Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information (ESI)

Highly efficient solid polymer electrolytes using ion containing polymer microgels

Suting Yan,[a] Jianda Xie,[b] Qingshi Wu,[a] Shiming Zhou,[c] Anqi Qu[a] and Weitai Wu*[a]

[a] *State Key Laboratory for Physical Chemistry of Solid Surfaces, and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, Fujian, China. E-mail: wuwtxmu@xmu.edu.cn*

[b] *School of Materials Science and Engineering, Xiamen University of Technology, Xiamen 361024, Fujian, China*

[c] *Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, Anhui, China*

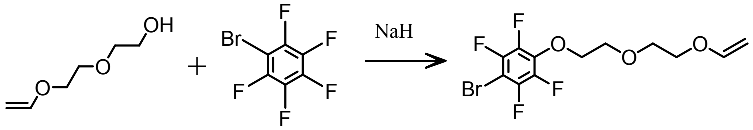
SI 1. Experimental Procedures

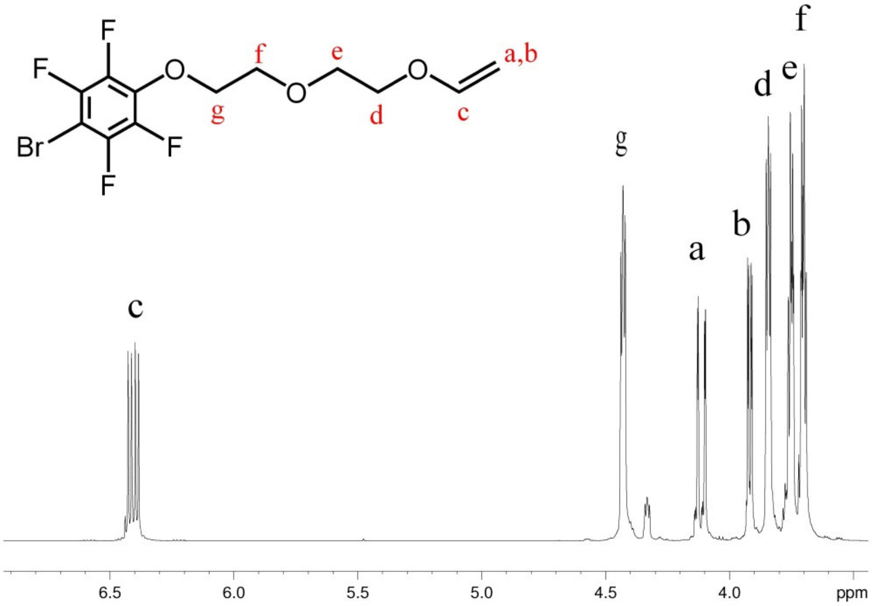
1.1. Materials

All chemicals were purchased from Aldrich. *N*-isopropylacrylamide (NIPAM) was recrystallized from a hexane-acetone (a 1:1 volume ratio) mixture and dried in vacuum. *N*,*N′*-methylenebisacrylamide (MBAAm), ammonium persulfate (APS), 2-(2-(vinyloxy)ethoxy)ethanol, 1-bromo-pentafluorobenzene, tris(pentafluorophenyl)borane, butyllithium (BuLi), NaH, tetrahydrofuran (THF), ethyl acetate, hexane, diethyl ether, acetone, anhydrous pentane, and other chemicals were used as received without further purification. The water used in all experiments was of Millipore Milli-Q grade.

