Supporting Information

Polyaromatic Perfluorophenylsulfonic Acids with High Radical Resistance and Proton Conductivity

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EXPERIMENTAL SECTION

Materials. *p*-Terphenyl (99+%, Acros), 2,2,2-trifluoroacetophenone (TFAp, 99%, Sigma-Aldrich), perfluoroacetophenone (PFAp, 98%, Matrix Scientific), triflic acid (TFSA, 99%, Acros), methanol (reagent grade, VWR), sodium hydrosulfide hydrate (NaSH \cdot xH₂O, >60% purity, Sigma-Aldrich), *N*,*N*-dimethylacetamide (DMAc, 99+%, Sigma-Aldrich), hydrochloric acid (HCl, reagent grade 37%, VWR), glacial acetic acid (ACS reagents, VWR), hydrogen peroxide solution (35%, Sigma-Aldrich), tetrahydrofuran (THF, VWR, reagent grade), hexane (VWR, reagent grade), *N*-methyl-2-pyrolidone (NMP, reagent grade, Sigma-Aldrich), chloroform-*d* (99.8% D, Sigma-Aldrich), and DMSO-*d*₆ (99.96% D, Sigma-Aldrich) were all used as received. Dichloromethane (DCM, Analytical, VWR) was dried over molecular sieves prior to use.

Preparation of precursor homopolymer P100. A 10 mL one-neck flask was charged with PFAp (0.74 g, 2.8 mmol), *p*-terphenyl (0.46 g, 2.0 mmol), and anhydrous DCM (2.7 ml). The reaction mixture was cooled to 0 °C using an ice bath before adding of TFSA (2.7 mL, 30.8 mmol) dropwise and the reaction mixture was stirred for 30 min. The temperature was then increased to room temperature and the reaction mixture was stirred at this temperature

for 48 h. The resulting highly viscous dark-blue, inhomogeneous reaction mixture was poured slowly into methanol. The precipitated white fiber of P100 was washed thoroughly with hot methanol and then dried at room temperature under vacuum for 24 h (yield 98%, 1.13 g).

Preparation of precursor copolymers P55, P72 and P83. The IEC of the copolymers was controlled by adjusting the molar ratio between PFAp and TFAp. The synthesis of copolymer P55 is given as an example. To a 10 mL flask was added PFAp (0.51 g, 1.96 mmol), TFAp (0.14 g, 0.84 mmol), *p*-terphenyl (0.46 g, 2.0 mmol), and anhydrous DCM (2.7 ml). The reaction mixture was cooled to 0 °C, TFSA (2.7 mL, 30.8 mmol) was added dropwise to the solution, and the reaction mixture was stirred for 30 min. The reaction mixture was heated to room temperature and held at this temperature for 48 h. The resulting dark-blue viscous reaction mixture was poured slowly into methanol. The white solid was washed with hot methanol and then dried at room temperature under vacuum for 24 h (yield 93%, 0.99 g).

Sulfonation. The synthesis of SP100 is given as an example. First, 1 g of precursor polymer P100 (corresponding to 2.10 mmol repeating units) was dissolved in DMAc (10 mL) at 90 °C. The reaction solution was cooled to room temperature before portion-wise additions of NaSH (0.65 g, 6.30 mmol). The green-blue mixture was kept for 24 h and then acidified by slowly adding a portion of aqueous HCl solution (1 M, 10 mL) over a period of 10 min. The obtained pale yellow solid was then filtered off and dried at 50 °C under vacuum for 24 h. The oxidation of the thiol groups to sulfonic acid ones was carried out with glacial acetic acid (10 mL) and hydrogen peroxide solution (7 mL) at 50 °C for 24 h, followed by 1 h at 110 °C. All solvents were then removed by vacuum distillation and the remaining gel-like product was dispersed swollen in deionized water (10 mL). The mixture was further purified by dialysis (MWCO = 3500 Da) in deionized water for 48 h, followed by freeze-drying in order to obtain the final sulfonated polymer (yield 83%, 0.927 g).

