

SUPPLEMENTARY MATERIAL

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1. STRUCTURAL ANALYSIS

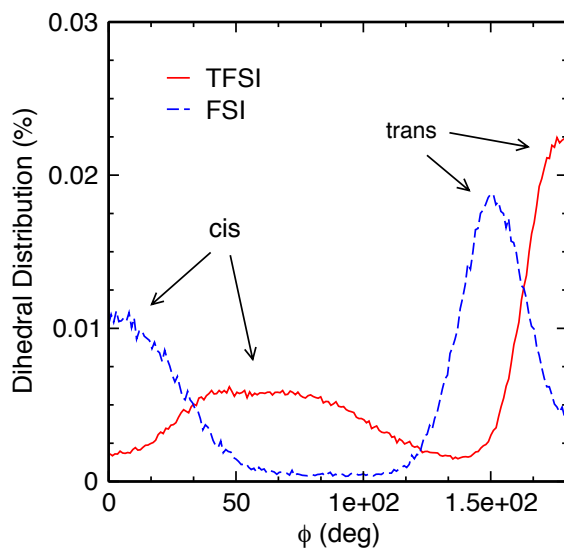


FIGURE S1. Distribution of the C-S-S-C dihedral and the F-S-S-F dihedral in $[\text{TFSI}]^-$ and $[\text{FSI}]^-$, respectively, at $T = 298$ K. Values of ϕ close to 180° represent trans conformations, while smaller values represent cis conformations.

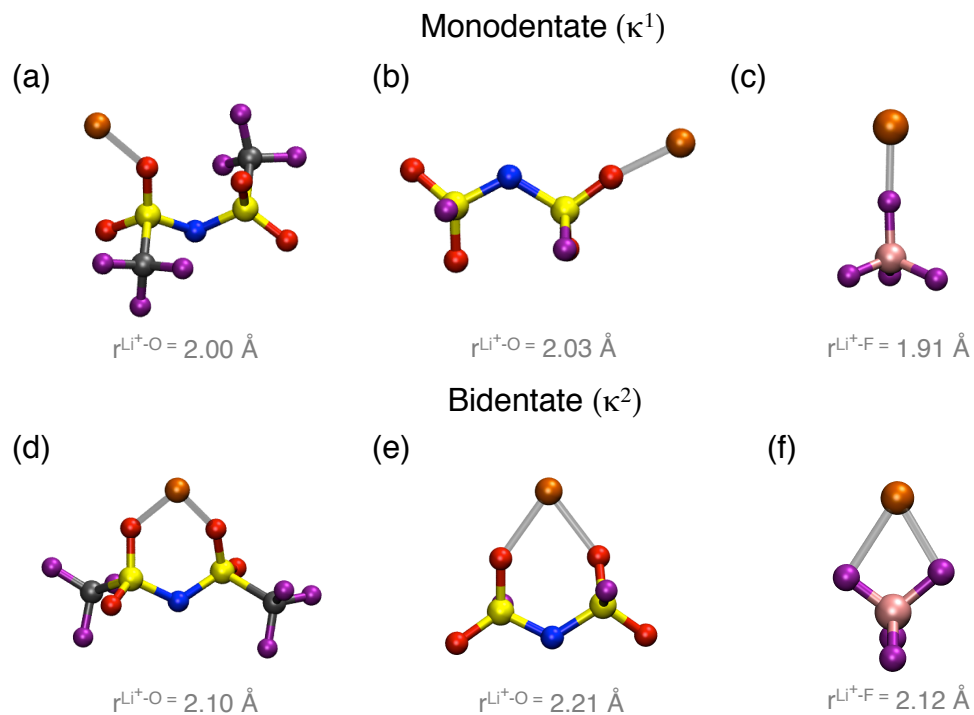


FIGURE S2. Depiction of monodentate (a-c) and bidentate (d-f) binding states for Li[TFSI], Li[FSI], and Li[BF₄]. Average bond distances at $T = 298 \text{ K}$ are included.

