Two Phosphonium Ionic Liquids with High Li+ Transport Number

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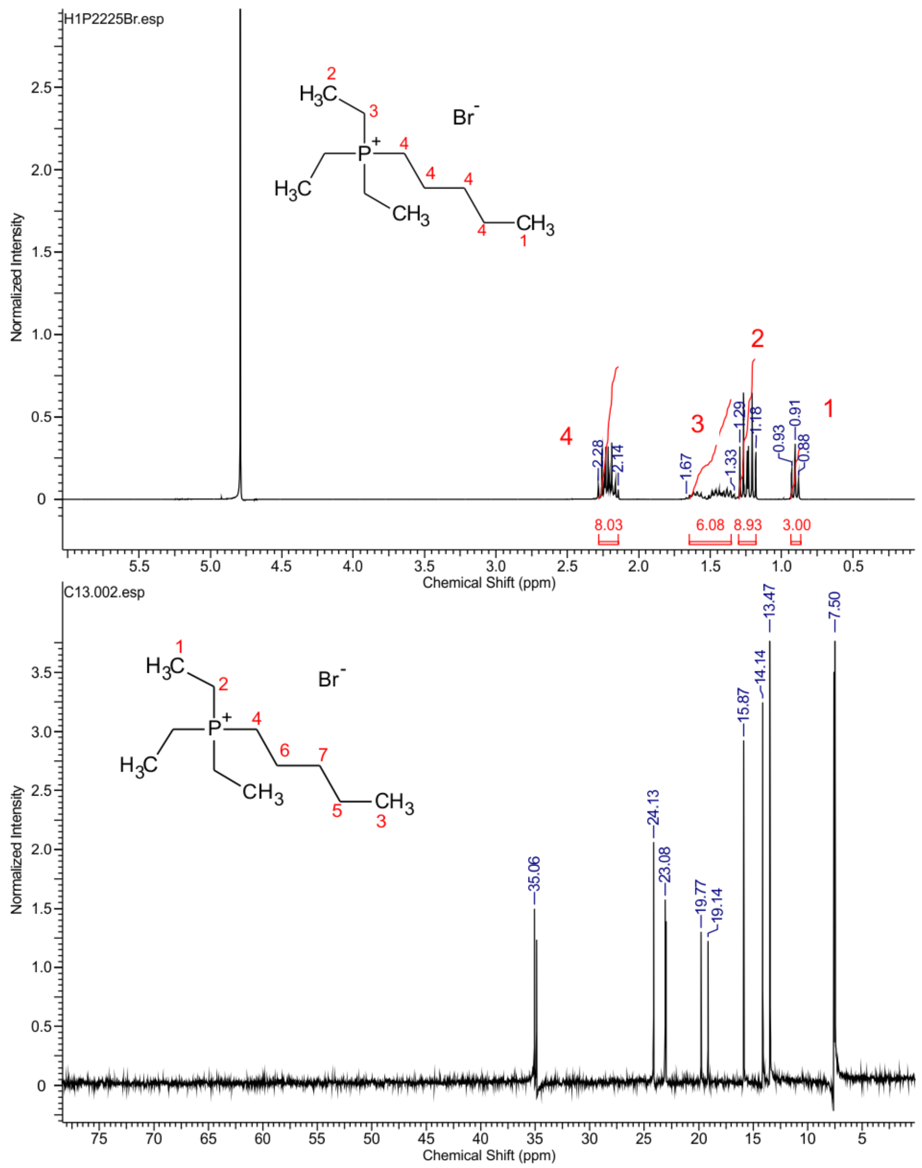

Figure S1: ^{1}H (a) and ^{13}C (b) NMR of $P_{2225}Br$.

