off, washed with methanol, and dried under vacuum. Yield: 79%. T_g = 168.5°C. ^1H NMR (DMSO- d_6): δ = 0.95–1.5 (e), 1.5–2.07 (d, d', l), 3.99–4.25 (c, c'), 6.48–6.62 (g, f), 6.96–7.07 (a), 6.62–8.01 (h–j), 8.03–8.56 (b) ppm.

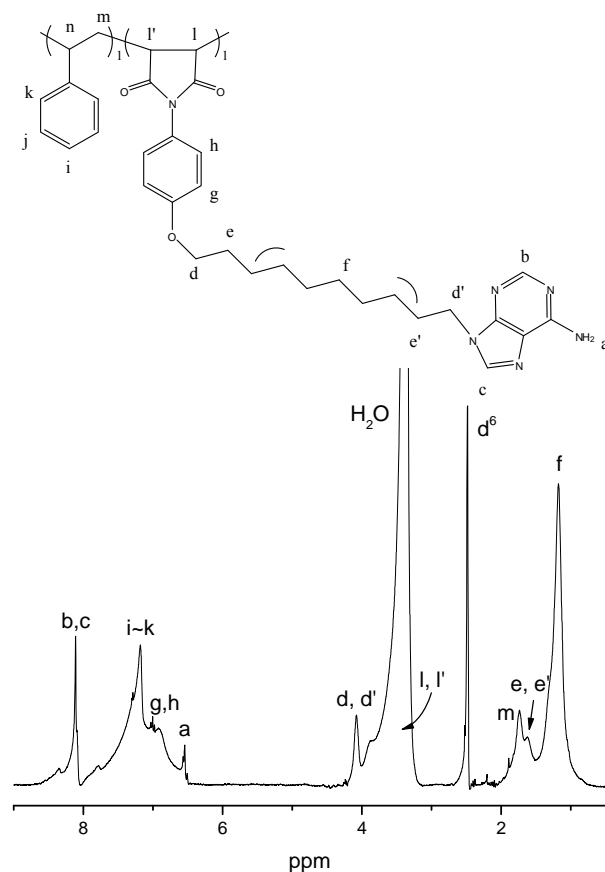
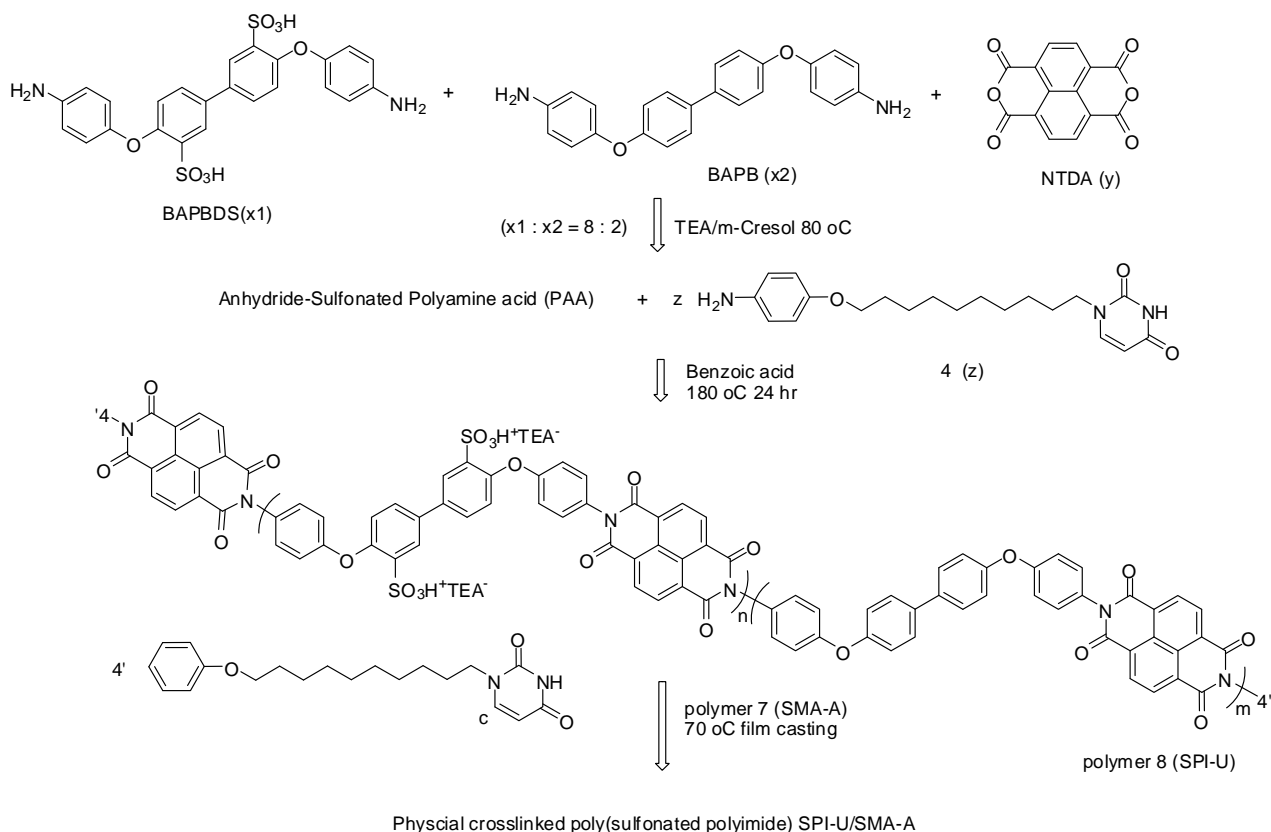


