Supplementary Information

to accompany

Electrochemical and physicochemical properties of small phosphonium cation ionic liquid electrolytes with high lithium salt content

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Content

1 Preparation of trimethyl(isobutyl)phosphonium bis(fluorosulfonyl)imide ($P_{111i4}FSI$)

Isobutylphosphine (CYTOP®141, Cytec Industries) was reacted with trimethyl phosphate (>3 mol) at a temperature 110-130 °C using the process described in US patent 7,829,744 B2.
The trimethyl(isobutyl)phosphonium dimethylphosphate intermediate was further reacted with 1.05 equivalents of potassium bis(fluorosulfonyl)imide (KFSI) in the presence of dichloromethane. The organic phase was treated with saturated $NaHCO_3$ in water followed by additional washes with H_2O, hexanes, and a number of washes with deionized H_2O and checked for the presence of any residual halide with the use of $AgNO_3$ in water. After removal of the volatiles on the Rotovap, the resulting product was additionally purified using short-path evaporator. Its structure was confirmed by ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR analyses (deuterated acetone ($(CD_3)_2CO$)).

2 Nuclear Magnetic Resonance spectra of $P_{111i4}FSI$

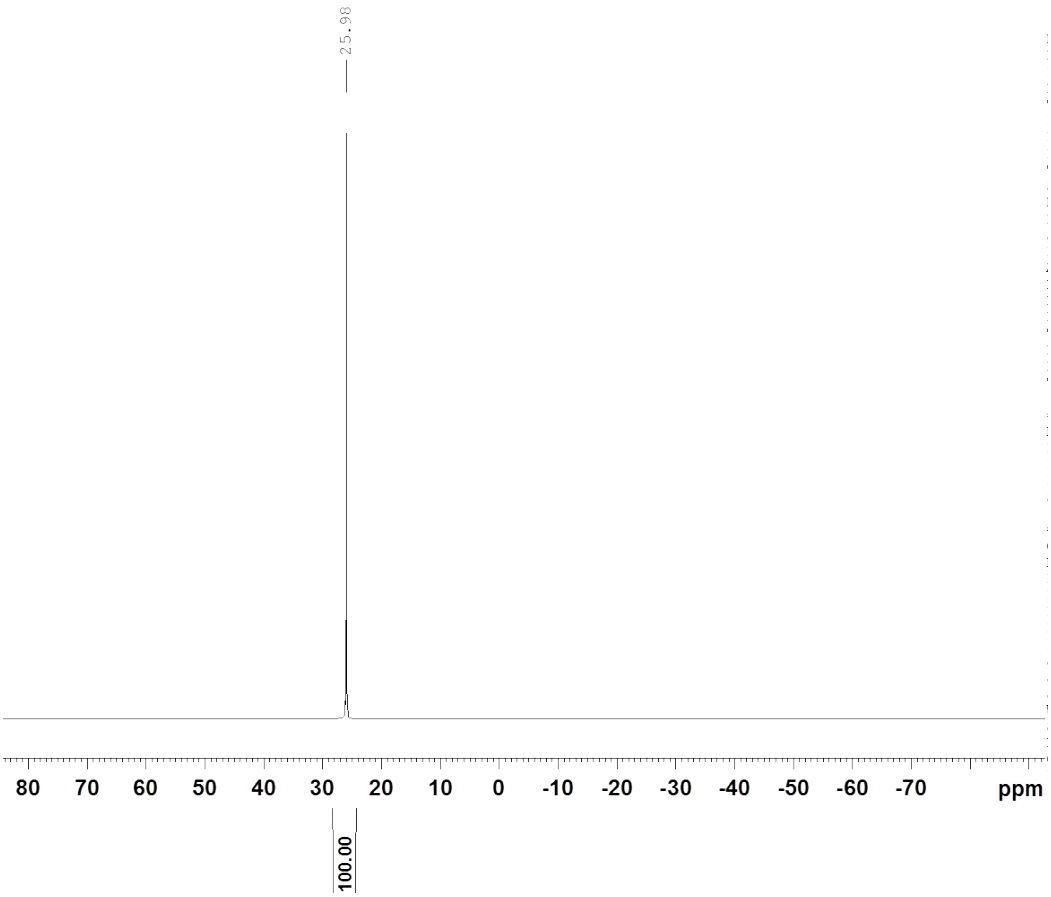

Figure S3 ^{31}P NMR spectrum of $P_{111i4}FSI$

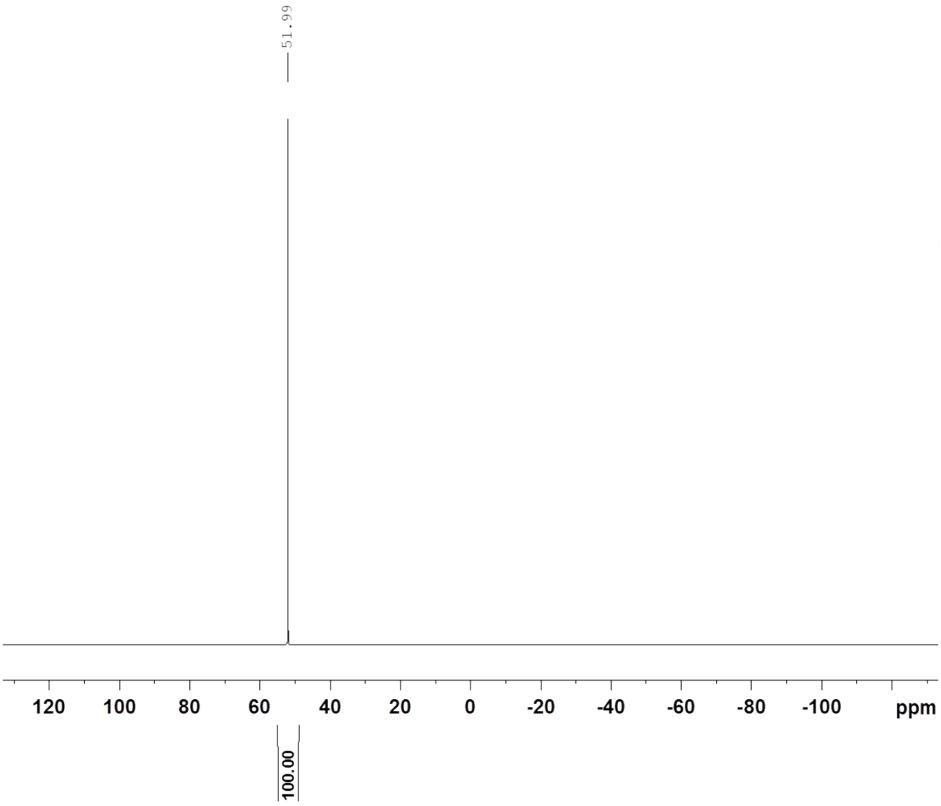

Figure S4 ^{19}F NMR spectrum of $P_{111i4}FSI$

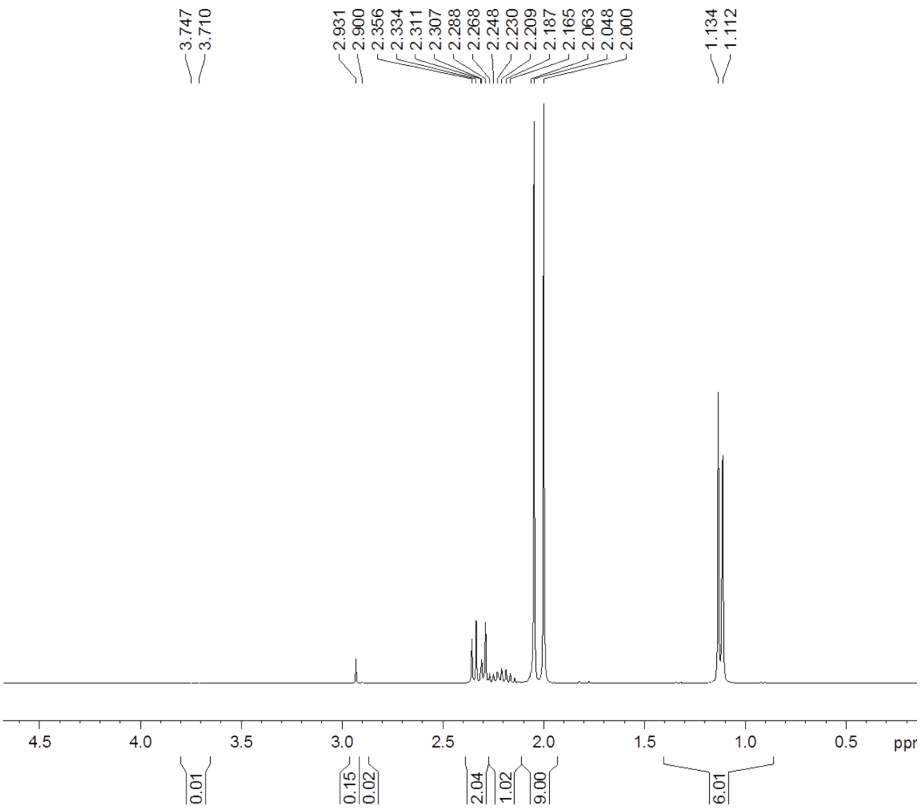

Figure S5 ^{1}H NMR spectrum of $P_{111i4}FSI$