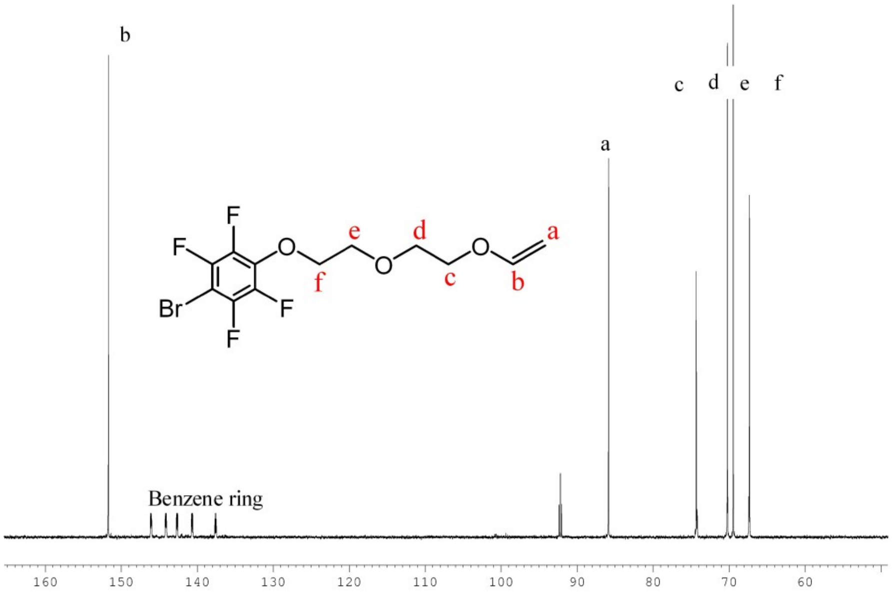
1.2. Synthesis of the LiTB

Typically, to a mixture of NaH (0.367 g, 60% in mineral oil) dispersed in dry THF (4.7 mL), 2-(2-(vinyloxy)ethoxy)ethanol (1.0 mL) was added at 0 °C via addition funnel. The mixture was stirred for 3 h before being transferred into a solution of 1-bromo-pentafluorobenzene (687.0 μL) in dry THF (4.7 mL). The mixture was allowed to react overnight to complete the reaction. The solution was condensed, and the residue was purified by column chromatography on SiO_2 with ethyl acetate/hexane (10/1 in volume ratio) as eluent to obtain 1-bromo-2,3,5,6-tetrafluoro-4-(2-(2-(vinyloxy)ethoxy)ethoxy)benzene as a colorless liquid. See below for ^{1}H and ^{13}C NMR spectra, respectively.





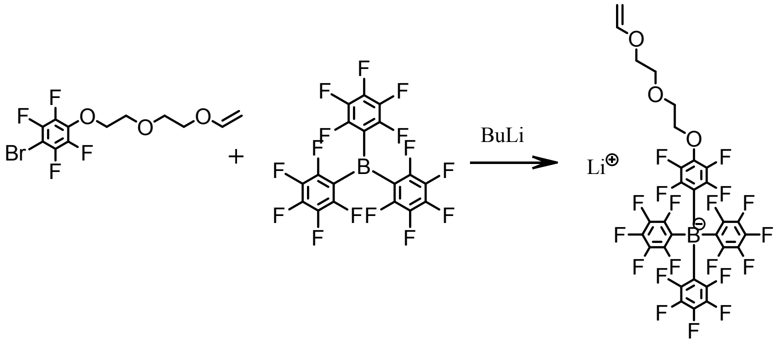
^{1}H NMR



^{13}C NMR

A solution of 1-bromo-2,3,5,6-tetrafluoro-4-(2-(2-(vinyloxy)ethoxy)ethoxy)benzene (1.000 g, 2.790 mmol) in diethyl ether (5.4 mL) was cooled to −78 °C by dry ice/acetone. A portion of BuLi (1.3

mL, 2.5 M) in hexane solution was added dropwise to the mixture over 30 min. The mixture was stirred at −78 °C for another hour before the solution of tris(pentafluorophenyl)borane (1.300 g, 2.54 mmol) in diethyl ether (5.35 mL) was added. The reaction mixture was allowed to warm up to room temperature while stirring overnight to complete the reaction. The mixture was dried by vacuum distillation and anhydrous pentane (three times) was used to wash the yellow residue. The upper pentane solution was removed by syringe, and the lower yellow phase was further dried in a vacuum oven at 50 °C for 24 h to give LiTB as a yellow powder. See Fig. S1, S2 and S3 below for ^{1}H, ^{13}C and ^{11}B NMR spectra.



1.3. Synthesis of the TPM

LiTB (8.2×10^{-3} mol L^{-1}), NIPAM (8.5×10^{-2} mol L^{-1}), MBAAm (3.5×10^{-3} mol L^{-1}), and water (25.0 mL) were added into a 100 mL round-bottom flask equipped with a stirrer, a N_2 gas inlet, and a condenser under stirring. After 30 min, the solution temperature was raised to 70.0 °C and the polymerization was initiated by adding APS (3.4×10^{-3} mol L^{-1}). The polymerization reaction was allowed to proceed for 6 hours. The solution was centrifuged twice (Thermo Electron Co. SORVALL® RC-6 PLUS superspeed centrifuge) with the supernatant discarded and the precipitate redispersed in deionized water (25.0 mL). The obtained polymer microgels were further purified by 3 days of dialysis (Spectra/Por® molecularporous membrane tubing, cutoff 12000-14000 Dalton MWCO) against water at room temperature.

