Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information

Nanostructured multi-block copolymer single-ion conductors for safer high-performance lithium batteries

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Table S1. Characteristic properties of the PES-FPES block copolymer backbone and the SI ionomer

Code	**PES/FPES (kg mol^{-1})**	**M_n^{a} (kg mol^{-1})**	**M_w^{a} (kg mol^{-1})**	**I_p**	**wt% FPES**
PES-FPES	15/15	126	378	3.0	50
SI	15/15	264	724	2.7	28

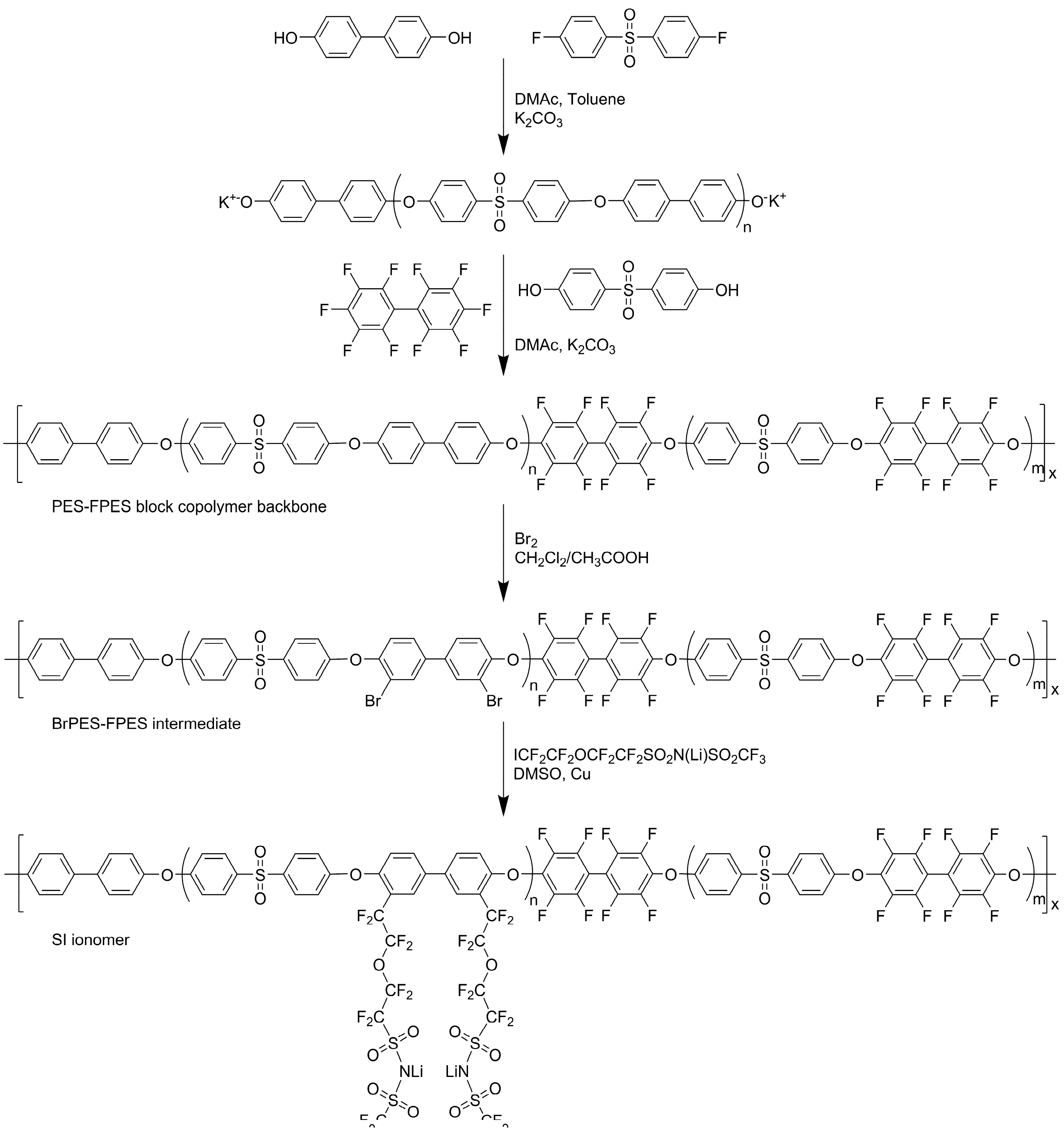


Figure S1. The synthesis procedure for the PES-FPES block copolymer backbone and the SI ionomer.

Figure S2. Photograph of an exemplary SI-S55 membrane.

