

**Design and synthesis of a single ion conducting block copolymer electrolyte with
multifunctionality for lithium ion batteries**

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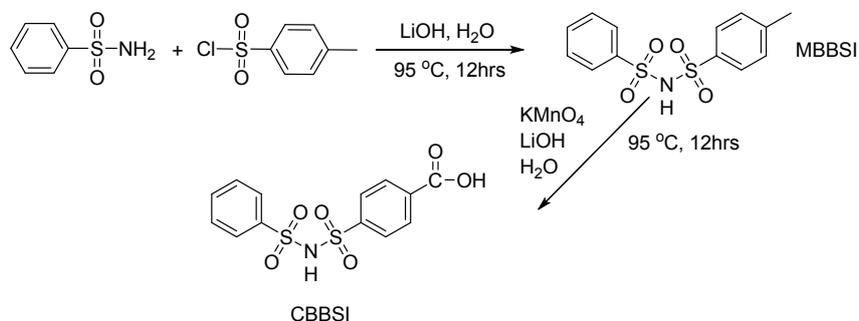
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1. Synthesis of bis(phenylsulfonyl imide) isophthalate amide (BPSIIA)

1.1. Synthesis of the 4-carboxyl benzene benzene sulphonyl imide (CBBSI)



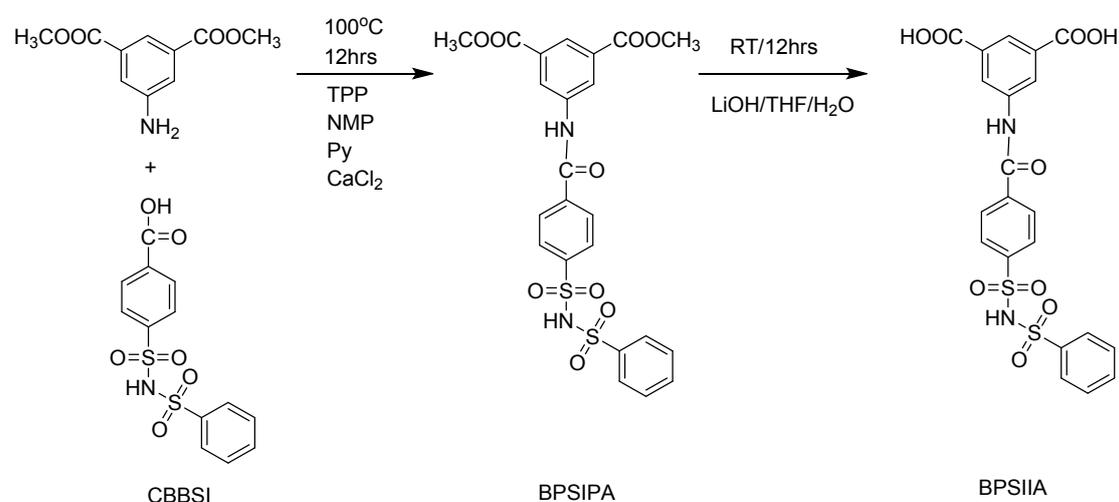
Scheme S1: Synthesis of 4-methyl benzene benzene sulphonyl imide (MBBSI) and 4-carboxyl benzene benzene sulphonyl imide (CBBSI).

Synthesis of the 4-methyl benzene benzene sulphonyl imide (MBBSI). The 4-carboxyl benzene benzene sulphonyl imide (CBBSI) was synthesized according to the procedure described by our previous works (Scheme S1).¹ P-toluenesulfonamide (34.244 g, 200 mmol) and sodium hydroxide (8.450 g, 210 mmol) were firstly dissolved in deionized water at 90 °C. Benzenesulfonyl chloride (17.662 g, 100 mmol) was then added into the solution within 2 hours followed by another 12 hours at 90 °C for completely reaction. The pH value of the reaction solution was adjusted the pH to 7 using dilute hydrochloric acid at 50 °C followed by stirring for another 12 hours. After the excessive p-toluenesulfonamide was removed by filtration, the row product was precipitated by adjusting the pH value of the filtrate to 1 using concentrated hydrochloric acid. The white precipitate was collected via vacuum filtration and dried in the oven at 80 °C. The final product was purified by recrystallization using deionized water. The yield was 59.1%. ¹HNMR (DMSO-d₆): 7.70, 7.67 (d, 2H), 7.58, 7.55 (d, 2H), 7.49, 7.47, 7.45, 7.42 (m,

3H), 7.23, 7.22 (d, 2H) and 2.34 (s, 3H) (Fig. S1a), ESI-MS $[M-H]^-$ at m/z 311.38 calculated for $C_{13}H_{13}NO_4S_2$.