1.4. Conductivity Measurements

The conductivity was measured in a glovebox by using an AC impedance spectroscopy (Solartron frequency analyser 1260) over a frequency range of 10^{-3}−10^{7} Hz. The conductivity was measured using a four-electrode probe (BekkTech LLC). Platinum wires were used as working/counter electrodes to apply a current to the sample (1.0×1.0×0.1 cm), and two platinum wires apart were used as reference electrodes.

1.5. Electrochemical Characterization

The lithium/TPM-material/stainless-steel cells were assembled in the glove box through lamination processes. The electrochemical cells were sealed in a coffee bag to carry out the experiments outside the glove box. The cells were equilibrated at 60 ^{o}C in a oven. Then cyclic voltammetries were carried out using a Solartron 1470 cell test system.

1.6. Battery Tests

Carbon-coated $LiFePO_4$ active materials were used to formulate the composite cathode. Carbon black was used to ensure the electronic percolation into the electrode volume. A composition of 60/30/10 (weight%) of $LiFePO_4$/TPM/carbon black was used. A mixture of the components with water enabled the production of an ink that was casted onto a surface-treated aluminium current collector. After evaporation of water at room temperature a composite electrode was obtained. Further drying in a vacuum oven at 60 ^{o}C for 72 h was done before the cathode was stored for two weeks in the glove box. Lithium/TPM-material/cathode batteries were assembled through lamination processes and sealed in a coffee bag. Batteries were tested using a Solartron 1470 cell test system.

1.7. Other Characterizations

XPS measurements were carried out by using a Omicron photoelectron spectrometer (Al Kα with 1 486.6eV operating at 15kV, 30W and 600μm spot size) and an Omicron Sphera II hemispherical electr on nergy analyzer. The base pressrer of the systems was 1.0×10^{-9} mbar. FTIR spectra were recorded with a Thermo Electron Corporation Nicolet 380 Fourier transform infrared spectrometer. TEM images were taken on a JEOL JEM-1400 transmission electron microscope at an accelerating voltage of 100 kV. TECNAI F-30 high resolution transmission electron microscopy operating at 300 kV, and JEM-2100 high resolution transmission electron microscopy operating at 200 kV. Scanning electron microscopy (SEM) images were obtained on Hitachi S4800 scanning electron microscope with a field emission electron gun. UV-vis absorption spectra were recorded on a Shimadzu UV-2550 UV-Vis spectrometer. The pH value was measured on a EUTECH PH 700 instruments. Dynamic light scattering (DLS) was performed on a 90Plus multi angle particle sizing analyzer equipped with a BI-9000AT digital autocorrelator (Brookhaven Instruments, Inc.). A He-Ne laser (35 mW, 659 nm) was used as the light source. All samples were passed through Millipore Millex-HV filters with a pore size of 0.80 μm to remove dust before the DLS measurements. Glass transition temperatures (T_g) were determined using a TA Q100 differential scanning calorimeter (DSC) with 10 K/min heating and cooling rates.

SI2. Figures.