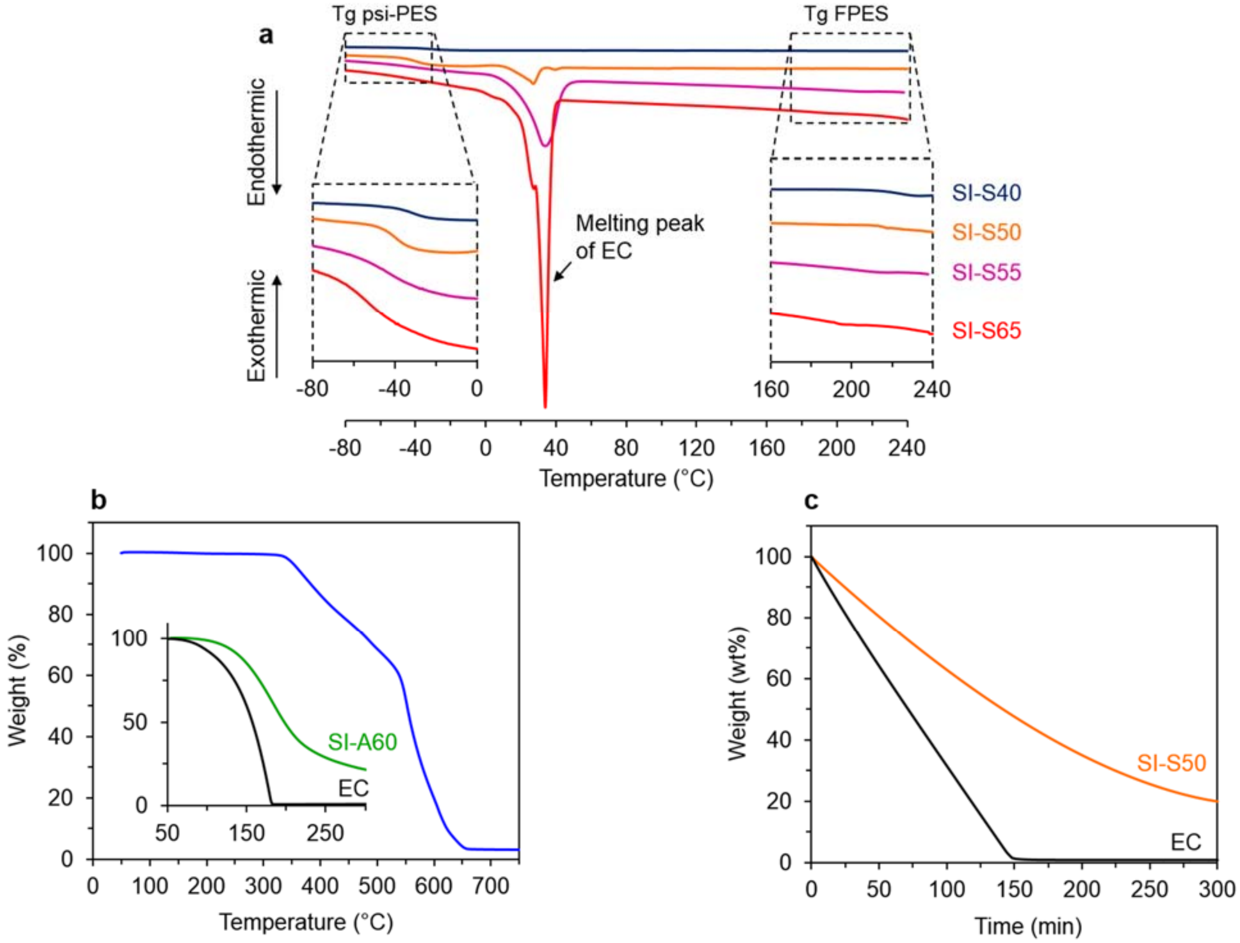


Figure S3. Thermal characterization of SI membranes: a) DSC curves of SI-S40 (dark blue), SI-S50 (orange), SI-S55 (pink), and SI-S65 (red) electrolyte membranes; b) TGA curve for the dried SI-A0 membrane (blue). Inset: Normalized TGA curves for the SI-A60 membrane (green) in comparison with that for pure EC (black); c) Evaporation rate of EC in SI-S50 membrane (orange) in comparison with that of EC absorbed in Celgard® 2500 separator (black), measured at 100 °C, applying a 40 mL min^{-1} argon flow.

Video S1 is attached as Electronic Supplementary Information, showing a SI-S55 membrane (thickness: 65-80 µm) exposed to mechanical strain by stretching the membrane between two glass pipettes. One can nicely see that the glass is bending, while the membrane itself is remaining very stable (being slightly, but reversibly stretched). This video nicely underlines the good mechanical stability of these membranes, as the membrane does not show any indication of mechanically induced damage under the given conditions.