Synthesis of the 4-carboxyl benzene benzene sulfonyl imide (CBBSI): 4-carboxyl benzene benzene sulfonyl imide (CBBSI) was obtained by oxidizing the methyl group of the MBBSI into carboxyl acid group by using potassium permanganate ($KMnO_4$). MBBSI (15.174 g, 48.7 mmol), lithium hydroxide monohydrate (2.045 g, 48.73 mmol) was completely dissolved in 300 mL of deionized water at 95 °C. $KMnO_4$ (19.252 g, 121.8 mmol) was added into the solution over 2 hours and left the solution for overnight at 95 °C. Manganese oxide and unreacted potassium permanganate were removed by vacuum filtration. The final product was precipitated by adding concentrated hydrochloric acid into the filtrate and the final desired product was acidified for 5 times to completely replace K^+ by H^+ with a yield of 82.6 %. 1H NMR ($DMSO-d_6$): 7.92, 7.90 (d, 2H), 7.76, 7.73 (d, 2H), 7.66, 7.64 (d, 2H), 7.43, 7.41, 7.38, 7.36, 7.34 (m, 3H) (Fig. S1b), ESI-MS $[M-H]^-$ at m/z 341.36 calculated for $C_{13}H_{11}NO_6S_2$.

1.2. Synthesis of the bis(phenylsulfonyl imide dimethyl-5-isophthalate amide (BPSIIA)



Scheme S2: Synthesis of bis(phenylsulfonyl imide) isophthalate amide (BPSIIA).

Synthesis of the bis(phenylsulfonyl imide dimethyl-5-isophthalate amide (BPSIPA)).

The bis(phenylsulfonyl imide) isophthalate amide (BPSIIA) was synthesized by following the synthesis of the precursor bis(phenylsulfonyl imide dimethyl-5-isophthalate amide (BPSIPA) (Scheme S2). CBBSI (3.4136 g, 10 mmol), dimethyl-5-aminoisophthalate (2.092 g, 10 mmol), calcium chloride (2.80 g, 25 mmol) and TPP (2.6 ml, 20mmol) were added into a mixture of NMP (10 ml) and pyridine (7.5 ml) in an argon-filled glove box. The reaction was then transferred into fumehood and connected to argon atmosphere. The reaction was kept at 100 °C for 12 hours with stirring and poured into 80 ml cold methanol to precipitate out the product. The white precipitate (BPSIPA) was continuously washed with methanol and deionized water. The product was dried in vacuum oven at 80 °C for overnight. The yield was 95 %. ¹HNMR (DMSO-d₆): 10.76 (s, 1H), 8.83, 8.81 (d, 1H), 8.75 (s, 2H), 8.23(s, 1H), 8.03, 8.01, 8.98 (t, 2H), 7.82 (s, 2H), 7.70, 7.68 (d, 2H), 7.41 (s, 2H), 2.49(s, 6H) (Fig. S2a), ESI-MS [M-H]⁻ at m/z 531.53 calculated for C₂₃H₁₉N₂O₉S₂.

Synthesis of the bis(phenylsulfonyl imide isophthalate amide (BPSIIA)). BPSIPA

(14.867 g, 27.91 mmol) was dissolved in a mixture of 400 mL THF and 80 mL of water under stirring. LiOH·H₂O (4.883 g, 91.70 mmol) was dissolved in water (25 ml) and then added into the above solution dropwise under stirring. Adjust pH of the solution to 7 with dilute hydrochloric acid. THF was removed by rotavaporation under reduced pressure. The reaction was kept at room temperature for 12 hrs. After reaction, the pH of the solution was firstly adjusted to be neutral and the solvents were removed under reduced pressure. The residue was redissolved in water, the product was generated by acidified the solution to pH=1 using aqueous HCl. The precipitate was filtered and washed with a small amount of water. The final product (12.9 g) was obtained after

dried at 100 °C for 24 hrs. The yield was 92 %. ¹H NMR (DMSO-d₆): 10.68 (s, 1H), 8.90, 8.88 (d, 1H), 8.68 (s, 2H), 8.23 (s, 1H), 8.02, 8.00, 8.97 (t, 2H), 7.81, 7.79 (d, 2H), 7.70, 7.68 (d, 2H), 7.42, 7.41, 7.38 (t, 2H) (Fig. S2b), ESI-MS [M-H]⁻ at m/z 503.01 calculated for C₂₁H₁₅N₂O₉S₂.