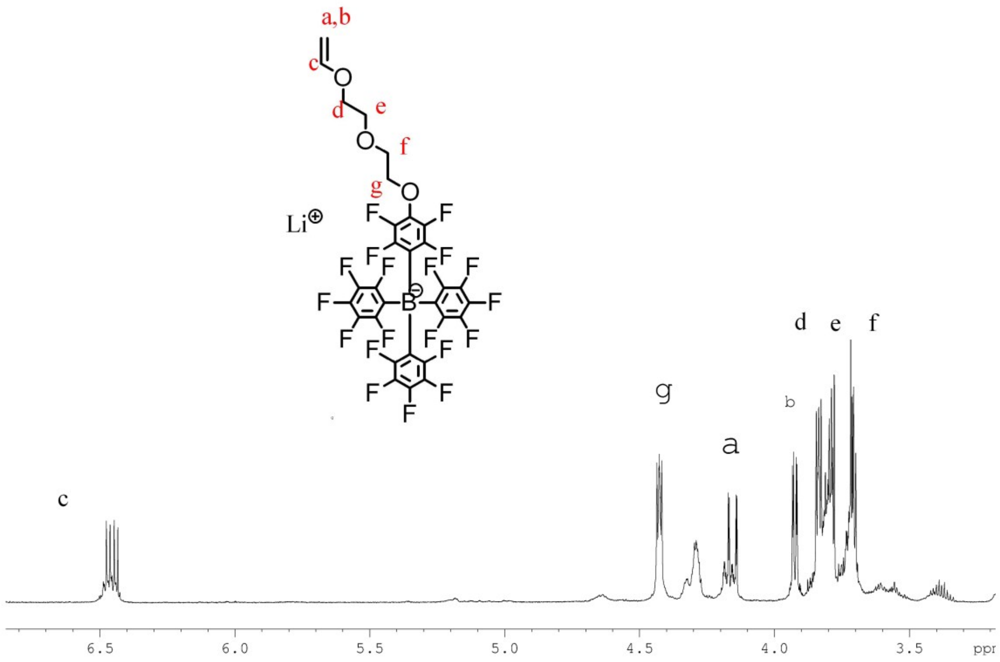


Fig. S1 ^{1}H NMR spectrum of LiTB (in d6-acetone).

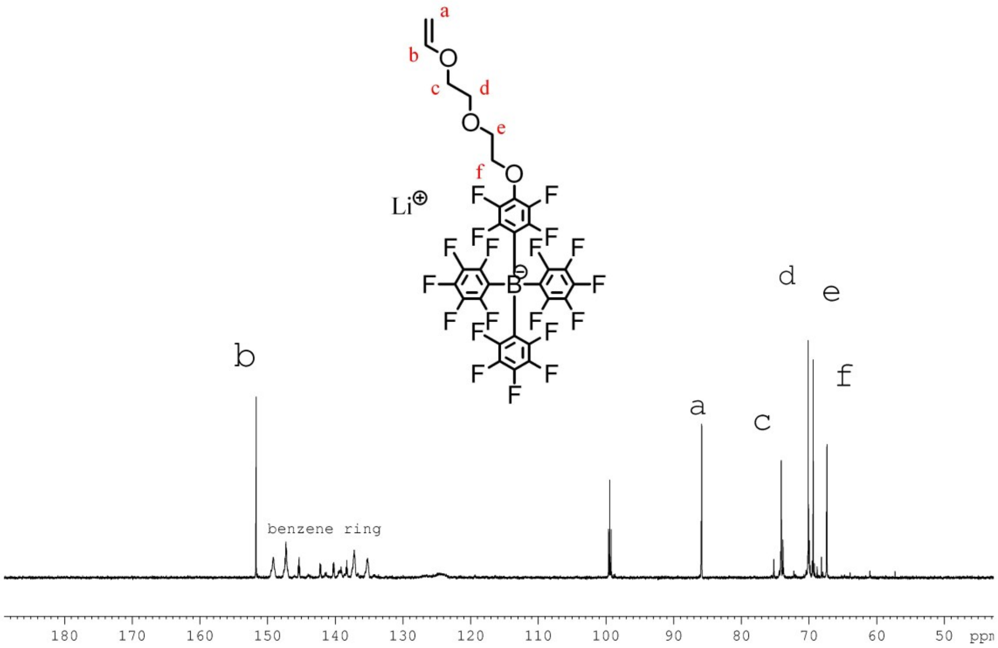


Fig. S2 ^{13}C NMR spectrum of LiTB (in d6-acetone).