Table S2. Enthalpy (ΔH), melting point (T_m) of EC, and glass-transition temperature (T_g) for the psi-PES block obtained by performing DSC of EC-doped SI membranes

Sample	**ΔH (kJ g^{-1} EC)**	**T_m of EC (°C)**	**$T_{g,exp}$ (°C)**	**$T_{g,theo}$[a] (°C)**
SI-0	0	//	150 ± 3	150
SI-15	0	//	51 ± 3	46
SI-35	0	//	-25 ± 3	-26
SI-40	0	//	-30 ± 3	-38
SI-45	0	//	-39 ± 3	-48
SI-50	21.2 ± 2	31 ± 2	-45 ± 3	-58
SI-55	76.2 ± 2	32 ± 2	-46 ± 3	-66
SI-60	83.8 ± 3	32 ± 2	-50 ± 3	-74
SI-65	95.2 ± 3	34 ± 2	-50 ± 3	-80
SI-70	110.3 ± 3	35 ± 2	-50 ± 3	-87
EC	160.1 ± 3	37 ± 2	-114 ± 3	-114

[a]Calculated based on the Flory-Fox equation as follows:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

where w_1 and w_2 are the weight fraction of the psi-PES block in the SI ionomer and the EC solvent, respectively, in the blended system (considered as being composed of only the psi-PES block and EC), while T_{g1} and T_{g2} are the T_g of the psi-PES block in dried SI membranes (150 °C) and EC (-114 °C), respectively. The FPES block does not have any impact on this calculation as its T_g is essentially independent from the EC content.

Video S2 and **Video S3** are attached as Electronic Supplementary Information, showing a Whatman glass fiber separator (to avoid any impact of the separator itself) drenched with a 1M solution of $LiPF_6$ in 1:1 mixture of EC and DMC (UBE), serving as reference, and an SI-S55 membrane, respectively, both exposed to a flame several times. This comparison highlights the inherently safer, self-extinguishing nature of the EC-containing membranes compared to the easily flammable liquid organic electrolyte.

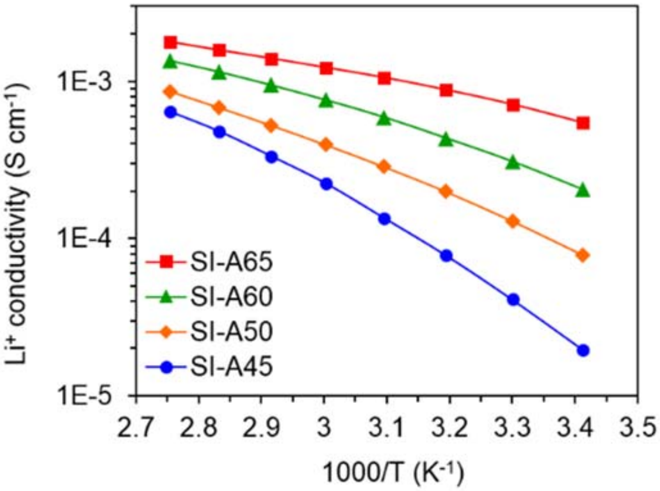


Figure S4. Ionic conductivity of DMAc-cast, EC-doped SI membranes (SI-Ax) as a function of temperature (x = 45-blue circles, 50-orange diamonds, 60-green triangles, and 65-red squares).

Table S3. Self-diffusion coefficients and the calculated transference numbers for a solution of LiTFSI in EC and the SI-A50 membranes as function of temperature

LiTFSI (0.52 mol kg^{-1})			
T (°C)	**D_{Li} (× 10^{-10} m^2s^{-1})**	**D_F (× 10^{-10} m^2s^{-1})**	**t^+**
25	1.30 ± 0.03	1.87± 0.02	0.41 ±0.02
40	2.01 ± 0.05	3.01± 0.07	0.40 ±0.02
55	2.78 ± 007	4.35± 0.11	0.39 ±0.02
70	3.80 ± 0.09	5.45± 0.13	0.41 ±0.02
90	5.30 ± 0.09	7.61± 0.19	0.41 ±0.02
SI-A50			
30	0.43 ± 0.01	no measurable diffusion	1
50	0.77 ± 0.02	no measurable diffusion	1
70	1.34 ± 0.03	no measurable diffusion	1
90	1.94 ± 0.04	no measurable diffusion	1

Table S4. Solvent content (SC) and lithium concentration (C_{Li}) of EC-doped SI membranes

