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Supporting Information:

Elucidation of Transport Mechanism and Enhanced Alkali Ion Transference Numbers in Mixed Alkali Metal–Organic Ionic Molten Salts

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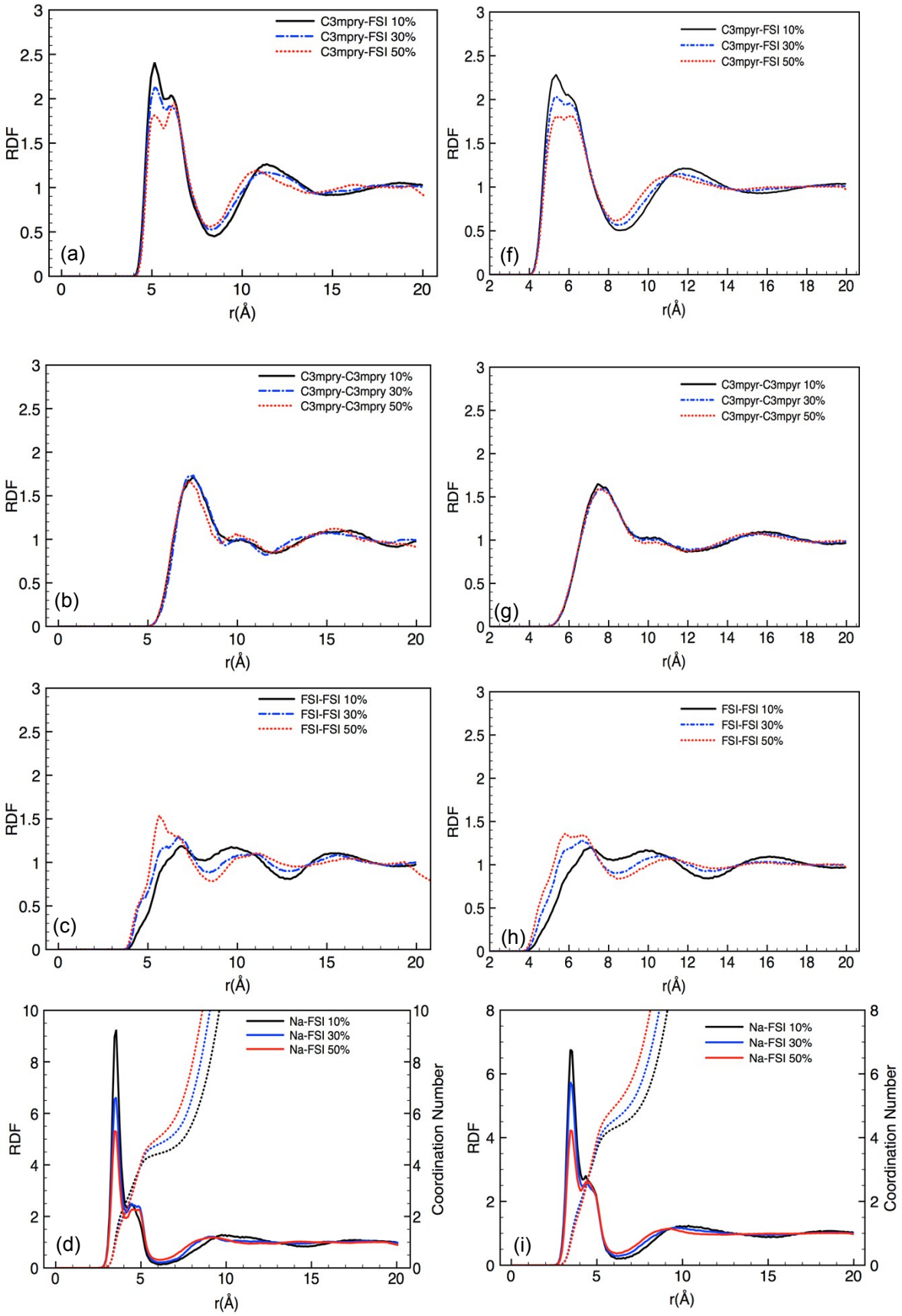
Table S1. Lennard-Jones potential parameters for the Li and Na ion.

Atom	σ(Å)	ε (kcal/mole)	Atom	σ(Å)	ε (kcal/mole)
Li	2.026	0.0183	Na	3.328	0.0028

Table S2. Statistics of number and percentage of alkali metal ions according to their largest mean square displacements calculated for 3ns.