Membrane Preparation. All membranes were prepared by means of solution casting of polymers dissolved in NMP. All the polymer were dissolved in NMP to give a 10% (w/v) solution. The solution was filtrated through a 5 μ m PTFE syringe filter onto a Petri dish (\emptyset = 5 cm) which was then placed in a ventilated casting oven at 85 °C for at least 24 h. The membranes were peeled off and then soaked in deionized water to remove residual solvent. The membranes were acidified by treating in boiling 1 M H₂SO₄ solution for 2 h, and were then washed with boiling deionized water for 2 h.

Characterization. ¹H and ¹⁹F spectra were obtained with Bruker DRX 400 spectrometer at 400.13 MHz, using either deuterated dimethyl sulfoxide (DMSO- d_6 , $\delta = 7.26$ ppm) or chloroform (CDCl₃, $\delta = 2.50$ ppm) solutions of the polymers. Size exclusion chromatography (SEC) was conducted to determine the molecular weight, polydispersity index (D), and intrinsic viscosity ([η]) of the precursor copolymer in chloroform solutions at 35 °C, employing a Viscotek GPCmax equipped with three consecutive columns (KF-805, KF-804, KF-802.5) calibrated with polystyrene (PS) standard samples ($M_n = 30$ kDa, Polyscience Inc.; 96 kDa, Polymer Laboratories; 650 kDa, Water Associates) and a refractive index detector (Viscotek TDA).

The thermal stability of the precursor polymer films and the corresponding phosphonated and sulonated polymer membranes was investigated by thermogravimetric analysis (TGA) using a TGA Q500 instrument (TA Instruments). The measurements were performed under nitrogen at a heating rate of 10 °C min⁻¹ up to 800 °C. Prior to the heating ramp, the samples were preheated at 150 °C during 10 min to remove water and any solvent residues. The degradation temperatures ($T_{d,95}$ and $T_{d,onset}$) were determined at the point where 95% of the sample weight remained, and was calculated from the TGA curves by extrapolating from the curve at the peak of decomposition back to the initial weight of the polymer, respectively.

Chemical stability was measured using Fenton's reagent (3% H₂O₂ aqueous solution containing 2 ppm Fe²⁺). The residual weight (*RW*) was calculated from the membrane weight before and after immersion in Fenton's reagent at 80 °C for 1 h. The dissolution time (τ) was measured by submerging the membranes in Fenton's reagent at 80 °C.

The glass transition temperature (T_g) of the polymers was evaluated by differential scanning calorimetry (DSC) using a Q2000 DSC instrument (TA instruments) at a heating rate of 10 °C min⁻¹ under nitrogen. The samples were subjected to a heating-cooling-heating cycle between 30 and 400 °C. The collected data during the second heating scan were used to evaluate the T_g which was taken as the midpoints of the transitions recorded.

Water uptake (WU) was calculated based on the weights of membranes in the acid form by using the equation:

Water uptake (%) =
$$(W_{\rm w} - W_{\rm d})/W_{\rm d} \times 100$$
 (1)

, where W_w and W_d represent the weight of the wet and dried samples respectively. The weights of dry samples were obtained after drying the membranes under vacuum at 50 °C for at least 24 h. The weights of wet samples were measured after immersing the membranes in water at 20, 40, 60, and 80 °C for 12 h and removing the excess water from the surface.

The weight based ion exchange capacity (IEC) of the membranes in acid form was measured by the titration method. The dry membrane was immersed in 1.0 M NaCl solution for 1 day with vigorous stirring. The released protons were titrated with a 0.01 M NaOH solution using phenolphthalein as an indicator, before calculating IEC as:

IEC (mequiv
$$g^{-1}$$
) = ($V_{\text{NaOH}} \times N_{\text{NaOH}}$)/ W_{d} (2)

, where V_{NaOH} and N_{NaOH} are the volume and normality of NaOH solution, respectively, and W_{d} is the weight of dry membrane.

The proton conductivity of each membrane sample was conducted both under fully hydrated conditions as a function of temperature and under reduced relative humidity (RH) at

80, 100, and 120 °C. The former measurement was performed in a sealed cell (size: 1.4 cm \times 1.4 cm \times 1.0 cm) containing water with the membrane fully hydrated. A two-probe method was used in the range 20 to 120 °C by employing a Novocontrol high-resolution dielectric analyzer V 1.01S in the frequency range 10⁰ to 10⁷ Hz at 50mV. The humidity dependence of the proton conductivity from 30 to 90% at 80, 100, and 120 °C by a four-probe method with a Gamry potentiostat/galvanostat/ZRA in the frequency range 10⁻¹ to 10⁶ Hz equipped with a Fumatech MK3 conductivity cell. The humidity was equilibrated by deionized water in a closed system.