Sample codes	**SC (wt%)**	**C_{Li} (mol kg^{-1})**
SI-0	0	1.04 ± 0.03
SI-30	30 ± 2	0.78 ± 0.03
SI-35	35 ± 2	0.68 ± 0.03
SI-40	40 ± 2	0.62 ± 0.03
SI-45	45 ± 2	0.57 ± 0.03
SI-50	50 ± 2	0.52 ± 0.03
SI-55	55 ± 2	0.47 ± 0.03
SI-60	60 ± 2	0.42 ± 0.03
SI-65	65 ± 2	0.36 ± 0.03
SI-70	70 ± 2	0.31 ± 0.03

Table S5. Comparison of the overpotential for SI-S55 and SI-A55 SIC membranes in dependence of the applied current (absolute and per cm^2)

I (mA)	**i (mA cm^{-2})**	**EWE (V)**	
		SI-S55	**SI-A55**
0.01	0.0065	0.001	0.002
0.02	0.013	0.002	0.005
0.05	0.033	0.005	0.012
0.1	0.065	0.093	0.020
0.2	0.13	0.019	0.037
0.5	0.33	0.047	0.087

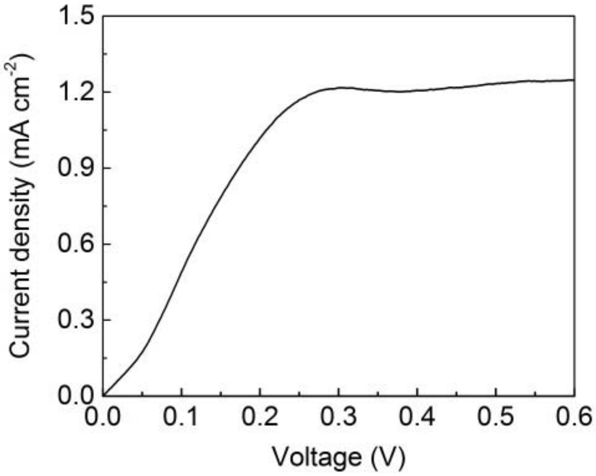


Figure S5. Determination of the limiting current density of EC-doped SI-S55 membranes by means of linear sweep voltammetry performed on symmetric Li/Li cells, applying a sweep rate of 0.05 mV s^{-1} and conducted at 50 °C. The limiting current density, i.e., the current at which the ion concentration at the electrolyte surface turns zero, is determined as the value at which it reaches a plateau, i.e., the evolving current does not change anymore independent of the applied voltage.[1,2]

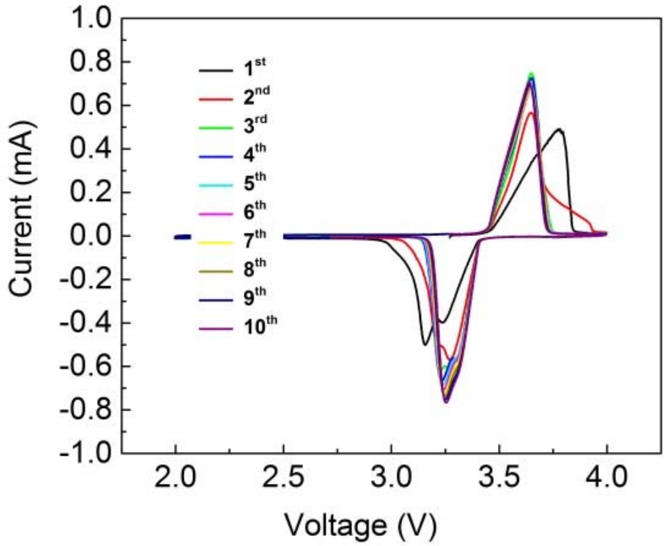


Figure S6. Cyclic voltammetry performed on pouch-type Li/LiFePO$_4$ (LFP) full-cells comprising SI-S55 SIC membranes. Li/LFP full-cells were subjected to 10 continuous cyclic sweeps in a potential range from 2.0 to 4.0 V vs. Li/Li$^+$, applying a sweep rate of 0.05 mV s^{-1}, conducted at 50 °C. The LFP composite electrode tapes were prepared according to Kim *et al*.[3] In brief, LFP (Clariant) and conductive carbon (KJB, Akzo Nobel) as well as PEO (Dow Chemical, WSR 301, MW = 4,000,000), LiTFSI (lithium bis(trifluoromethane)sulfonimide, 3M), and *N*-methyl-*N*-butyl-pyrrolidinium TFSI (PYR$_{14}$TFSI) were intimately mixed and subsequently combined to obtain a paste-like mixture. This mixture was annealed overnight at 100 °C and eventually cold-calendared to obtain 0.05 mm thick cathode tapes.