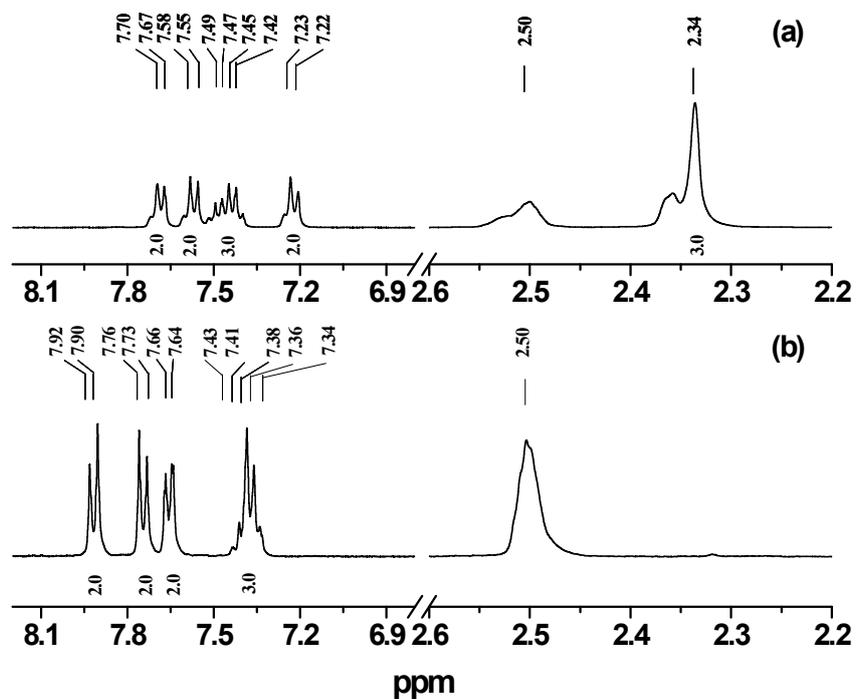


Figure S1. ¹H NMR spectra of MBBSI (a) and CBBSI (b).

The ¹H NMR spectra of the MBBSI and CBBSI are shown in Figure S1. It displays clear defined peaks with the correct integration ratio corresponding well with the number of protons in the respective compounds. The absence of a signal at 2.34 ppm in CBBSI (Figure S1b), which was assigned to the methyl group in MBBSI (Figure S1a), suggests that the MBBSI was successfully oxidised to yield CBBSI.