Fig. S6. ^1H -NMR spectra of monomer polymer 7.

Controlled-molecular-weight alkane-uracil-terminated sulfonated polyimide oligomers (SPI-U, Polymer 8). In a one-pot high temperature imidization process, control over the molecular weight and end group functionality was achieved using stoichiometrically adjusted amounts of the monomers (Scheme 2). A completely dried 150-mL four-neck flask was charged with BAPBDS (7.61 g, 14.4 mmol), BAPB (1.32 g, 3.60 mmol), *m*-cresol (80 mL), and TEA (8 mL), with stirring under an Ar flow. After BAPBDS had completely dissolved, NTDA (4.96 g, 18.5 mmol) and benzoic acid (3 g) were added. The reaction mixture was heated at 80 °C for 1 h and then monomer **4** (0.32 g, 0.9 mmol) was added and the mixture heated for another 4 h. Isoquinoline (2.4 g) was added and the mixture heated at 180 °C for 24 h. The resulting polymer solution was precipitated into IPA. The polymer was filtered off, purified through Soxhlet extraction with methanol overnight, and then dried at 120 °C in vacuo for at least 24 h (yield: 92%). Sulfonated polyimide (SPI) was

synthesized and purified using the same procedure, but without the addition of monomer **4** (yield: 94%). M_n (determined using ^1H NMR spectroscopy): SPI-U = 25,400 g mol^{-1} ; SPI-U₃₂₅₀ = 3250 g mol^{-1} . Intrinsic viscosity (IV, in *m*-cresol at 30 °C): SPI = 0.88 dL g^{-1} ; SPI-U = 0.39 dL g^{-1} ; SPIs-U₃₂₅₀ = 0.26 dL g^{-1} . Polymer **8**: ^1H NMR (DMSO-*d*₆): δ = 0.71–2.02 (e, f), 3.92–4.33 (d, d'), 5.44–5.57 (b), 6.94–7.28 (h), 7.28–7.57 (g), 7.57–8.0 (j), 8.6–9.2 (k), 11.16–11.32 (a) ppm. IR: ν = 1705 (C=O_{sym}), 1659 (C=O_{asym}), 1368 (C–N imide), 1197 (S=O_{asym}), 1034 (S=O_{sym}) cm^{-1} .

Scheme S2. Schematic representation of the preparation of the crosslinked SPI-U/SMA-A with an m:n ratio of 8:2.