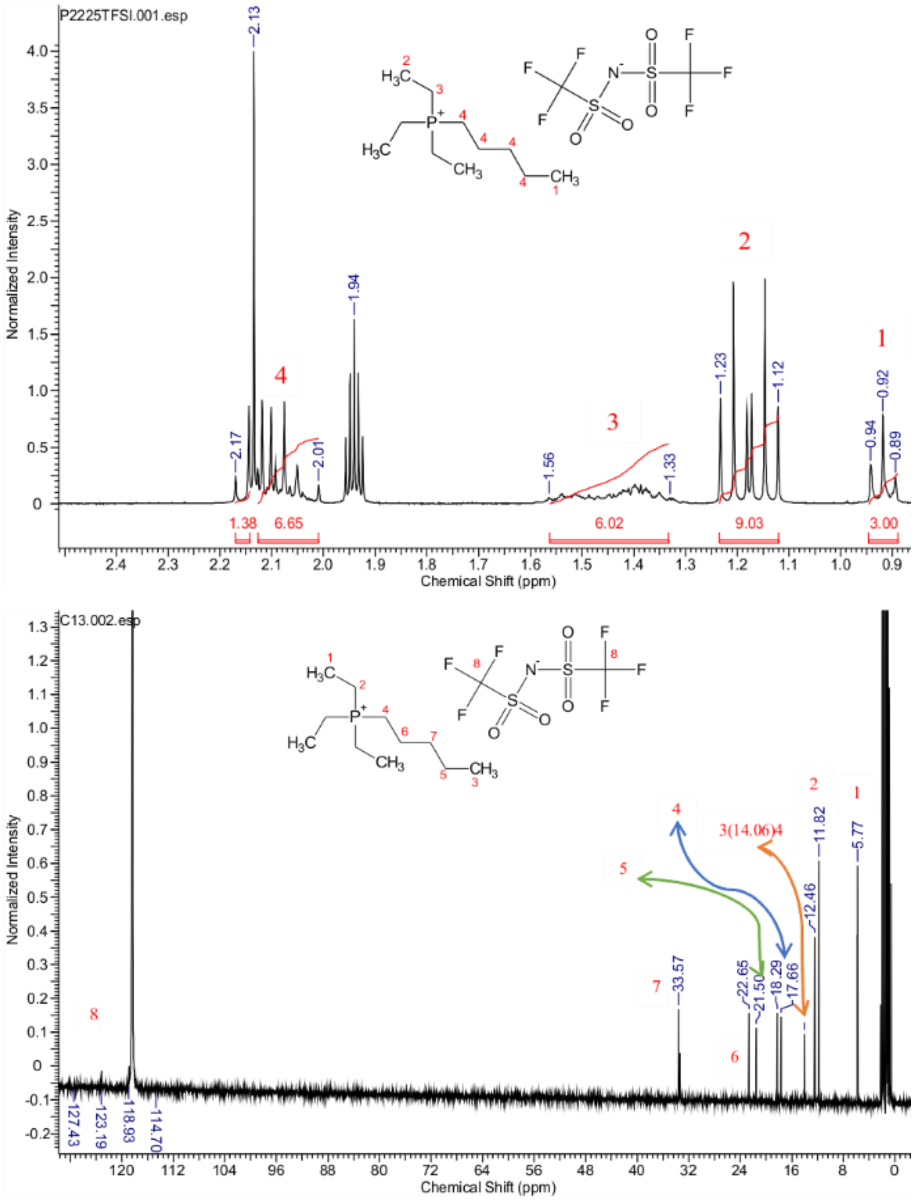

Figure S2: ^{1}H (a) and ^{13}C (b) NMR of $[P_{2225}][Tf_2N]$.

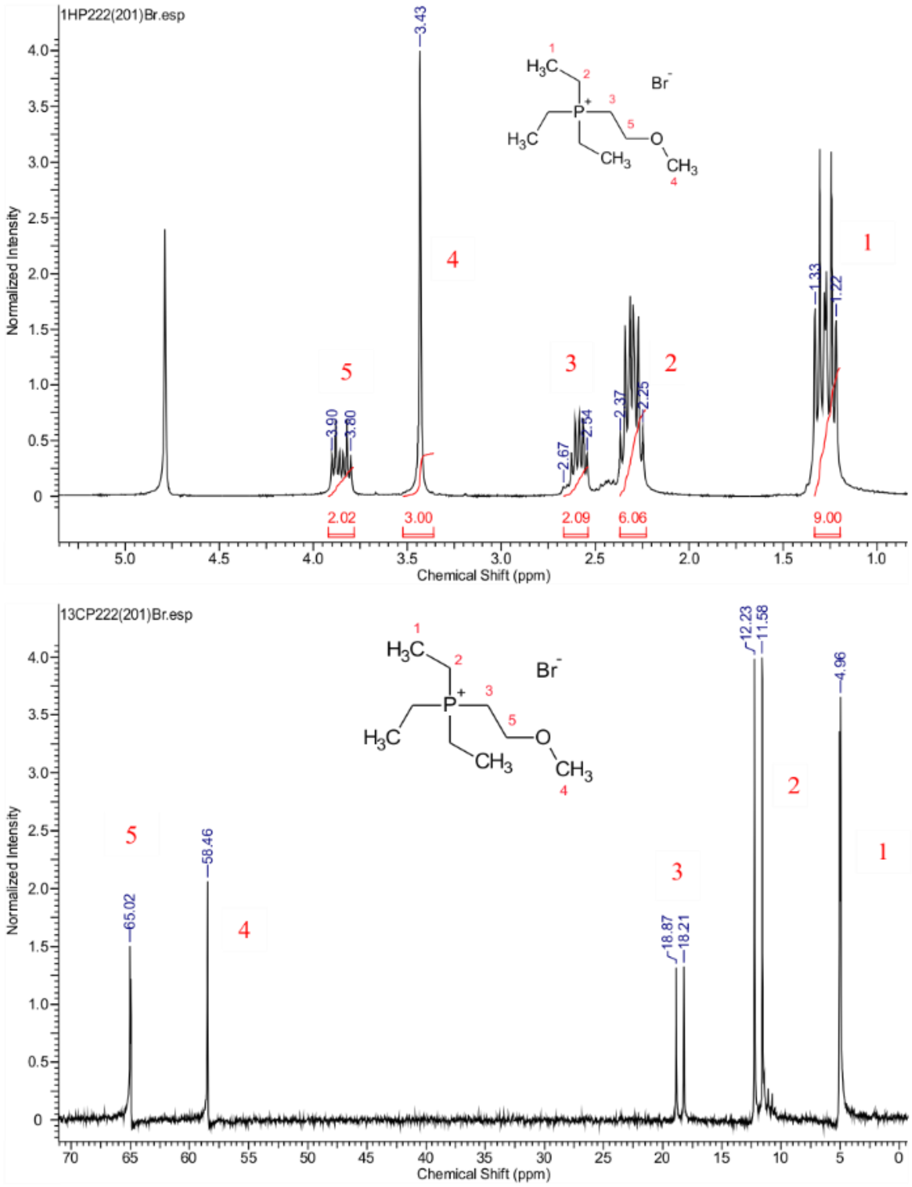

Figure S3: ^{1}H (a) and ^{13}C (b) NMR of $P_{222(2O1)}Br$.