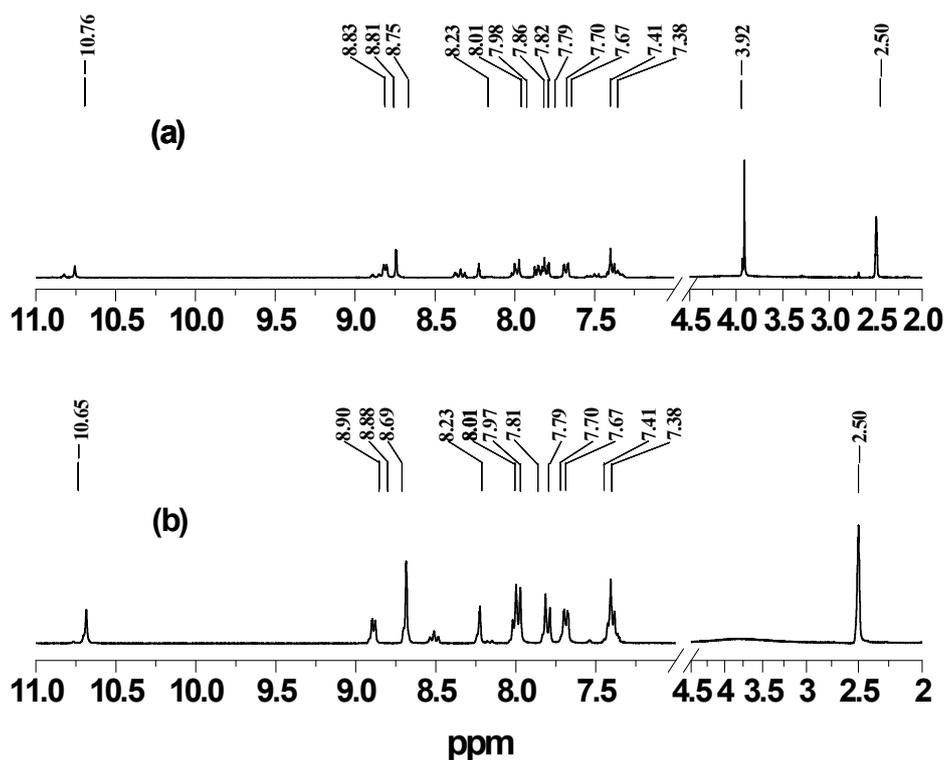


Figure S2. ^1H NMR spectra of BPSIPA (a) and BPSIIA (b).

The ^1H NMR spectra of the BPSIPA and BPSIIA are shown in Figure S2. It displays clear defined peaks with the correct integration ratio corresponding well with the number of protons in the respective compounds. The absence of the signal at 3.92 ppm in BPSIIA (Figure S2b) corresponding to the methyl group in BPSIPA (Figure S2a) suggest that BPSIPA was successfully hydrolysed to yield BPSIIA.

2. Methods

^1H NMR spectra of all synthesized materials were recorded on Bruker AV300 using DMSO- D_6 solvent. FTIR spectra were recorded using Bio-Rad Excalibur FTIR spectrometer in the 400-4000 cm^{-1} frequency range and spectral resolution of 4. The individual polymers were mixed with KBr and made into a plate. Molecular weight and polydispersity index (PDSI) were measured using GPC using THF as an eluent. The enthalpy were analyzed using TA Instrument 2920. This analysis was performed under nitrogen atmosphere at a heating rate of 10 $^\circ\text{C}/\text{min}$.

Thermal gravimetric analysis (TGA) of blended PEEIA-co-LiPEEPSI) was performed on SDT TA Instruments 2960 Simultaneous DTA-TGA, at 10.00 °C/min ramp up to 800 °C under nitrogen atmosphere. Powder XRD was performed on D5005 Bruker AXS diffractometer using sample size of 70 - 110 mg and Cu-K α radiation ($\lambda = 1.5410$ nm) as the source at 40 kV voltage in the scanning range 1.4° - 60° at room temperature. Surface morphology of the blended polymer was studied using JEOL JSM-6701F field emission scanning electron microscopy. The sample was imaged after being sputter-coated with platinum. Tensile strength and tensile strain of SIPE was measured using Instron 5544 at room temperature, with an elongation rate of 1.00mm/min and sensitivity set at 40%. The membranes were measured according to ASTM D882, REF ASTM.

The amount of solvent uptake is calculated by Equation (3):

$$\eta = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \quad (1)$$

where W_{dry} and W_{wet} are the weight of the membrane before and after the absorption of EC/PC solvent.

High solvent uptake of 141% as seen in Table 3 was attributed to the high porosity of Li(PEEIA-co-PEEPSI)/PVDF-HFP with pore size of 200 nm as shown in 11 (c). High solvent uptake is essential for forming high ionic conducting SIPE.

The electrochemical stability of the SIPE membrane was determined using the CHI instrument by performing cyclic voltammetry (CV) in a sandwich cell using two stainless-steel electrodes as a working electrode and a counter electrode in the voltage range of 1.5 - 7 volts and at a scan rate of 0.2 mV s⁻¹.² In order to obtain a more accurate measurement of electrochemical stability, a slow

scan rate was used. Lithium ion transference number (t_{Li^+}) was measured using a Li|SIPE membrane|Li battery cell. The cell was subjected to a combination of AC impedance and DC polarization method described by Evans et al. [58] lithium ion transference number was calculated using Equation (2):

