## **Supporting Information**

## Nanostructured block copolymer single-ion conductors for low-temperature, high-voltage and fast charging lithium-metal batteries

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## **Supporting Experimental Information**

The lithium concentration (C<sub>Li</sub>, meq Li<sup>+</sup> per g of electrolyte) in the dried ionomer films was obtained determined from both <sup>19</sup>F NMR spectra and acid-base titration of the ionomers in their acidic form as described elsewhere<sup>[1]</sup>. The molecular mass (Mw, Mn) and polydispersity index (Ip) were determined by size exclusion chromatography coupled multi-angle laser light scattering (SEC-MALLS) with differential refractometer SOPARES RI2000 coupled to a multi-angles light scattering detector WYATT DAWN EOS at 690 nm by using 2xPLgel-Mixed-D as a column. The elution solvent was 0.1 M solution of NaNO<sub>3</sub> in dimethylformamide (Alfa Aesar-HPLC grade 99.7%), with flow rate of 1 mL/min. Injection of the sample solution was carried through the polypropylene filter of 0.2 µm.

Sample	C <sub>Li</sub> , (meq. Li <sup>+</sup> g <sup>-1</sup> ) (NMR)	C <sub>Li</sub> , ( <i>meq. Li</i> <sup>+</sup> g <sup>-1</sup> ) (titration)	M <sub>n</sub> (kg mot <sup>-1</sup> )	M <sub>w</sub> (kg mot <sup>1</sup> )	Ip
SI05-05	1.02	$1.00\pm0.02$	150	396	2.6
SI10-05	1.18	$1.15 \pm 0.03$	165	362	2.2
SI15-05	1.28	$1.25\pm0.04$	126	408	3.2

Table S1. Li concentration and molecular weights of copolymer samples

For testing the electrochemical stability window of the electrolytes, linear sweep voltammetry (LSV) was performed with a VMP3 potentiostat (Biologic) at 0.1 mV s<sup>-1</sup> in two-electrode 2032 coin cells. For the anodic sweep, a platinum (Pt) foil ( $\emptyset = 6$  mm) was used as working electrode (WE) and a lithium foil ( $\emptyset = 12$  mm) as combined counter (CE). For the cathodic sweep, a nickel (Ni) foil ( $\emptyset = 12$  mm) was used as WE and a lithium foil was used as CE.



**Figure S1.** Electrochemical stability window of PTFSI-10/5-70 compared with 1M LiTFSI in PC for the anodic scan; inset: magnification of the onset of the current evolution at elevated potentials.



**Figure S2.** Cycling stability of a Li||LFP cell at 20 °C with PTFSI-10/5-70 as the electrolyte (cut-off voltages: 2.5 V and 4.1 V).



**Figure S3.** Cycling stability of a Li||NMC<sub>111</sub> cells at 20 °C with PTFSI-10/5-70 as the electrolyte (cutoff voltages: 2.8 V and 4.2 V).



**Figure S4.** Cycling stability of Li||NMC<sub>622</sub> cells at 0.5C after the rate capability tests at (a) 20 °C and (b) 0 °C (cut-off voltages: 2.8 V and 4.2 V).



**Figure S5.** Cycling stability of a Li||NMC<sub>111</sub> cell at 20 °C using PTFSI-10/5 with 70 wt% adiponitrile as the electrolyte (cut-off voltages: 2.8 V and 4.2 V).

## Bibliography

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