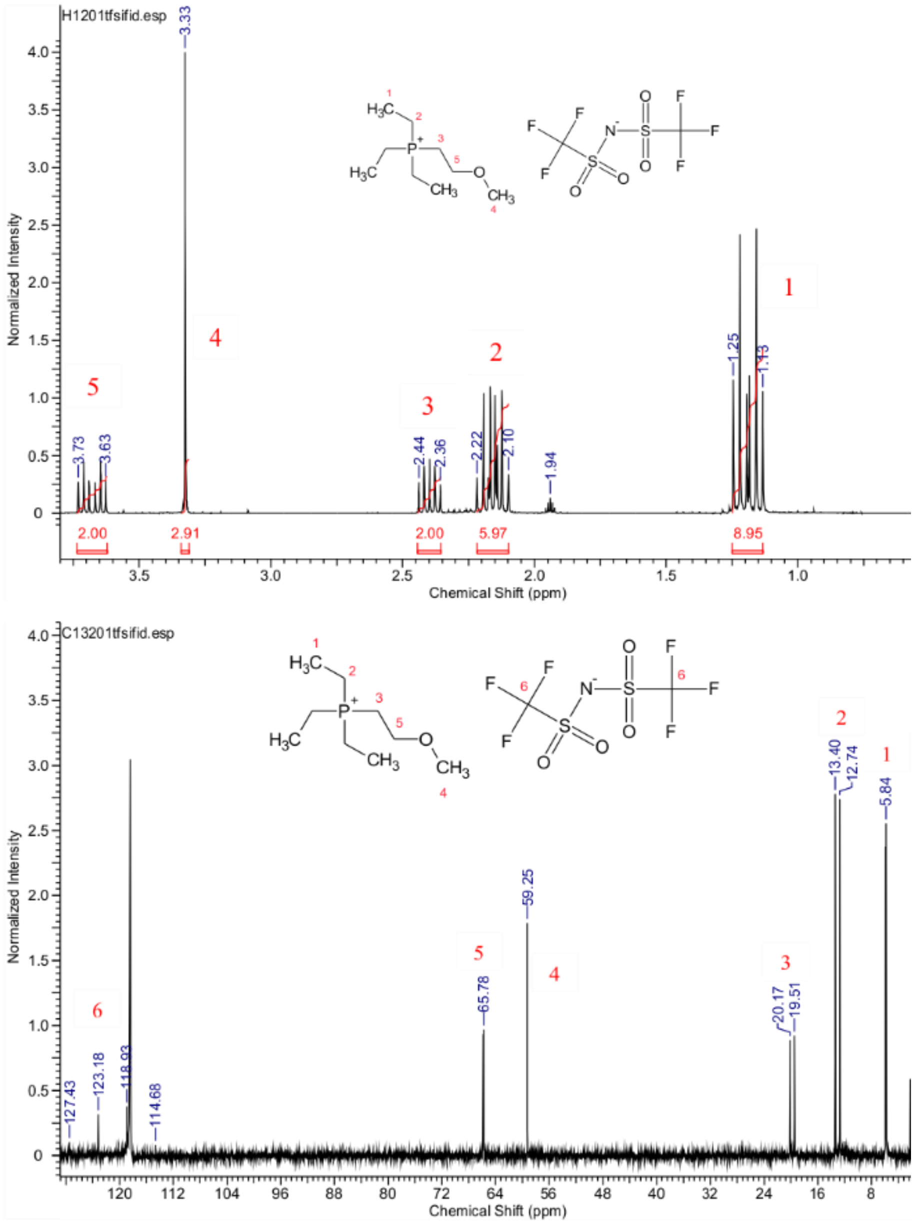

Figure S4: ^{1}H (a) and ^{13}C (b) NMR of $[P_{222(2O1)}][Tf_2N]$.