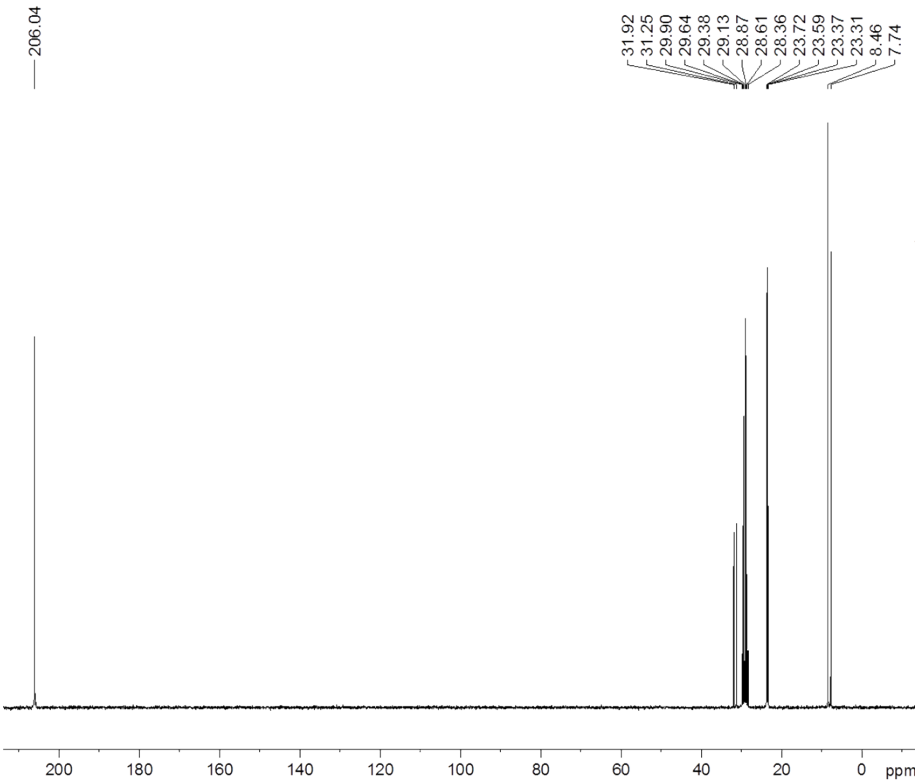

Figure S6 ^{13}C NMR spectrum of $P_{111i4}FSI$

3 Electrospray mass spectra of $P_{111i4}FSI$

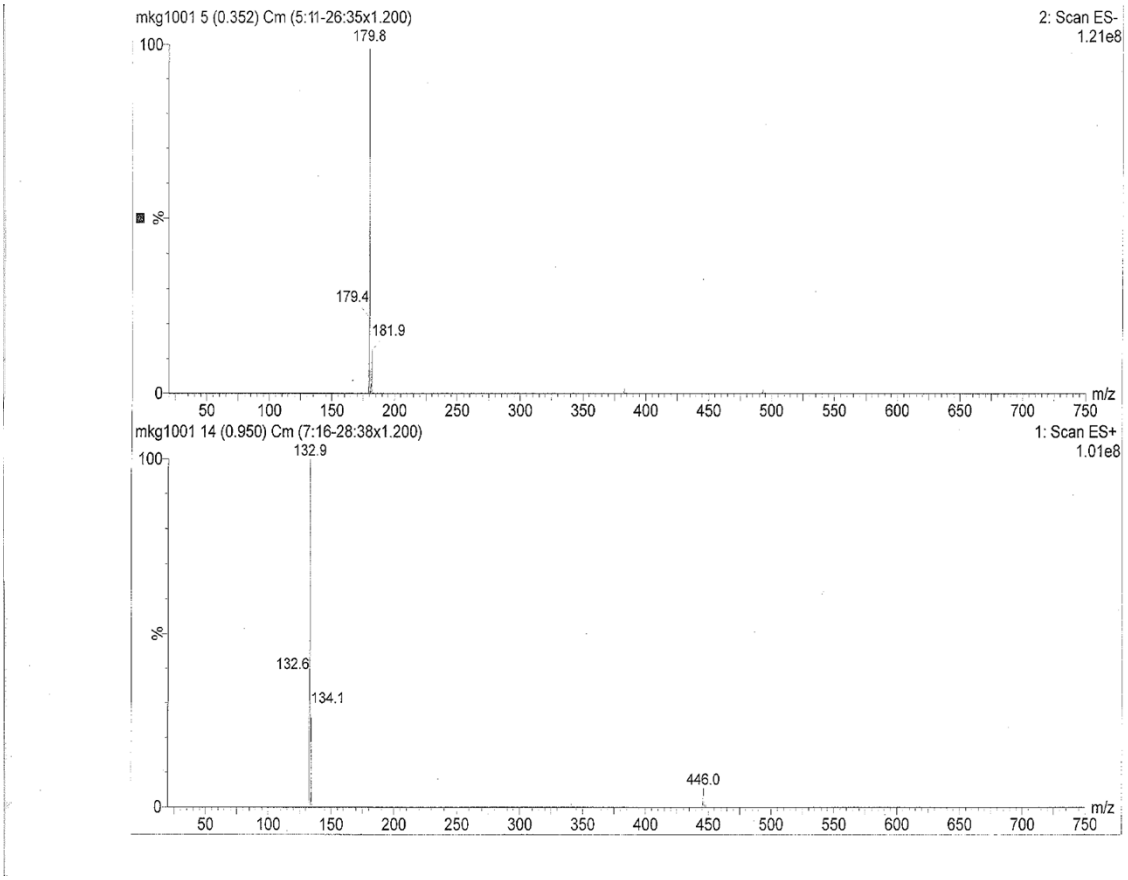

Figure S7 Mass spectra of $P_{111i4}FSI$

4 Transport properties – VTF parameters

(a) (b)

Figure S1 VTF plots of ionic conductivity (a) and dynamic viscosity (b) for $P_{111i4}FSI$ electrolytes and various concentrations of LiFSI

Table S1 VTF equation parameters of ionic conductivity from -40 to 120°C (

$$\sigma = \sigma_0 exp\left\{\frac{-B}{T - T_0}\right\})$$

LiFSI concentration	**Molar ratio Li^+: P^+**	**Ln σ_0 / mS.cm^{-1}**	**B (K)**	**T_0(K)**	**R (correlation coefficient)**
2.0	0.19:0.31	6.36±0.09	791±24	160±2	0.9999
3.2	0.25:0.25	6.07±0.0.02	768±5	173±0.3	0.9999
