Supplementary information

A Class of *sp*^{3} Boron-Based Single-ion Polymeric Electrolytes for Lithium Ion Batteries

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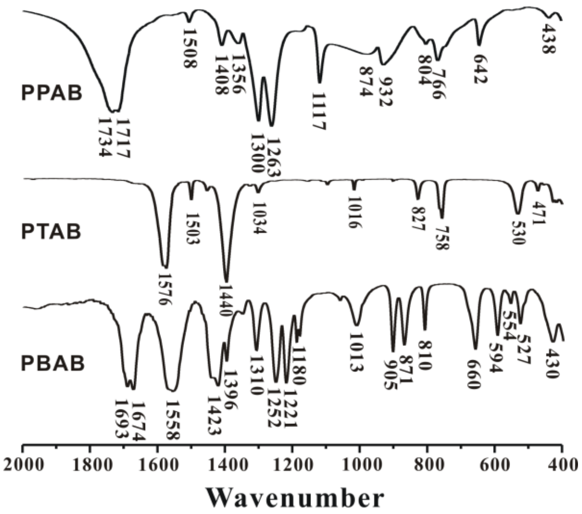

Figure S1. The FTIR spectra of PPAB, PTAB and PBAB.

The IR spectra of PPAB, PATAB and PBAB exhibit the characteristic absorption B-O bands associated with the stretching modes in the range of 1000cm^{-1} to 1400cm^{-1}.[1] Specifically, pronounced features are observed at 1356cm^{-1}, 1300cm^{-1}, 1263cm^{-1} and 1117cm^{-1} for PPAB, 1440cm^{-1} and 1034cm-1 for PTAB, and 1310cm^{-1}, 1252cm^{-1}, 1221cm^{-1} and 1013cm^{-1} for PBAB, respectively.

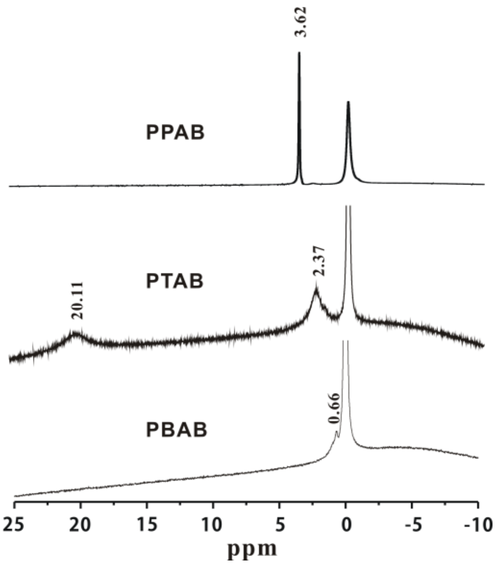

Figure S2. The ^{11}B NMR spectra of PPAB, PTAB and PBAB.

The ^{11}B NMR spectra display sharp peaks at 3.62ppm, 2.37ppm and 0.66ppm for PPAB, PTAB and PBAB, respectively, clearly indicating that all boron atoms adopt a *sp*^{3} configuration.

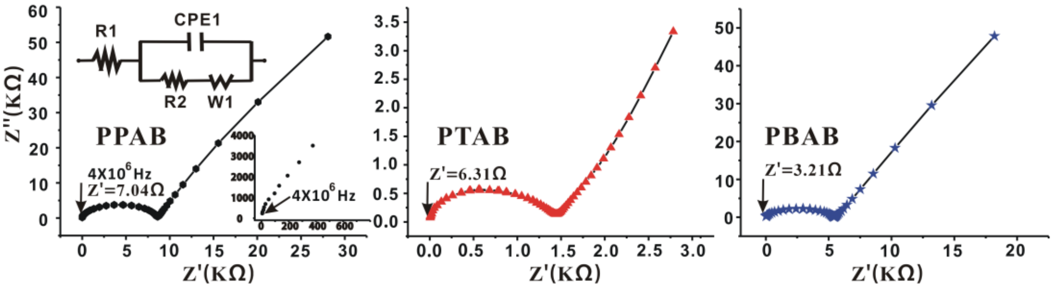

Figure S3. Electrochemical impedance spectroscopy of novel sp3 Boron-Based 3-D frameworks