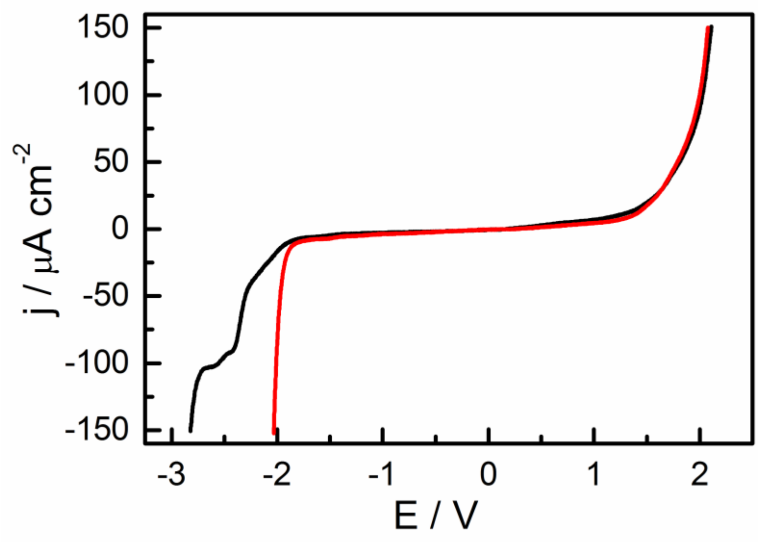

Figure S5: Electrochemical windows of $[P_{2225}][Tf_2N]$ (black line) and $[P_{222(2O1)}][Tf_2N]$ (red line) obtained by two linear voltammetry starting from open circuit potential. Scan rete of 10 mV s^{-1} and +/- 150 μA cm^{-2} of current cut off. EW: glassy carbon, CE: Pt, RE: Ag.

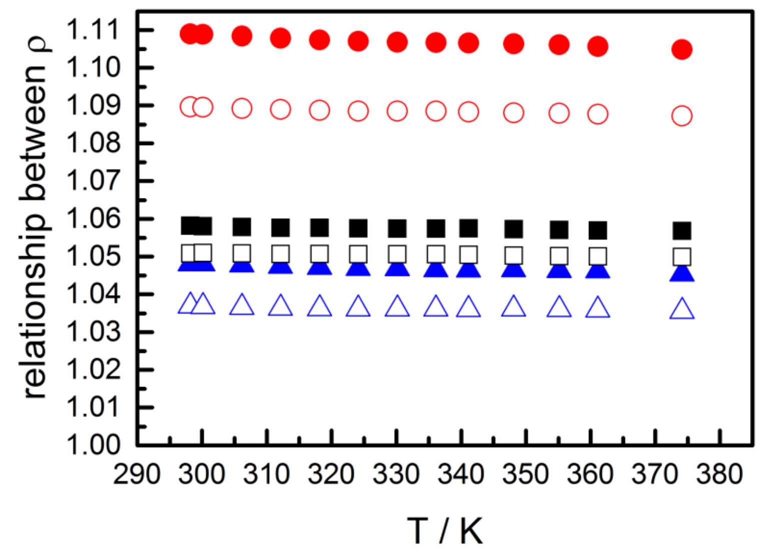

Figure S6: relationship between the densities in the range of temperature studied. For $[P_{2225}][Tf_2N]$, 1.0 mol L^{-1}/neat (■) 2.0 mol L^{-1}/neat (●) and 2.0 mol L^{-1}/1.0 mol L^{-1} (▲); and for $[P_{222(2O1)}][Tf_2N]$, 1.0 mol L^{-1}/neat (□), 2.0 mol L^{-1}/neat (○) and 2.0 mol L^{-1}/1.0 mol L^{-1} (△).

Table S1: VTF parameters for viscosity.

	η_0 (mPa s)	B (K)	B/T_0	
$[P_{2225}][Tf_2N]$	0.0953	946	5.91	17%*
$[Li]_{0.25}[P_{2225}]_{0.75}[Tf_2N]$	0.0836	1237	7.73	31%
$[Li]_{0.39}[P_{2225}]_{0.61}[Tf_2N]$	0.0822	1563	9.77	65%
$[P_{222(2O1)}][Tf_2N]$	0.131	809	5.06	
$[Li]_{0.25}[P_{222(2O1)}]_{0.75}[Tf_2N]$	0.128	1068	6.68	32%
$[Li]_{0.39}[P_{222(2O1)}]_{0.61}[Tf_2N]$	0.0945	1327	8.29	64%

*compared to $[P_{222(2O1)}][Tf_2N]$

Table S2: VTF parameters for conductivity.

	σ_0 (S cm^{-1})	B (K)	B/T_0	
$[P_{2225}][Tf_2N]$	0.196	741	4.63	7%*
$[Li]_{0.25}[P_{2225}]_{0.75}[Tf_2N]$	0.334	1035	6.47	40%
$[Li]_{0.39}[P_{2225}]_{0.61}[Tf_2N]$	0.470	1320	8.25	78%
$[P_{222(2O1)}][Tf_2N]$	0.539	692	4.33	
$[Li]_{0.25}[P_{222(2O1)}]_{0.75}[Tf_2N]$	0.410	895	5.59	29%
$[Li]_{0.39}[P_{222(2O1)}]_{0.61}[Tf_2N]$	0.675	1136	7.10	64%