MSD (Å^2)	Number of Li ion	Percentage_Li (%)	Number of Na ion	Percentage_Na (%)
> 100	5	13.9	1	2.7
> 60	9	25	5	13.9
40-60	17	47.2	3	8.3
< 40	10	27.8	28	77.8


C3mpry-FSI 10%
C3mpry-FSI 30%
C3mpry-FSI 50%
(a)
RDF
r(Å)
C3mpyr-FSI 10%
C3mpyr-FSI 30%
C3mpyr-FSI 50%
(f)
C3mpry-C3mpry 10%
C3mpry-C3mpry 30%
C3mpry-C3mpry 50%
(b)
C3mpyr-C3mpyr 10%
C3mpyr-C3mpyr 30%
C3mpyr-C3mpyr 50%
(g)
FSI-FSI 10%
FSI-FSI 30%
FSI-FSI 50%
(c)
(h)
Na-FSI 10%
Na-FSI 30%
Na-FSI 50%
(d)
(i)
Coordination Number

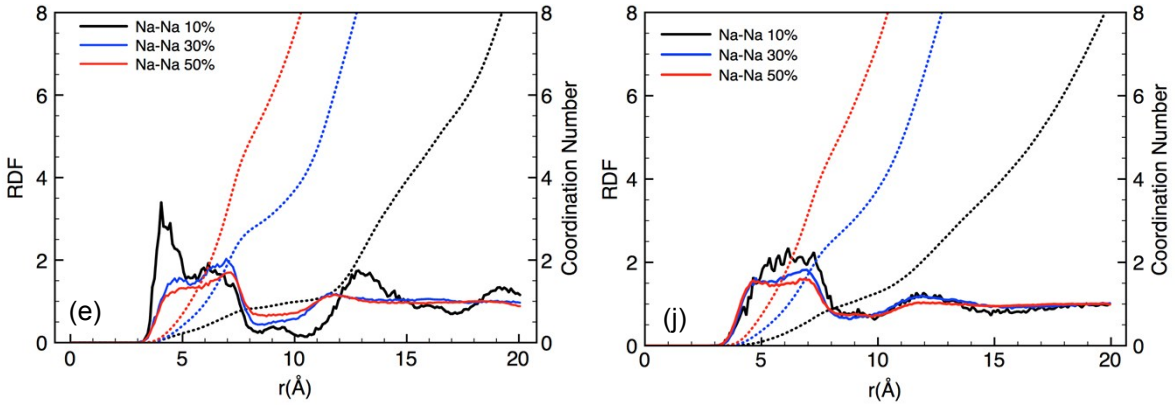


Figure S1. RDFs calculated between the mass center of the C3mpyr cation, FSI anion, and the Na ion at (a)-(e) 293K and (f)-(j) 393K.

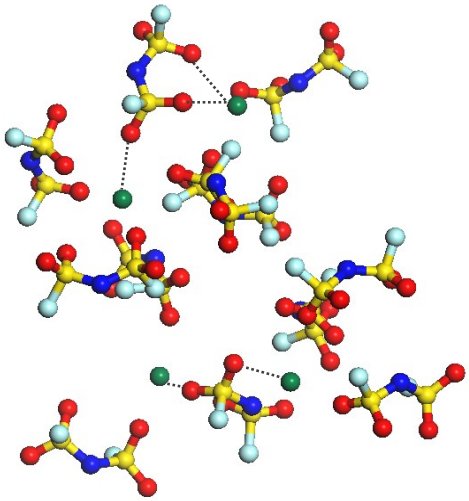


Figure S2. A snapshot illustrates that one FSI anion was shared by one more Na ions (green particles). The dotted lines indicate the interaction between the Na ion and FSI oxygen.