The ionic conductivity of the above GPEMs were determined in the SS|GPEM|SS cells by electrochemical impedance spectroscopy (EIS) over a frequency range of 0.1–4X10^6 Hz and the Nyquist plots are shown in Fig. S3. Each diagram of Nyquist plots includes a suppressed semicircle in the high frequency regime that corresponds to bulk resistance and a straight line in the low frequency regime that reflects the interfacial resistance controlled by the diffusion of the charged particles. This electrochemical behavior is typical for single ion electrolytes with the impedance accounting for both the bulk resistance and the interfacial resistance. Using the equation, $\sigma = L/(R*A)$, where L and A stand for the thickness and the area of the composite membrane, respectively, and R is the membrane resistance (Table S2).

Table S1. Molecular weights of PPAB, PTAB and PBAB

	M_n(X10^4)	M_w(X10^4)	M_w/M_n
PPAB	0.74	0.89	1.21
PTAB	0.38	1.32	3.52
PBAB	2.95	3.42	1.16

The Gel Permeation Chromatography (GPC) analysis gives molecular weights of these polymers in the range of 3,750–29,400 with the polydispersity indices between 1.16 and 3.52, suggesting a relatively narrow distribution of the molecular weights.

Table S2. The membrane thickness (L), the area of the composite membrane (A), and the membrane resistance (R) of PPAB, PTAB and PBAB.

	L(μm)	R(Ω)	A(cm^2)
PPAB	126.98	7.04	1.43
PTAB	160.69	6.31	1.43
PBAB	266.76	3.21	1.43

Experimental section

Preparation of lithium tetramethanolatoborate ($LiB(OCH_3)_4$) with a high purity with a yield of 92% based on the procedure described by Barthel et al.[27] 1H NMR (DMSO-d6): δ3.16 (s, 12H); 13C NMR (DMSO-d6): δ48.95 (s, 4C); 11B NMR (referenced to BF3•Et2O in DMSO-d6): δ 3.37; (ESI-MS) m/z=135.00.

The silylation reactions were carried out under argon atmosphere by reacting the selected organic acids with hexamethyldisilane (HMDS) in anhydrous 1,2-dichloroethane (DCE) at 100°C till all acids were consumed (roughly, 6 hrs). The low boiling point solvent and the unreacted hexamethyldisilane were then removed under reduced vacuum. The silylation derivatives were characterized with 1H NMR ($CDCl_3$): for pyromellitic acid, □□ 7.96 ppm (2H, s), □□0.39 ppm (18H, s); for terephthalic acid, □ 8.83 ppm (4H, s), 0.42 ppm (18H, s); for 1, 2, 3, 4-butanetetracarboxylic acid, δ 3.80 (2H, d), δ 3.12 (2H, d), δ0.20 (18H, s).

The second step reaction was done by stirring lithium tetramethanolatoborate and the chosen silylation derivative in a small amount of anhydrous N,N-Dimethylformamide (DMF) for PPAB and PTAB at 50 °C for 3 days, and for the synthesis of PBAB the reaction was carried out in anhydrous acetonitrile (AN) at 45°C for 1 day and subsequently at 70°C for another 3 days. In all cases, the second step reaction was conducted at argon atmosphere to ensure all boron atoms in the polymers maintain only the sp^3 configuration in the final products. The raw products were purified via recrystallization using DMF followed by further purification through washing continuously using acetonitrile. After drying at 120°C under vacuum for 24 hrs, the products were collected for characterizations with a variety of spectroscopic techniques. Due to the intrinsic high polarization arising from the large delocalized anions in the polymer backbones and the highly exposed lithium cations, these compounds are very sensitive to moisture and must be kept in a glove box with argon.

1 L. Larush-Asraf, M. Biton, H. Teller, E. Zinigrad, D. Aurbach, *J Power Sources* **2007**, 174, 400-407.