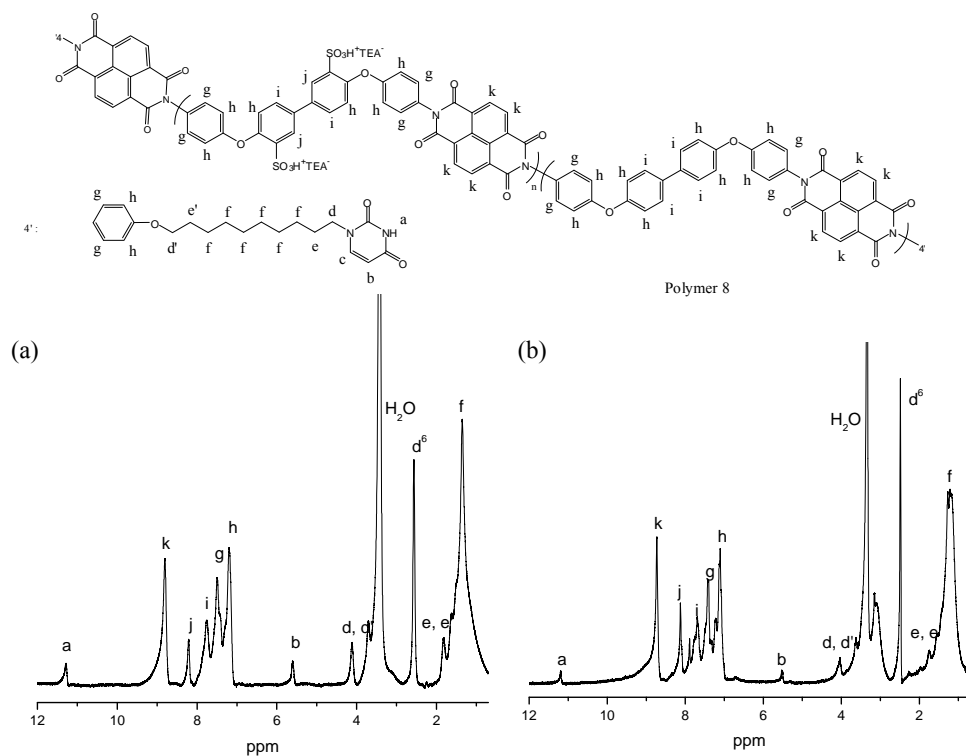


Fig. S7. $^1\text{H-NMR}$ spectrum of polymer 8. (a) $\text{SPI-U} = 3250 \text{ g mol}^{-1}$; (b) $\text{SPI-U}_{3250} = 25,400 \text{ g mol}^{-1}$

Membrane preparation.

SPI and SMA-A were dissolved in *m*-cresol and stirred at 70 °C for 3 h. The SPI/SMA-A solution was cast onto a glass Petri dish and then placed in an oven for at least 24 h and then heated at 120 °C to remove residual solvent. After cooling to room temperature, the membrane was removed from the dish by soaking it in deionized water. The blended films were then equilibrated in 1 M H_2SO_4 at room temperature for 24 h. All membranes were stored in water at room temperature prior to use. The SPI-U/SMA-A membrane was prepared using the same procedure, except for the addition of SPI-U (rather than SPI).

Ionic exchange capacity (IEC)

Previous studies have indicated that the formation of the acid-base complexes within PEMs give rise to perturbations when measuring the IEC. This is the result of the exchange of the acid protons of the PEMs being more difficult as compared to for other kinds of sulfonated polymers^{S2},

which was also the case in the present study. To eliminate this effect, the membrane was kept in the titration solution until the measurement was completed. The IEC values measured from this method were in good agreement with the theoretical values (Table S1).

S2. (a) J. Rozière, D. J. Jones, M. Marrony, X. Glipa, B. Mula, *Solid State Ionics*, 2001, **145**, 61.;(b) J. Jouanneau, R. Mercier, L. Gonon, G. Gebel, *Macromolecules*, 2007, **40**, 983.;(c) F. Zhang, N. Li, Z. Cui, S. Zhang, S. Li, *J. Membr. Sci.*, **2008**, **314**, 24.

Membrane Characterization.