Annex 1. Synthesis of the SI ionomer

SI ionomers were obtained *via* a three-step synthesis route (**Figure S1**): (i) The synthesis of the PES-FPES block copolymer backbone, (ii) the bromination of the PES-FPES block copolymer backbone to obtain the BrPES-FPES intermediate, and (iii) the coupling of BrPES-FPES with the perfluorosulfonimide ionic functions.

A1.1 Synthesis of the PES-FPES multiblock copolymers. In a typical protocol for the synthesis of the block copolymer PES-FPES 15/15, a 100-mL three-neck round bottom flask, equipped with a mechanical stirrer, a condenser, an argon inlet-outlet, and a Dean-Stark trap, was charged with DFDPS (4.000 g, 15.733 mmol) and BP (3.010 g, 16.164 mmol). DMAc (30 mL) was added to provide ~25% (w/v) of monomer in the solvent. As the mixture was completely dissolved, K_2CO_3 (6.701 g, 0.0485 mol) and 15 mL of toluene, serving as azeotroping agent, were added. The ratio of DMAc to toluene (v/v) was 2:1. The reaction bath was heated to 150 °C and kept at this temperature for 4 h to dehydrate the system. Then, the bath temperature was slowly increased to 160 °C to completely evaporate the toluene. Subsequently, the temperature of the reaction bath was decreased to 120 °C and the polymerization was allowed to proceed at this temperature for 24 h. Afterwards, the reaction bath was cooled down to 70 °C and K_2CO_3 (3.084 g, 0.0223 mol), a solution of 1.862 g DHDPS (7.439 mmol in 5 ml) in 5 mL DFBP (2.630 g, 7.870 mmol), and 20 mL of DMAc were added to the reaction medium. After 2 h the mixture was precipitated into 1000 mL of 1M HCl under magnetic stirring and kept for 8 h before being filtered and rinsed with distilled water, until a neutral pH was reached. The final product was dried under vacuum at 100 °C for 12 h.

^{1}H-NMR: ($CDCl_3$): δ (ppm) 7.91–7.89 (d, 4H), 7.83–7.81 (d, 4H), 7.52–7.50 (d, 4H), 7.09–6.98 (m, 12H).

^{19}F-NMR: ($CDCl_3$): δ (ppm) -137.81 (s, Ar–F), -138.20 (m, Ar–F), -153.28 (s, Ar–F), -153.68 (m, Ar–F).

A1.2 Synthesis of the BrPES-FPES intermediate. The bromination of PES-FPES was carried out in a mixture of distilled dichloromethane and acetic acid (10% v/v) by adding bromine (Br_2) at room temperature. In a typical procedure, 10 g of PES-FPES 15/15 (12.515 mmol of BP unit) was introduced into a 500-mL three-neck round bottom flask equipped with an argon inlet, a condenser, and a mechanical stirrer. Then 180 mL of dichloromethane (CH_2Cl_2) distilled from CaH_2 and 18 mL of distilled acetic acid were added. When the polymer was completely dissolved, 9.688 mL (0.188 mol) of Br_2 were drop-by-drop introduced to the reaction mixture and the latter was subsequently stirred for 24 h. Afterwards, the reaction mixture was poured into methanol and kept under agitation for 24 h. After that, the polymer was filtered and rinsed several times with methanol. The polymer thus obtained was dried under vacuum at 60 °C for 24 h. The overall yield for the bromination is ~95–98 %.

^{1}H-NMR ($CDCl_3$): δ (ppm) 7.91–7.89 (d, 4H), 7.85–7.82 (d, 4H), 7.77 (s, 2H), 7.45–7.43 (d, 2H), 7.08–7.06 (d, 6H), 6.96–6.94 (d, 4H)

^{19}F-NMR ($CDCl_3$): δ (ppm) -137.81 (s, Ar–F), -138.20 (m, Ar–F), -153.28 (s, Ar–F), -153.68 (m, Ar–F).