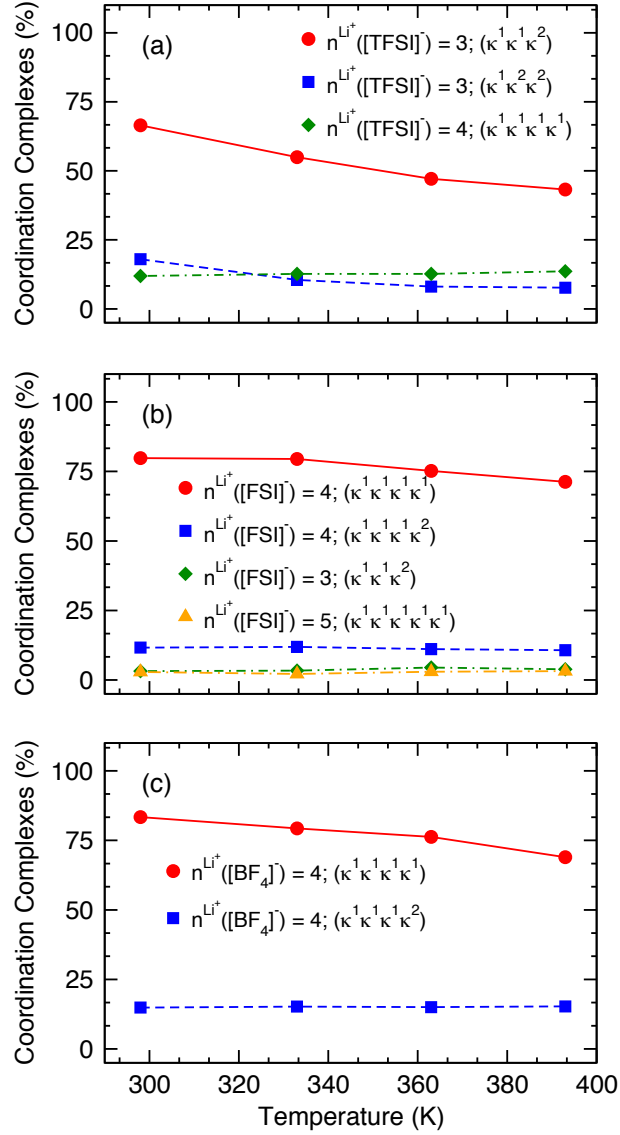


FIGURE S3. Most likely Li^+ -anion coordination shells found in (a) $[\text{pyr14}][\text{TFSI}]$, (b) $[\text{pyr13}][\text{FSI}]$, and (c) $[\text{EMIM}][\text{BF}_4]$ for a T range 298 K to 393 K. The values are averaged over simulations at $x_{\text{Li}^+} = 0.05$, and the shells are defined by the number of monodentate (κ^1) and bidentate (κ^2) anions in the shell.

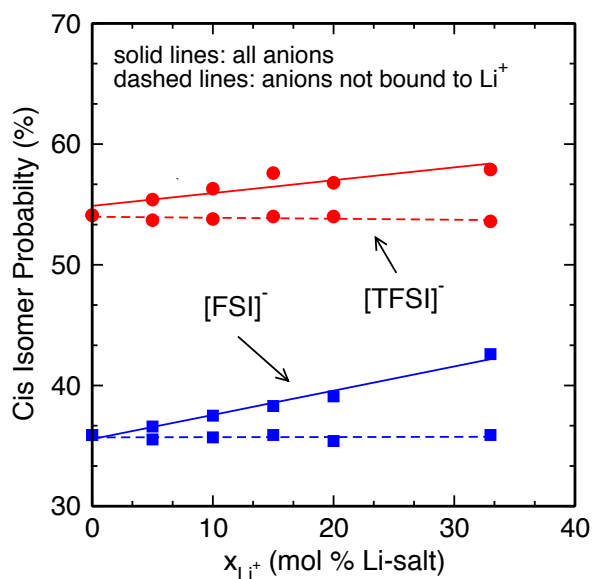


FIGURE S4. Distribution of cis and trans rotamers as a function of Li-salt mole fraction, x_{Li^+} , for anions not bonded with Li⁺ (dashed lines) and all anions in the system (solid lines).