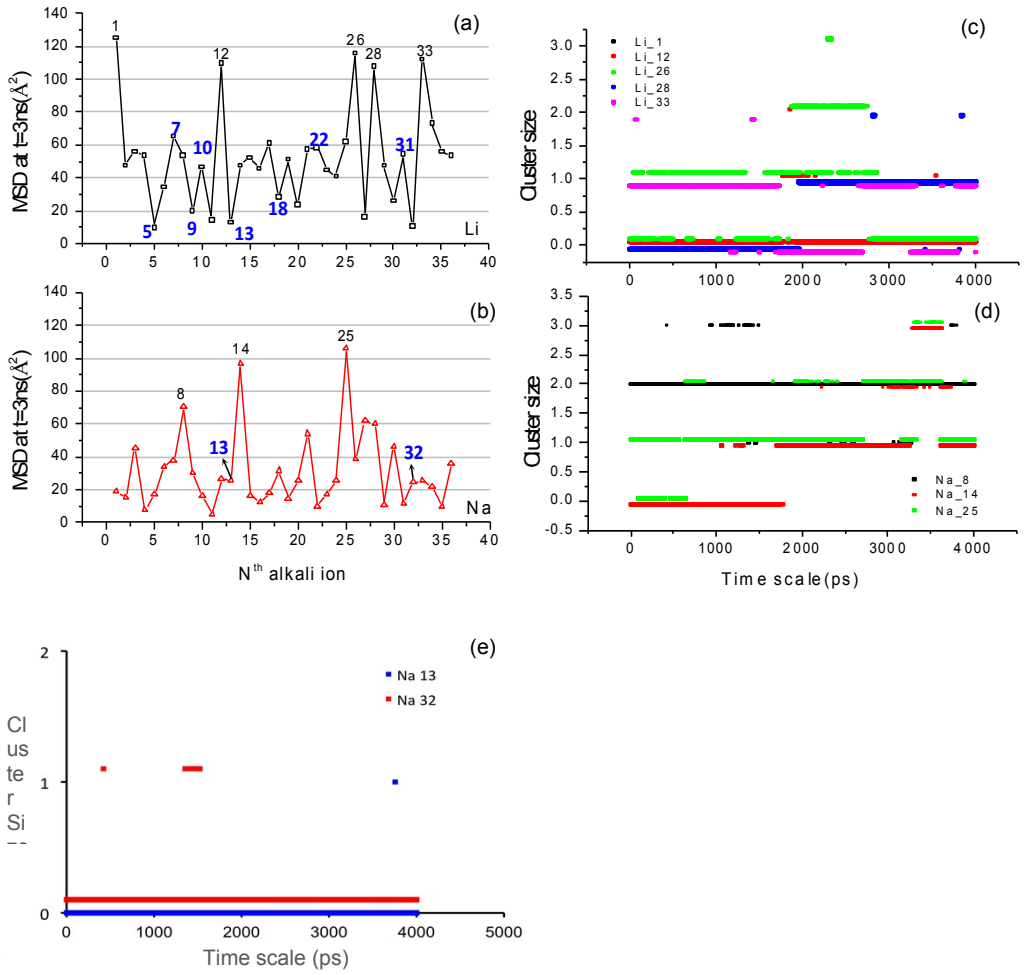


Figure S3. The largest mean square displacement calculated for 3ns for 36 Li (a) and Na (b) ions in the 16.7 mol% $P_{1224}PF_6$ systems; the cluster size for the five fastest Li_1, 12, 26, 28, 33 ions (c) and the three fastest Na_8, 14, 25 ions (d) was calculated in each time frame throughout 4000 ps simulation time. These Li and Na ions presenting to be a 'free' ion (cluster size=0) in most time were also marked in (a) and (b) in blue, and the time dependent cluster size changes of two relative 'free' Na_13 and Na_32 ions were given in (e).

The fastest metal ions decided from their mean square displacement were traced of their cluster size throughout a 4 ns simulation time. It shows that the cluster size of these ions would not always be same, but keep changing between several sizes, indicating the dissociation of their clusters happens during the diffusion. These relatively 'free' metal ions were also decided from the time dependent cluster size analysis with a typical distribution shown in Figure S3(e), and they were marked in

Figure S3(a) and (b) using atomic number (in blue) and their displacements suggest a either medium high or slow dynamics.

The statistics of the displacement of these alkali ions also demonstrates that the number of the fastest Li ions is apparently more than that of the Na ions. For example, Table S2 lists these results for 16.7mol% Li or Na doped systems. The mobility of alkali ions was evaluated according to their largest displacements in a 3 ns simulation time, and was divided into four levels. The fast motion of the metal ions is defined as having more than 60 $Å^2$ of a displacement, and this group includes 25% Li ions but only 13.9% Na ions. The 13.9% of the Li^+ even have a displacement more than 100 $Å^2$, comparing to only the 2.7% of the Na^+. 47.2% of Li ions have displacements between 40 and 60 $Å^2$, and the left 27.8% are regarded as the slowest ones (< 40 $Å^2$). Obviously, the majority 77.8% Na ions show their displacements in the slowest ion range.