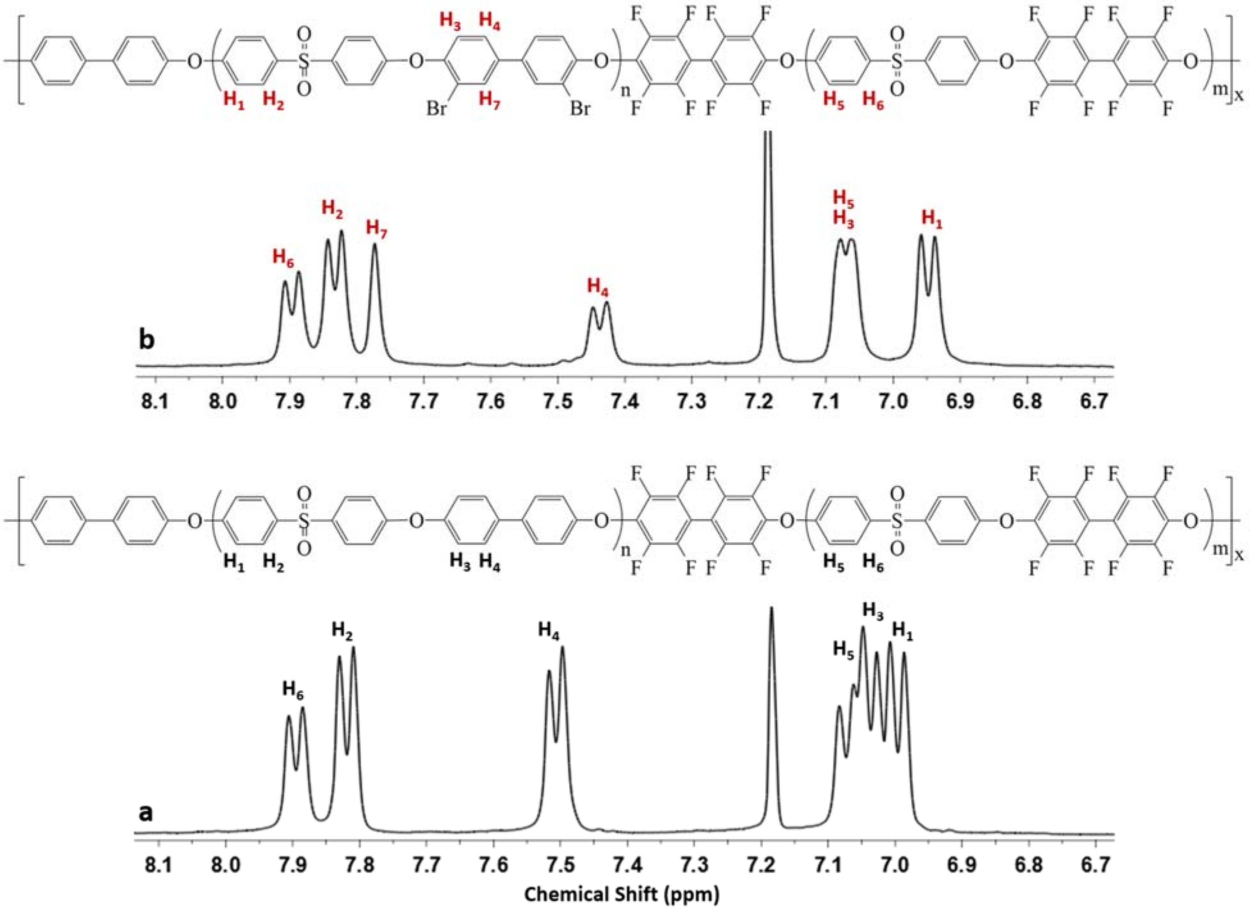
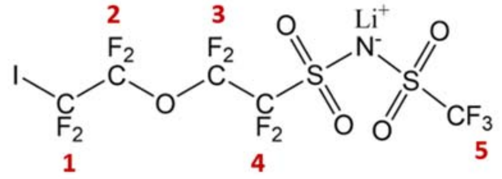


Figure A1. ^{1}H NMR spectra of (a) the PES-FPES block copolymer backbone and (b) the BrPES-FPES intermediate.

A1.3 Synthesis of the perfluorosulfonimide ionic functions (I-psiLi). For the synthesis of *N*-(trifluoromethanesulfonyl)-1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonamide lithium ($ICF_2CF_2OCF_2CF_2SO_2N^-(Li^+)SO_2CF_3$ or I-psiLi), 8.400 g (0.0563 mol) $CF_3SO_2NH_2$ were introduced into a 100-mL two-neck round bottom flask, charged with an air condenser and a magnetic stirrer. Then, 10.452 g (0.103 mol) of TEA, freshly distilled from CaH_2, and 20 mL of acetonitrile freshly distilled from CaH_2, were added. The mixture was stirred to dissolve the solid and 20.000 g (0.0469 mol) of $ICF_2CF_2OCF_2CF_2SO_2F$ were added. The mixture was heated to 40 °C and the reaction was allowed to proceed for ~36–40 h. The reaction progress was monitored by ^{19}F NMR spectroscopy. When the peak corresponding to SO_2F (44.77 ppm) disappeared, the reaction was stopped. The resulting red mixture was loaded into a rotary evaporator at 40 °C to remove the solvent. The residue was dissolved in (200–250 ml) dichloromethane, washed with 1000 mL of distilled water, and dried over magnesium sulfate. After removing the solvent once more by means of a rotary evaporator at 40 °C, a red oil was obtained.