*compared to $[P_{222(2O1)}][Tf_2N]$

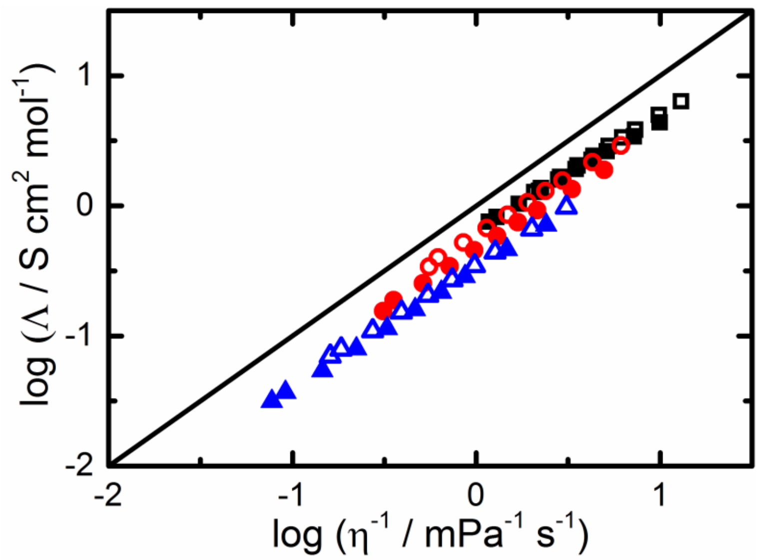

Figure S7: Walden plot of $[P_{2225}][Tf_2N]$ (■) $[Li]_{0.25}[P_{2225}]_{0.75}[Tf_2N]$ (●), $[Li]_{0.31}[P_{2225}]_{0.69}[Tf_2N]$ (▲), $[P_{222(2O1)}][Tf_2N]$ (□), $[Li]_{0.25}[P_{222(2O1)}]_{0.75}[Tf_2N]$ (○) and $[Li]_{0.31}[P_{222(2O1)}]_{0.69}[Tf_2N]$ (△). The line represents the KCl 0.01 mol L^{-1} solution, as closer of the line, higher is the IL ionicity.

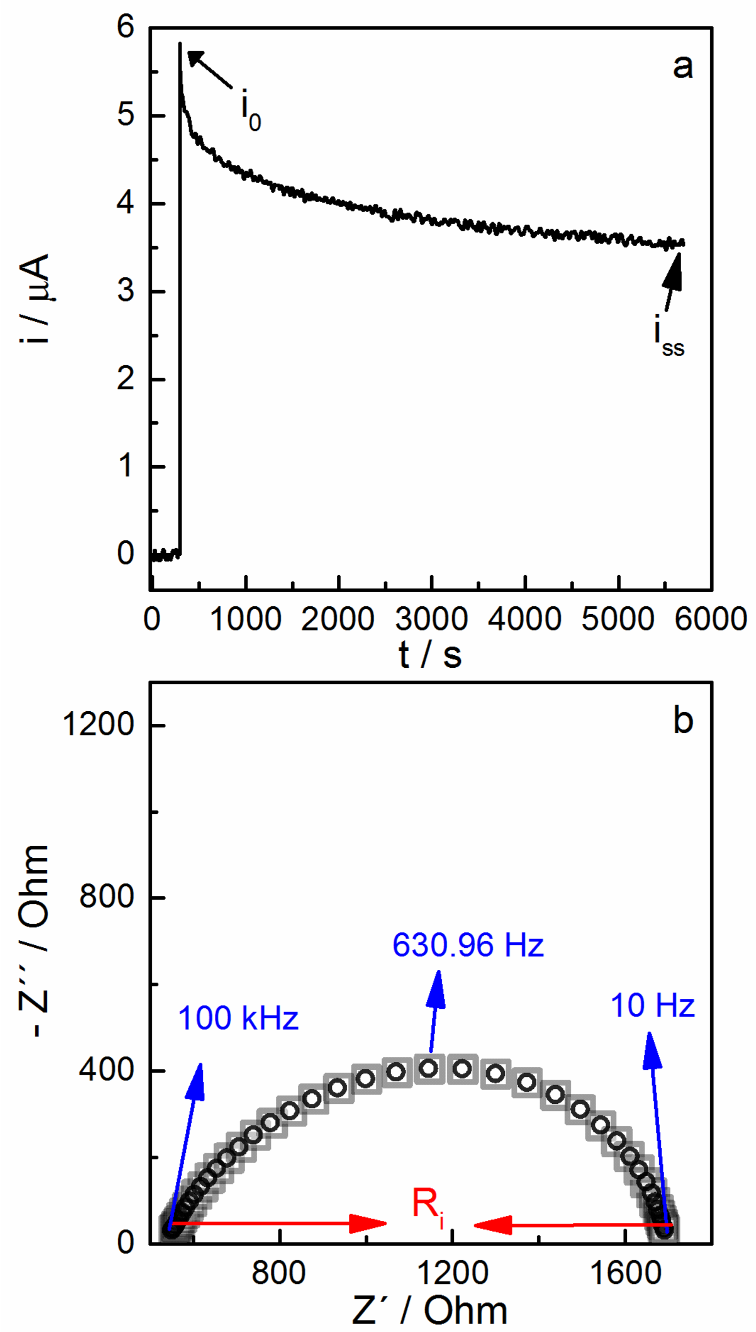

Figure S8: Experiments for calculation of Li^+ transport number in the mixture $[Li]_{0.25}[P_{222(201)}]_{0.75}[Tf_2N]$. (a) Current as a function of time at overpotential of 10mV; (b) Nyquist diagrams from 100kHz to 10Hz at OCP (■) and at overpotential of 10mV (○).