$^1\text{H NMR}$ spectra were recorded at 25 °C using an INOVA 500 MHz NMR spectrometer. *FTIR* recorded using Nicolet Avatar 320 *FTIR* spectrometer; 32 scans were collected at a spectral resolution of 1 cm^{-1} . The ionic exchange capacity (*IEC*) was measured using a conventional titration method (ASTMD2187). The water uptake (*WU*) was obtained using the equation $WU = W_s - W_d / W_d$, where W_s and W_d are the weights of the wet and dry membranes, respectively. The proton conductivity (σ , S cm^{-1}) was obtained using the equation $\sigma = l / (R \times S)$, where l is the distance between the reference electrodes and S is the cross-sectional area of the membrane. The activation energy (E_a , kJ mol^{-1}), the minimum energy required for proton transport, for each membrane was obtained from the gradients of Arrhenius plot using the following equation: $\sigma = -E_a / RT$, where σ is the proton conductivity (S cm^{-1}), R is the universal gas constant ($3.314 \text{ J mol}^{-1} \text{ K}$), and T is the absolute temperature (K). The methanol diffusion coefficient of the membrane was measured using a two-chamber liquid permeability cell. The methanol concentration (6M) in the water cell was determined periodically using a *GC-8A* gas chromatograph (Shtmadu, Tokyo, Japan). The hydrolytic durability to free radical attack was examined in the aqueous solution containing H_2O_2 (30 wt%) and ferrous ammonium sulfate (30 ppm) maintained at 30 °C (the area of each sample was 1.0 cm^2). Differential scanning calorimetry (*DSC*) was performed using a DuPont 910 *DSC-9000* controller operated under an atmosphere of dry N_2 . A DuPont Q100 thermogravimetric analyzer (*TGA*) was used to investigate the thermal stability of the membranes;

the samples (~10 mg) were heated from ambient temperature to 850 °C under a nitrogen atmosphere at a heating rate of 20 °C/min. The carbon, hydrogen, and nitrogen studies of the samples were obtained using a CHN-O-Rapid elemental analyzer (Foss. Heraeus, Germany) GC/MS spectra were acquired using a Micromass Trio 2000 mass spectrometer (Micromass, Beverly, MA). The resulting data were used to identify the real molecular weights of the samples.

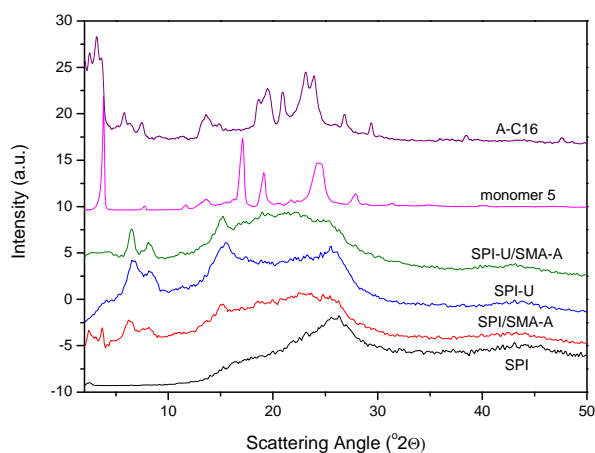


Fig. S8. WAXD data for SPI/SMA-A and SPI-U/SMA-A complexes.



Fig. S9. Optical micrograph of inverted vials 20-30 min at room temperature after vial inversion with (left) the elastic gel SPI-U/SMA-A and (right) the crosslinking SPI-U/SMA-A fluid after heating at 80 °C. All polymers and additives were dissolved in m-cresol.

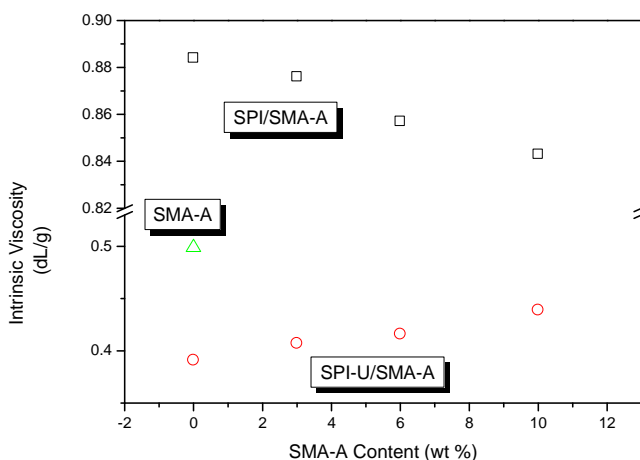


Fig. S10. The intrinsic viscosity of SMA-A, SPI/SMA-A, and SPI-U/SMA-A.