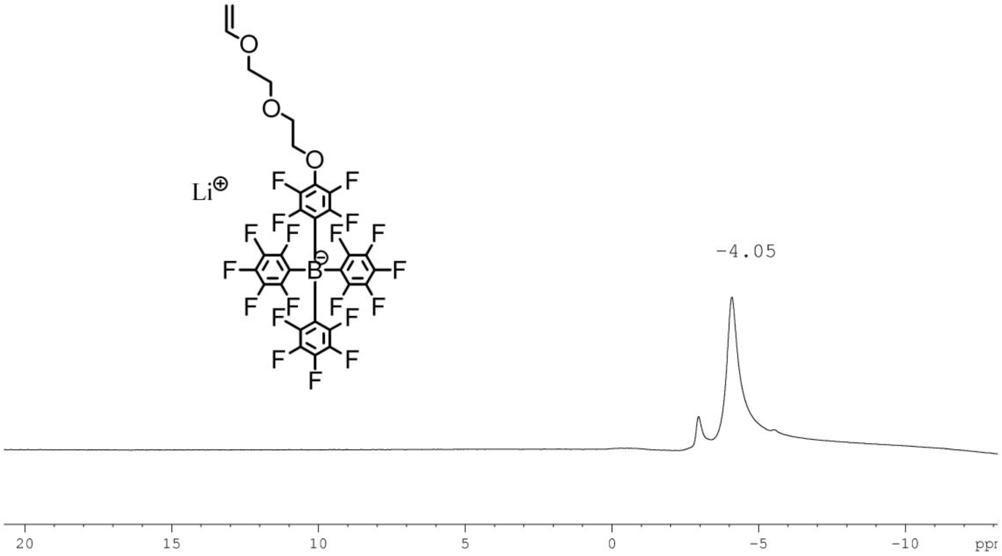


Fig. S3 ^{11}B NMR spectrum of LiTB (in d6-acetone).

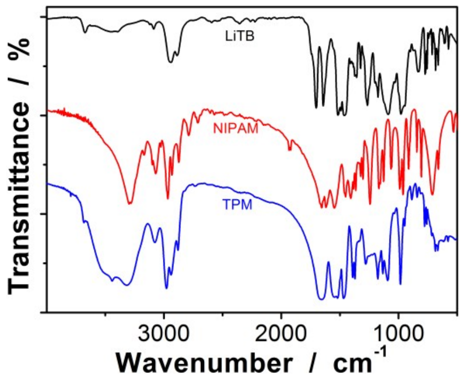


Fig. S4 FTIR spectra of LiTB, NIPAM, and the TPM.

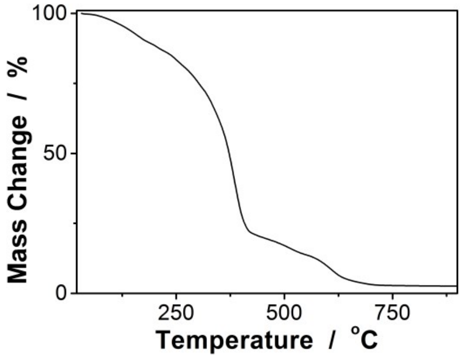


Fig. S5 TG curve of the TPM.

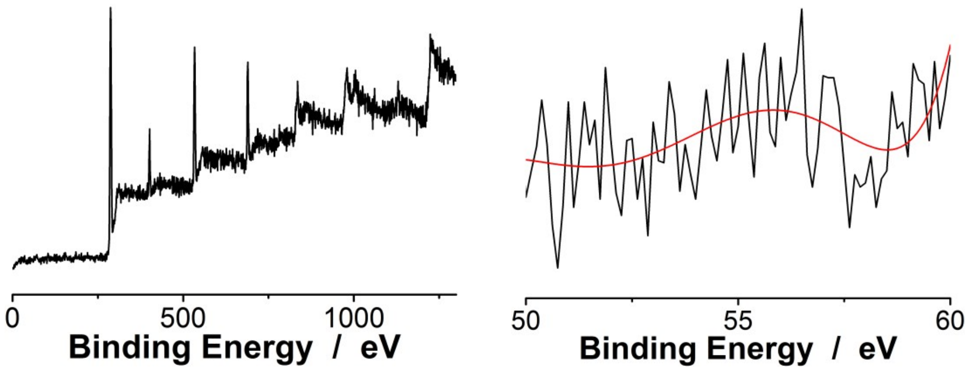


Fig. S6 XPS spectra of the TPM.

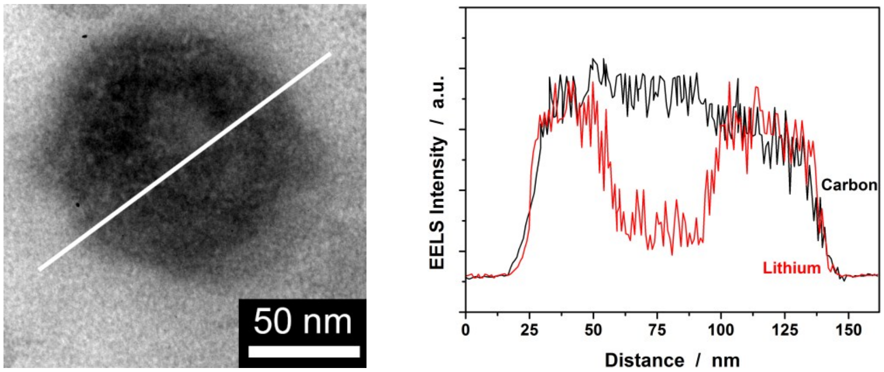


Fig. S7 EELS of the TPM along the line in the TEM image.