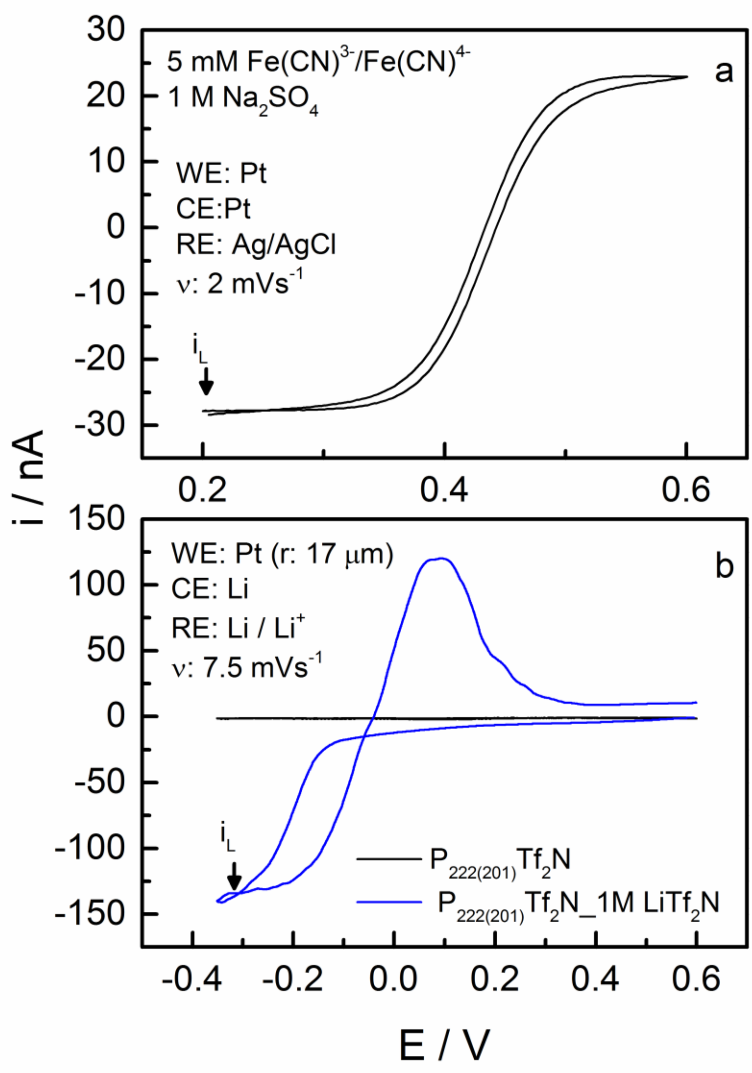

Figure S9. Calculation of microelectrode radius. The steady state for the disk microelectrode is: $i_L = 4nFD_{R/O}C^*_{R/O}r$, solving for r, $r_{average}$ = 17 µm. D_{Fe2+} and D_{Fe3+} can be obtain from the literature.[1] Diffusion coefficient of Li^+ in the mixture containing [$P_{222(2O1)}$], using the same equation above is 2.0 10^{-7} cm s^{-1}.