This red oil was dissolved in 0.5M LiOH (using a 5% excess of LiOH). After stirring the solution for 15 minutes, the water was removed by freeze-drying. The resulting viscous oil was dissolved in ethyl acetate, dried over magnesium sulfate, and the solvent was removed by means of a rotary evaporator. The residue was dried under vacuum at 40 °C for 24 h to obtain a light yellow solid. The final chemical yield of the I-psiLi synthesis was ~65–70 %.

^{19}F-NMR (Acetone-d6) δ (ppm): -69.36 (t, ICF_2), -82.06 (t, CF_2O), -86.37 (t, OCF_2), -117.18 (m, CF_2SO_2), -79.87 (s, CF_3).



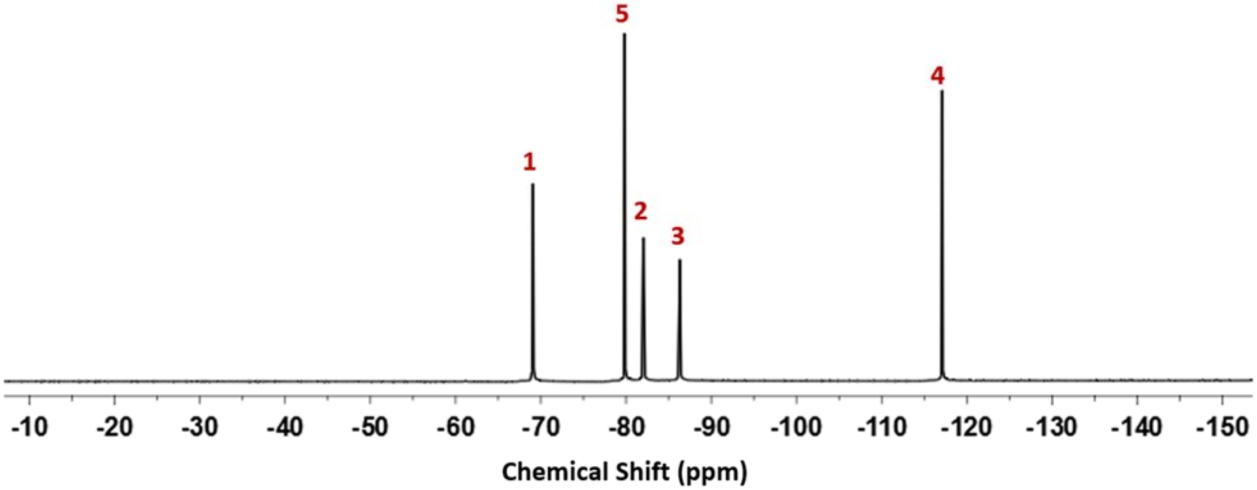


Figure A2. ^{19}F NMR spectrum of the perfluorosulfonimide ionic functions (I-psiLi).

A1.4 Synthesis of the SI Ionomer. The perfluorosulfonimide-based ionomers were synthesized *via* the Ullman coupling reaction of BrPES-FPES with lithium 1,1,2,2-tetra-fluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonimide (I-psiLi). In a typical procedure, 4.000 g (3.599 mmol of diphenyl units) BrPES-FPES 5/5, 3.43 g (54.0 mmol) powdrous copper, and 30 ml DMSO were added into a 100-mL three-neck round bottom flask, equipped with a mechanical stirrer, a condenser, an argon inlet-outlet, and an addition funnel. The mixture was stirred at 60 °C until the polymer was completely dissolved. Subsequently, the bath temperature was increased to 120 °C under continuous stirring for 2 h. Afterwards, 8.076 g (14.40 mmol) of I-psiLi were dissolved in DMSO (30% m/v) and added drop-by-drop to the reaction mixture, while the bath temperature was increased to 140 °C. The reaction was allowed to proceed at that temperature for 24 h. Afterwards, the copper powder was removed by centrifugation at 5000 rpm for 15 minutes. The ionomer was precipitated into 1000 mL 1M HCl and kept under strong agitation for 24 h. Finally, the polymer was filtered and washed with distilled water until a neutral pH was reached. The ionomer was then immersed in 1M LiOH for 12 h. The resulting ionomer was filtered and washed with deionized water until a neutral pH was reached. The powder finally obtained was dried at 80 °C under vacuum.