Figure S1. ¹H NMR spectra of the precursor copolymers in the Px series.

Sample	mol%	b PFAp	$M_{\rm n}^{\ \rm c}$	$M_{ m w}{}^{ m c}$	а	$[\eta]^{d}$	T_{g}^{e}	$T_{\rm d,onset}{}^{\rm f}$	
	charged ^a	obtained ^b	(kg mol ⁻¹)	(kg mol ⁻¹)		$(dL g^{-1})$	(°C)	(°C)	
P55	70	55	29	50	1.7	0.17	> 400	414	
P72	80	72	25	37	1.5	0.17	> 400	421	
P83	90	83	18	27	1.5	0.16	> 400	422	
P100	100	100	88	162	1.8	0.53	> 400	418	

Table S1. Synthesis and thermal data of the precursor polymers in the Px series.

^a mol% of PFAp in the ketone monomer feed (PFAp + TFAp). ^b mol% of PFAp residues in (co)polymer as calculated from ¹H NMR data. ^c Measured by SEC at 35 °C using chloroform as eluent. ^d Intrinsic viscosity in chloroform at 35 °C. ^e Measured by DSC. ^f Measured by TGA under N₂.

Table S2. Data of the PEMs in the SPx series and Nafion NR212.

PEM	IEC ^a (mequiv g ⁻¹)		water uptake ^b (wt%)		λ ^b ([H ₂ O]/[SO ₃ H])		(%)		σ^{d} (mS cm ⁻¹)		$T_{d,onset}^{e}$ (°C)	q_{max}^{f} (nm ⁻¹)	d ^f (nm)
	theor.	titrated	20 °C	80 °C	20 °C	80 °C	20 °C	80 °C	80 °C	120 °C			
SP55	1.17	1.13	6.0	9.8	3.0	4.8	5.9	5.9	42	50	285	2.6	2.4
SP72	1.45	1.41	16	21	6.5	8.4	4.5	7.6	104	131	283	2.6	2.4
SP83	1.62	1.58	22	30	7.6	12	8.2	11	136	171	284	2.8	2.2
SP100	1.85	1.83	25	39	7.5	12	10	21	203	257	277	2.9	2.2
NR212	-	0.92	22	45	14	27	12	18	208	264	281	1.97 ^g	3.2 ^g

^a Acid form. ^b Fully hydrated in acid form. ^c Thickness swelling in acid form, immersed. ^d Measured by EIS fully hydrated in acid form. ^e Measured by TGA in H⁺ form under N₂. ^f Measured by SAXS in H⁺ form in the dry state. ^g Data from Peng et al.^[1]



Figure S2. ¹H NMR (a) and ¹⁹F NMR (b) spectra of P55 and SP55, respectively, indicating complete and selective displacement of the fluorine atoms in the *para* positions of the PFAp residues. Spectra of P100 and SP100 recorded in CDCl₃ and DMSO- d_6 , respectively. The compositions of the Px copolymers were determined by comparing the intensity of the ¹H signals at 7.37 (g and h) and 7.44 ppm (c).



Figure S3. TGA profiles of the precursor polymers in the Px series. The values of $T_{d,onset}$ are collected in Table S1.



Figure S4. TGA profiles of the PEMs in the SPx series in the Na⁺ form. The values of $T_{d,onset}$ were 397, 402, 409 and 414 °C for sample SP55, SP72, SP83 and SP100, respectively. The corresponding value for NR212 (Na⁺ form) was 330 °C.



Figure S5. TGA profiles of the PEMs in the SP*x* series in the H⁺ form. The values of $T_{d,onset}$ are collected in Table S2.



Figure S6. ¹H NMR spectra before and after storage in Fenton's reagent at 80 °C during 1 h of (a) SP100, (b) SP83, (c) SP72 and (d) SP55 (all in H⁺ form). Spectra recorded in DMSO- d_6 (see Figure 1 and S2 for designation of signals).