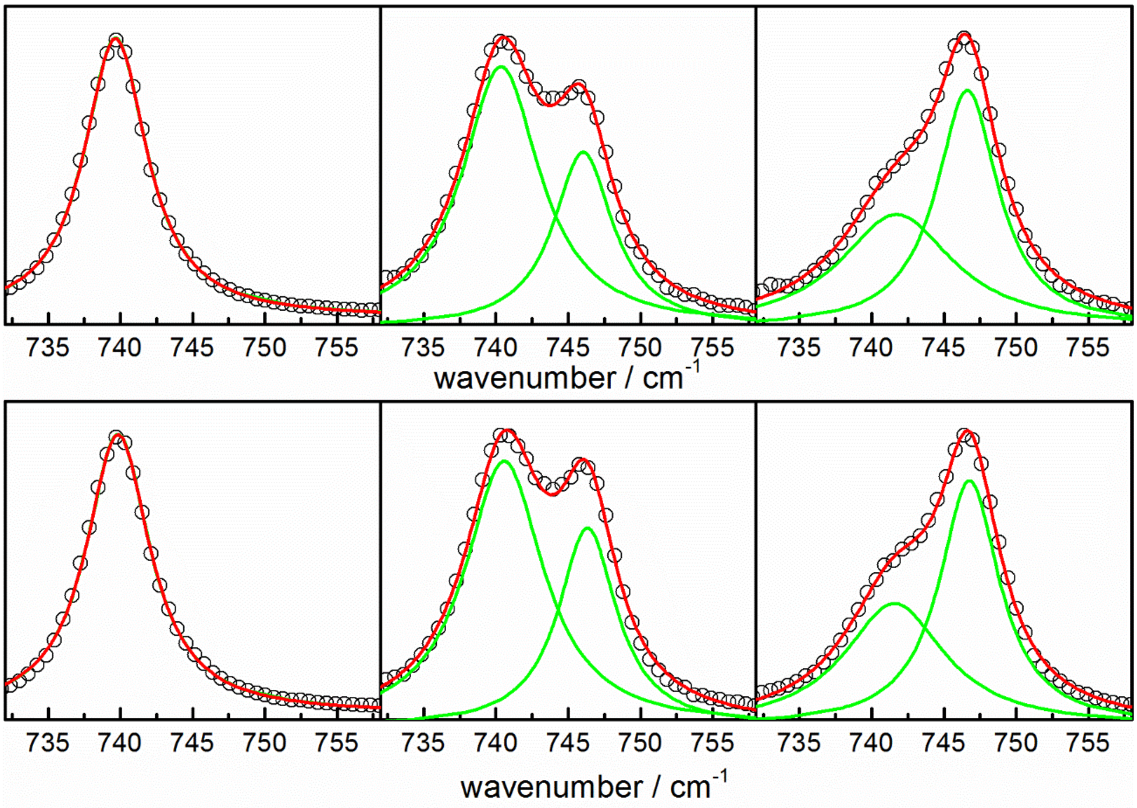

Figure S10: Raman spectra of $[P_{2225}][Tf_2N]$, $[Li]_{0.25}[P_{2225}]_{0.75}[Tf_2N]$ and $[Li]_{0.39}[P_{2225}]_{0.61}[Tf_2N]$ at the top and of $[P_{222(2O1)}][Tf_2N]$, $[Li]_{0.25}[P_{222(2O1)}]_{0.75}[Tf_2N]$ and $[Li]_{0.39}[P_{222(2O1)}]_{0.61}[Tf_2N]$ at the bottom. Circles represent the experimental data, green lines represent the two Gaussian components and the red lines represent the fits.

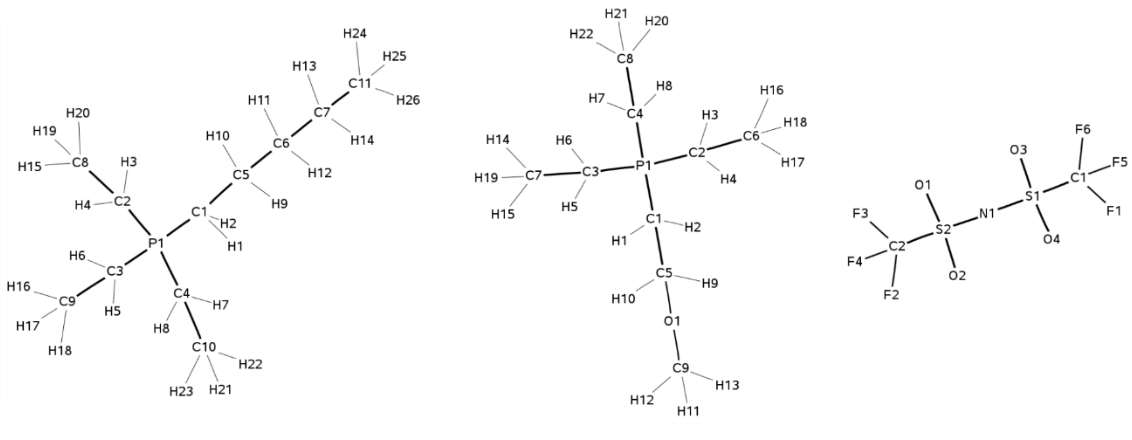

Figure S11: The cations P_{2225}^+ and $P_{222(2O1)}^+$ and the anion Tf_2N^- with their atoms enumerated as used in the MD simulations.

Table S3. Density, viscosity, ionic conductivity and diffusion coefficient (PGSE-NMR) for the neat IL $[P_{2225}][Tf_2N]$ and its Li^+ mixtures in the studied temperature range.

	$[P_{2225}][Tf_2N]$					**$[Li][P_{2225}][Tf_2N]$**						**$[Li][P_{2225}][Tf_2N]$**		
T °C	ρ g cm^{-3}	η mPa s	σ S cm^{-1}	D_{cat} cm^2 s^{-1}	D_{an} cm^2 s^{-1}	ρ g cm^{-3}	η mPa s	σ S cm^{-1}	D_{cat} cm^2 s^{-1}	D_{an} cm^2 s^{-1}	D_{Li+} cm^2 s^{-1}	ρ g cm^{-3}	η mPa s	σ S cm^{-1}
25	1.3039	85.301	0.0021	1.1 10^{-7}	1.3 10^{-7}	1.3797	319.92	0.000612	3.47 10^{-8}	3.62 10^{-8}	6.37 10^{-8}	1.446	1289.4	0.000159
27	1.3022	77.428	0.00227			1.3778	280.86	0.000741				1.444	1091	0.000186
33	1.2971	58.675	0.00286	1.5 10^{-7}	1.98 10^{-7}	1.3722	194.62	0.000995	5.61 10^{-8}	5.95 10^{-8}	9.82 10^{-8}	1.4378	685.18	0.000274
39	1.2921	45.421	0.00358	2.27 10^{-7}	2.47 10^{-7}	1.3666	139.17	0.00134	7.59 10^{-8}	8.09 10^{-8}	1.39 10^{-7}	1.4315	449.24	0.000403
45	1.287	35.818	0.00435	2.73 10^{-7}	3.29 10^{-7}	1.3611	102.29	0.00177	1.05 10^{-7}	1.06 10^{-7}	1.88 10^{-7}	1.4253	305.45	0.000575
51	1.282	28.788	0.00521	3.66 10^{-7}	3.69 10^{-7}	1.3557	77.064	0.00228	1.5 10^{-7}	1.62 10^{-7}		1.4193	214.65	0.000800
57	1.277	23.5	0.00612	4.81 10^{-7}	4.8 10^{-7}	1.3503	59.283	0.00291	1.83 10^{-7}	1.91 10^{-7}		1.4135	155.35	0.00109
63	1.2719	19.458	0.00711	5.93 10^{-7}	6.55 10^{-7}	1.3449	46.553	0.00359	2.3 10^{-7}	2.4 10^{-7}	4.09 10^{-7}	1.4076	115.34	0.00144
68	1.2676	16.793				1.3405	38.56					1.4028	91.963	
75	1.2619	13.863	0.00917			1.3341	30.208	0.00517				1.3962	68.007	0.00231
82	1.2562	11.583				1.3279	24.071					1.3895	51.771	
88	1.2514	10.015	0.01169			1.3226	20.105	0.00721				1.3837	41.721	0.00353
101	1.241	7.5314				1.3115	14.149					1.3711	27.45	