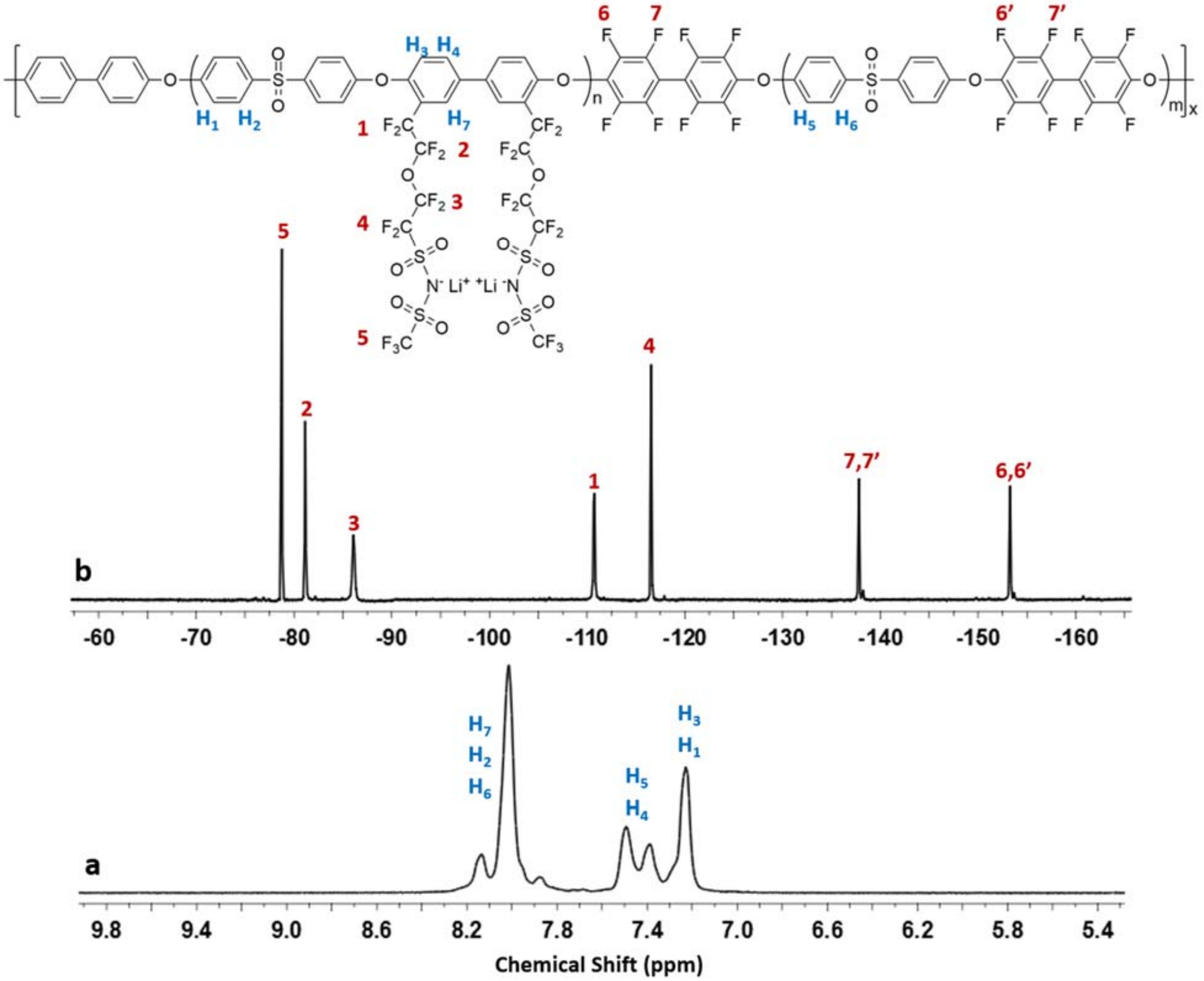


Figure A3. (a) ^{1}H NMR and (b) ^{19}F NMR spectra of the SI ionomer.

^{1}H-NMR: (DMSO.d6): δ (ppm) 8.09–7.82 (m), 7.45 (s), 7.35–7.32 (m), 7.27–7.05 (m).

^{19}F-NMR: (DMSO.d6): δ (ppm) -78.77 (d, CF_3SO_2), -81.16 (s, $–CF_2O$), -86.11 (s, $–OCF_2$), -110.70 (d, Ar–CF_2), -116.54 (s, CF_2SO_2), -137.81 (s, Ar–F), -138.20 (m, Ar–F), -153.28 (s, Ar–F), -153.68 (m, Ar–F).

References

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