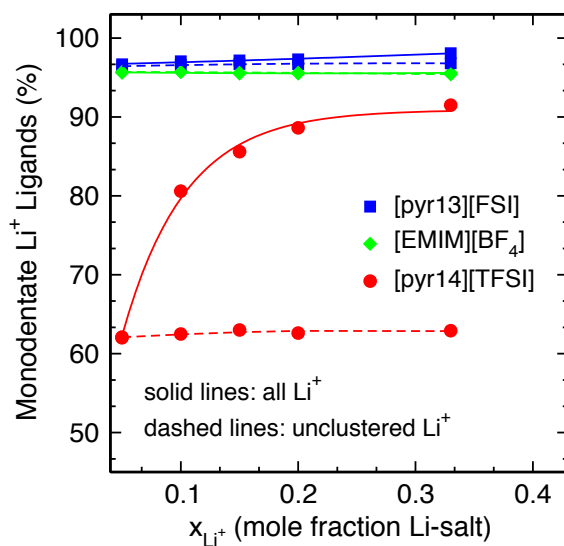


FIGURE S5. Distribution of monodentate bonds to Li⁺ as a function of Li-salt mole fraction, x_{Li^+} , for Li ions not associated with a cluster structures (dashed lines) and all Li ions in the system (solid lines).

2. COMPUTATIONAL AND EXPERIMENTAL THERMODYNAMICS

Measurements for neat [EMIM][BF₄] exhibit a significant hysteresis in conductivity, below -15°C (see Fig. S7). Similar hysteresis has been reported by J. Vila et al. for a number of [EMIM]-based ionic liquids. [1] The observed drop in conductivity occurs well above the solidification temperature tabulated by Galinski for [EMIM][BF₄]. [2] Ionic liquids based on [pyr14][TFSI] were not studied below room temperature in this work.

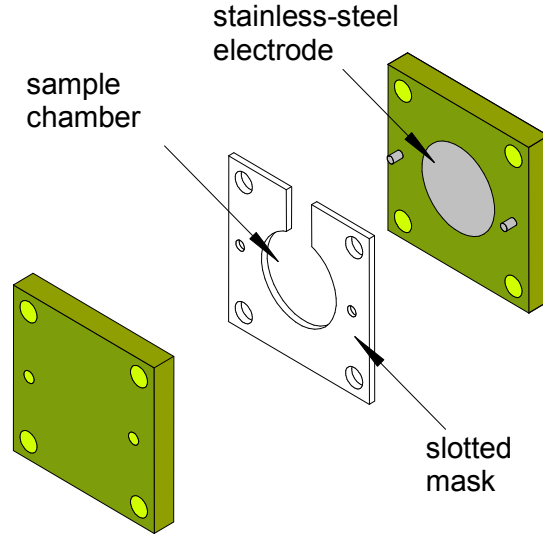
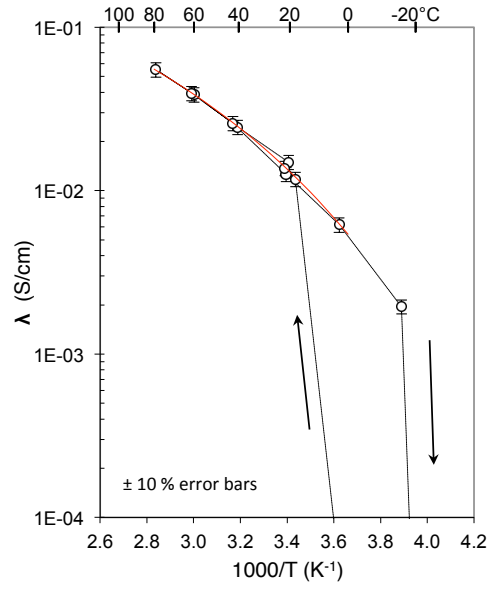


FIGURE S6. Conductivity fixture.

TABLE S1. Density and diffusion coefficient of [pyr14][TFSI] and [EMIM][BF₄] at $T = 298$ K for both neat samples and those having 0.5 m Li-salt doping.