Table S4. Density, viscosity, ionic conductivity and diffusion coefficient (PGSE-NMR) for the neat IL $[P_{222(2O1)}][Tf_2N]$ and its Li^+ mixtures in the studied temperature range.

	$[P_{222(2O1)}][Tf_2N]$					**$[Li][P_{222(2O1)}][Tf_2N]$**						**$[Li][P_{222(2O1)}][Tf_2N]$**					
T °C	ρ g cm^{-3}	η mPa s	σ S cm^{-1}	D_{cat} cm^2 s^{-1}	D_{an} cm^2 s^{-1}	ρ g cm^{-3}	η mPa s	σ S cm^{-1}	D_{cat} cm^2 s^{-1}	D_{an} cm^2 s^{-1}	D_{Li+} cm^2 s^{-1}	ρ g cm^{-3}	η mPa s	σ S cm^{-1}	D_{cat} cm^2 s^{-1}	D_{an} cm^2 s^{-1}	D_{Li+} cm^2 s^{-1}
25	1.3777	48.135	0.00384	$1.98\ 10^{-7}$	$2.04\ 10^{-7}$	1.4478	180.12	0.00142	$9.39\ 10^{-8}$	$6.58\ 10^{-8}$	$9.58\ 10^{-8}$	1.5013	622.45	0.000370	$4.39\ 10^{-8}$	1.3410^{-8}	$2.81\ 10^{-8}$
27	1.3758	44.28	0.00411			1.4459	161.01	0.00166				1.4991	541.96	0.000416			
33	1.3704	34.949	0.00498	$2.96\ 10^{-7}$	$3.07\ 10^{-7}$	1.4401	117.36	0.00218	$1.33\ 10^{-7}$	$1.09\ 10^{-7}$	$1.49\ 10^{-7}$	1.4927	365.49	0.000577	$5.94\ 10^{-8}$	$2.39\ 10^{-8}$	$4.89\ 10^{-8}$
39	1.365	28.096	0.00608	$3.85\ 10^{-7}$	$3.3\ 10^{-7}$	1.4343	87.838	0.0028	$1.83\ 10^{-7}$	$1.29\ 10^{-7}$	$2.06\ 10^{-7}$	1.4865	254.99	0.000797	$8.11\ 10^{-8}$	$4.12\ 10^{-8}$	$7.05\ 10^{-8}$
45	1.3596	22.967	0.00719	$5.2\ 10^{-7}$	$4.36\ 10^{-7}$	1.4286	67.315	0.00352	$2.48\ 10^{-7}$	$1.9\ 10^{-7}$	$2.61\ 10^{-7}$	1.4803	183.28	0.00108	$9.63\ 10^{-8}$	$6.5\ 10^{-8}$	$9.27\ 10^{-8}$
51	1.3543	19.042	0.00848	$6.04\ 10^{-7}$	$5.6\ 10^{-7}$	1.4229	52.67	0.00437	$2.9\ 10^{-7}$	$2.4\ 10^{-7}$		1.4743	135.31	0.00141	$1.27\ 10^{-7}$	$9.1\ 10^{-8}$	
57	1.3489	16.01	0.00987	$7.08\ 10^{-7}$	$7.21\ 10^{-7}$	1.4172	41.962	0.00534	$3.66\ 10^{-7}$	$3.0\ 10^{-7}$		1.4684	102.27	0.00181	$1.52\ 10^{-7}$	$1.21\ 10^{-7}$	
63	1.3436	13.62	0.0113	$8.88\ 10^{-7}$	$8.22\ 10^{-7}$	1.4116	33.993	0.0064	$4.48\ 10^{-7}$	$3.31\ 10^{-7}$	$5.32\ 10^{-7}$	1.4625	78.969	0.00229	$1.88\ 10^{-7}$	$1.62\ 10^{-7}$	$2.24\ 10^{-7}$
68	1.3392	11.982				1.4068	28.857					1.4575	64.602				
75	1.3331	10.152	0.0145			1.4001	23.334	0.0088				1.4506	49.752	0.00343			
82	1.3271	8.6924				1.3936	19.176					1.4438	39.089				
88	1.322	7.6717	0.0184			1.3882	16.369	0.01177				1.438	32.318	0.00501			
101	1.3112	5.9903				1.3767	11.996					1.4257	22.198				