3.8	0.27:0.23	6.35±0.0.04	844±8	171±0.5	0.9999

Table S2 VTF equation parameters of dynamic viscosity from 20 to 80°C (

$$\eta = \eta_0 exp\left\{\frac{B}{T - T_0}\right\})$$

LiFSI concentration	**Molar ratio Li^+: P^+**	**Ln η_0 / P**	**B (K)**	**T_0(K)**	**R (correlation coefficient)**
2.0	0.19:0.31	-4.84±0.38	589±100	188±11	0.9998
3.2	0.25:0.25	-5.69±0.39	863±117	173±10	0.9999
3.8	0.27:0.23	-5.16±0.64	742±170	186±15	0.9996

5 Electrochemical measurements of tri(methyl)isobutylphosphonium bis(fluorosulfonyl)imide ($P_{111i4}FSI$)

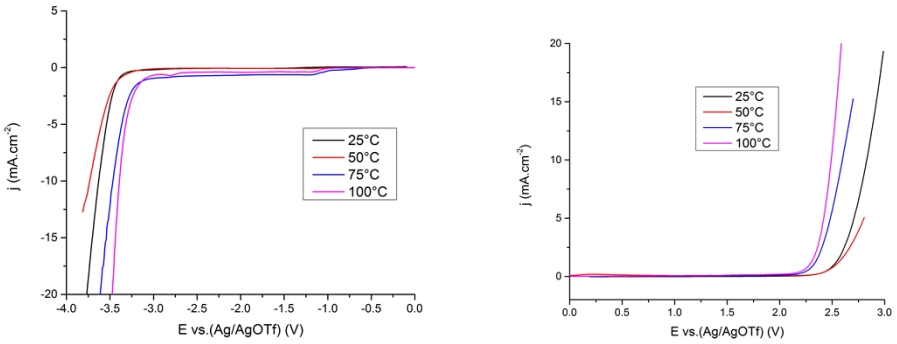

Figure S2 Linear sweep voltammograms for neat $P_{111i4}FSI$ at a glassy carbon working electrode with a potential sweep rate of 20mV.s^{-1} at different temperatures 25-50-75-100°C.