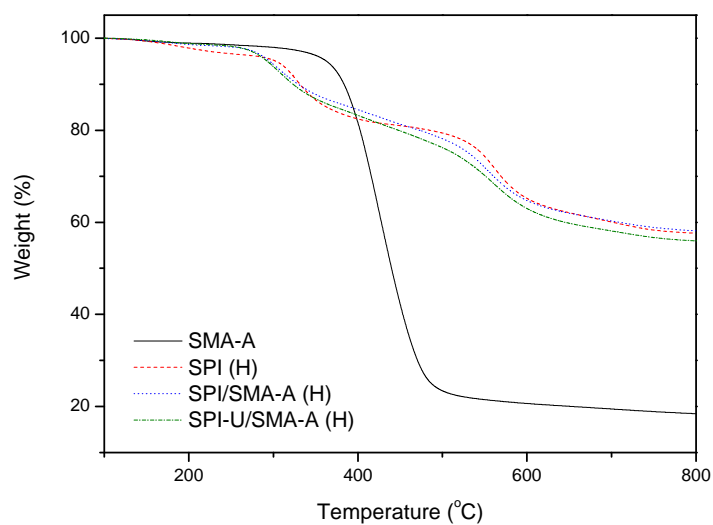


Fig. S11. TGA curves for the SMA-A, SPI (H), SPI/SMA-A (H), and SPI-U/SMA-A.

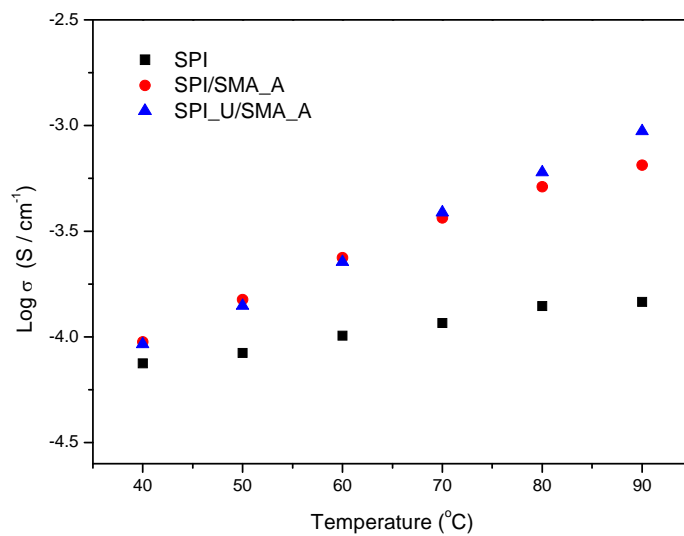


Fig. S12. Temperature dependence of the proton conductivity for the SPI, SPI/SMA-A, and crosslinked SPI-U/SMA-A at anhydrous condition.

Table S1. Characterization Data for SPI, SPI/SMA-A, and SPI-U/SMA-A

Membrane	SMA-A Content (wt%)	Proton conductivity (mS cm ⁻¹)		Methanol permeability (× 10 ⁻⁷ cm ² s ⁻¹) ^a	Selectivity (× 10 ³ S s cm ⁻³) Φ	Oxidative Stability (h) ^b	
		at 30 °C/90% RH	at 80 °C/50% RH			τ_1^c	τ_2^c
SPI	0	78.1	19.0	8.52	9.2	21	30
SPI/SMA-A	10	65.5	35.3	4.47	14.7	27	36
SPI-U/SMA-A	10	46.8	51.1	0.94	49.8	29	41
Nafion 117	0	93.0	26.0	13.1	7.1	-	-

^a Measured at room temperature.

^b Measured at 30 °C in 30% H₂O₂ containing 30 ppm FeSO₄.

^c τ_1 and τ_2 refer to the expended times required for the membranes to begin to dissolve and to completely dissolve in solution, respectively.

Table S2. Characterization of SPI, SPI/SMA-A, and SPI-U/SMA-A.

Membrane	SMA-A Content (wt%)	Ion exchange capacity (meq/g)			Water uptake (wt %) ^c	$\lambda(\text{H}_2\text{O}/\text{SO}_3\text{H})$
		Calculated IEC _{th} ^a	Titration IEC _{tit} ^b	IEC _{tit} /IEC _{th} (%)		
SPI	0	2.19	1.99	90.9	76.4	21.3
SPI/SMA_A	10	1.98	1.74	87.9	55.3	17.6
SPI-U/SMA-A	10	1.92	1.68	87.5	48.7	16.1
Nafion 117	0	-	1.02	-	35.6	19.4

^a IEC calculated from DS.

^b IEC measured with titration.

^c Measured at room temperature.