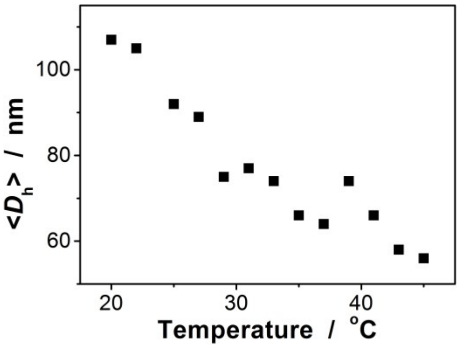


Fig. S8 Temperature-dependent <D_h> values for the TPM.

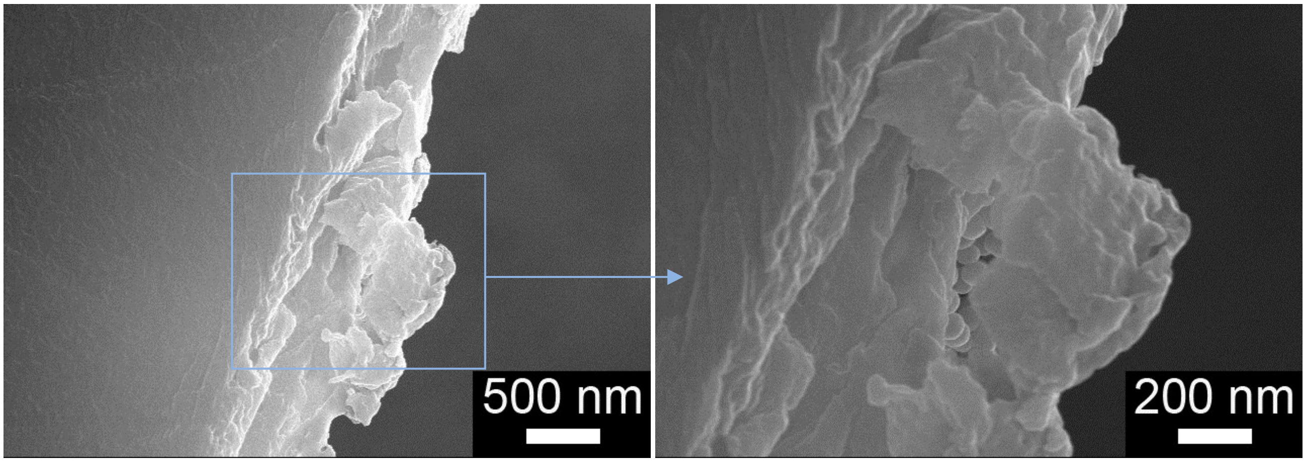


Fig. S9 SEM images of the materials fabricated by the TPM.

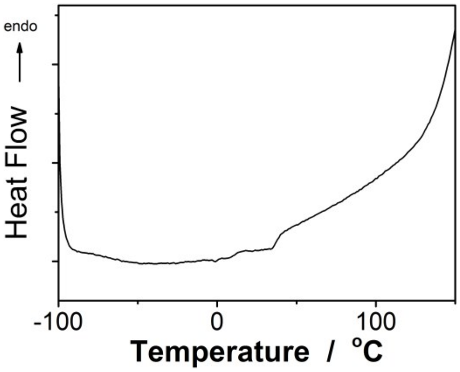


Fig. S10 DSC curve of the TPM.

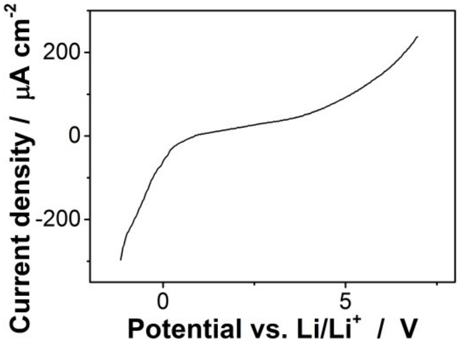


Fig. S11 Linear scan voltammetry (LSV) of a symmetric lithium cell with the TPM-material as electrolyte (Li/TPM-material/Li cell).