$$t_{Li^+} = \frac{I_s(\Delta V - I_o R_o)}{I_o(\Delta V - I_s R_s)} \quad (2)$$

Where ΔV is the potential applied across the cell; I_o and I_s are the initial and steady-state current determined by DC polarization; R_o and R_s are the initial and steady-state resistances of the passivation layers on the Li electrode determined by AC impedance. Ionic conductivity of the SIPE membrane was measured by means of Electrochemical Impedance Spectroscopy (EIS) using Zahner electrochemical workstation model, PGSTAT, with the EIS module over a frequency range 4×10^6 to 1 Hz and an oscillating voltage of 5 mV. The electrolyte membrane was placed in a stainless steel cylindrical device of 1.5 cm diameter. The device was left in the 80 °C oven overnight before taking measurements to ensure maximum contact between the membrane and the device. Nyquist plot of imaginary vs real impedance were obtained and fitted with Simulated Impedance Measurement (SIM) software: The ionic conductivities were obtained by fitting the measured resistance into Equation (1):

$$\sigma = \frac{l}{AR} \quad (3)$$

where σ is the ionic conductivity; l is the membrane thickness; A is the area of the membrane; R is the resistance obtained from the Nyquist plot.

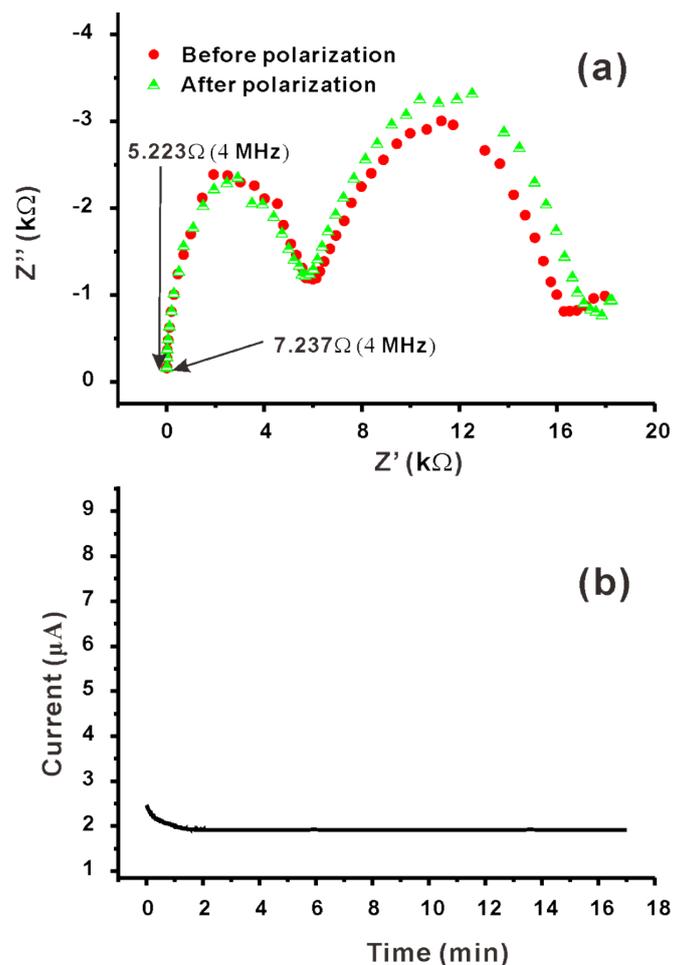


Figure S3. Impedance spectra (a) and time dependence response of DC polarization (b) for Li|Li(PEEIA-co-PEEPSI)/PVDF-HFP membrane|Li symmetric cell at room temperature, polarized with a potential of 100 mV.

Table S1. The measured parameters and the calculated t_{Li^+} of the PVDF-HFP/PEEIA-co-LiPEEPSI membrane.

| Electrolyte | $I_0(\mu A)$ | $I_s(\mu A)$ | $R_0(\Omega)$ | $R_s(\Omega)$ | t_{Li^+} |
|---------------------|--------------|--------------|---------------|---------------|------------|
| Li(PEEIA-co-PEEPSI) | 2.47 | 2.25 | 5.223 | 7.237 | 0.91 |

Reference

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- 2 A. Ghosh, C. S. Wang, P. Kofinas, *J Electrochem Soc.*, **2010**, *157*, A846-A849.