	ρ (g/cm ³)	D^+ (m ² /s)	D^- (m ² /s)	D^{Li} (m ² /s)
[pyr14][TFSI] (neat)	-	0.1338E-10	0.1029E-10	-
[pyr14][TFSI] (0.5 m Li-salt)	1.44	0.0473E-10	0.0270E-10	0.0248E-10
[EMIM][BF ₄] (neat)	-	0.3339E-10	-	-
[EMIM][BF ₄] (0.5 m Li-salt)	1.31	0.2329E-10	-	0.0765E-10

FIGURE S7. Conductivity of neat [EMIM][BF₄].TABLE S2. T dependence of the ionic conductivity of [pyr14][TFSI] in both the neat form and that having 0.5 m Li-salt doping.

T (K)	λ (mS/cm)	
	[pyr14][TFSI] (neat)	[pyr14][TFSI] (0.5 m Li-salt)
293.0	2.31	1.22
313.0	4.98	2.85
333.0	8.90	5.55
353.0	13.8	8.54

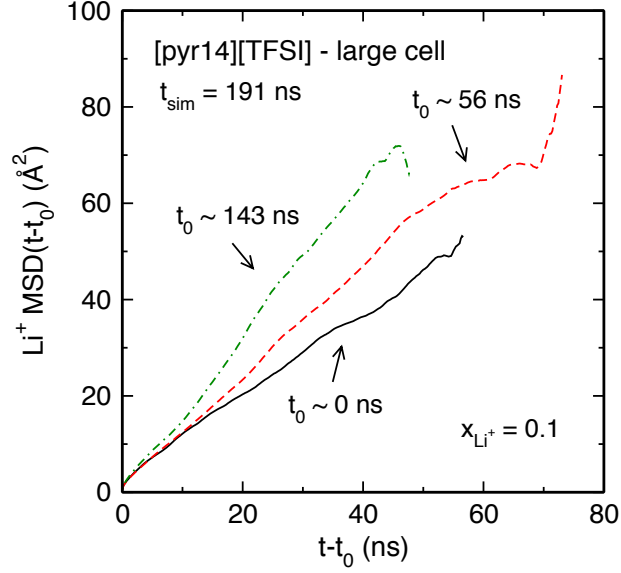


FIGURE S8. Deviation of computed Li^+ MSD as a function of initial state over the course of a 191 ns simulation at $T = 298$ K. The difference between D^{Li^+} taken from the initial trajectory (black solid line) and the final trajectory (green dashed-dotted line) is a factor ~ 2 .

TABLE S3. T dependence of the ionic conductivity of $[\text{EMIM}][\text{BF}_4]$ in both the neat form and that having 0.5 m Li-salt doping.

T (K)	λ (mS/cm)	
	$[\text{EMIM}][\text{BF}_4]$ (neat)	$[\text{EMIM}][\text{BF}_4]$ (0.5 m Li-salt)
352.1	63.6	43.6
334.4	47.3	31.1
332.2	43.4	29.7
314.5	29.5	19.3
313.5	28.0	18.4
297.6	17.6	11.0
295.0	16.4	9.7
294.1	15.5	9.6
275.5	7.38	4.0

TABLE S4. T dependence of the ionic conductivity of neat [pyr13][FSI].

T (K)	λ (mS/cm)
253.7	1.4
265.0	2.6
274.6	3.9
277.3	4.4
295.1	8.0
295.2	7.9
296.5	8.3
313.5	13.1
318.1	14.6
333.1	20.0
335.1	20.1
353.1	28.2

TABLE S5. T dependence of the ionic conductivity of a 0.5 m solution of Li[FSI] in [pyr13][FSI].

T (K)	λ (mS/cm)
253.8	0.9
255.3	1.0
264.8	1.7
275.0	2.9
284.1	4.2
293.8	6.0
294.5	6.2
294.8	5.4
307.3	8.6
319.5	12.7
333.5	17.0
339.3	19.4
343.0	20.7
353.0	24.6

REFERENCES

- [1] J. Vila, C. Franjo, J. M. Pico, L. M. Varela, and O. Cabeza. *Port. Electrochim. Acta*, 51:5567–5580, 2006.
- [2] M. Galiński, A. Lewandowski, and I. Stępnia. *Electrochim. Acta*, 51:5567–5580, 2006.