Electronic Supplementary Information

Structural study on a specific Li-ion ordered complex in dimethyl carbonate-based dual-cation electrolytes

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Details in MD simulations.

Data curation of the MD simulation was done at intervals of 0.1 ps during the last 500 ps, after which the X-ray weighted structure factors $S^{MD}(q)$ and the radial distribution functions $G^{MD}(q)$ were estimated. Based on previous studies, the OPLS-AA-based force fields that incorporate intermolecular Lennard–Jones (LJ) and coulombic interactions as well as intramolecular interactions of bond stretching, angle bending, and torsion of dihedral angles, were employed for DMC,[1, 2] SBP+,[2-4] EMI+,[5] and BF4–.[6] The partial charges for the DMC, SBP+, EMI+, and BF4– were obtained from DFT calculations (ChelpG method, Fig. S1). The $S^{MD}(q)$ values were determined from the MD simulations trajectories using Eq. S-1.

$$S^{MD}(q) = \begin{cases} \dfrac{\Sigma_i \Sigma_j \left\{ \frac{n_i(n_j-1)f_i(q)f_j(q)}{N(N-1)} \right\}}{\left\{ \Sigma_k \left(\frac{n_k f_k(q)}{N} \right) \right\}^2} \int_0^{r_{max}} 4\pi r^2 \rho_0 \left(g_{ij}^{MD}(r) - 1 \right) \dfrac{\sin qr}{qr} dr + 1 \,(i = j) \\[4mm] \dfrac{\Sigma_i \Sigma_j \left\{ \frac{2n_i n_j f_i(q)f_j(q)}{N^2} \right\}}{\left\{ \Sigma_k \left(\frac{n_k f_k(q)}{N} \right) \right\}^2} \int_0^{r_{max}} 4\pi r^2 \rho_0 \left(g_{ij}^{MD}(r) - 1 \right) \dfrac{\sin qr}{qr} dr + 1 \,(i \neq j) \end{cases}$$

$$(S-1)$$

where r_{max} is the upper integration limit (25 Å), N is the total number of atoms within the cubic simulation box as defined by $N = \Sigma_k nk$, and $g^{MD}{}_{ij}(r)$ is the atom–atom pair correlation function for atoms i and j. $G^{MD}(q)$ was obtained from the calculated $S^{MD}(q)$ using an inverse Fourier transform.

Table S1. Compositions (number of salts and solvent), box lengths of the system, and densities (d) for MD simulations.

| Sample	Li-BF4	SBP-BF4 (or EMIBF4)	DMC	Box length / Å	d / g cm^{-3}		c_{Li} / mol dm^{-3}	c_{SBP} / mol dm^{-3}
					MD	Exp.		
1.0 M LiBF4/DMC	200	–	2252	68.75	1.142	1.143	1.0	–
2.0 M SBPBF4/DMC	–	400	1630	69.62	1.142	1.143	–	2.0
*1 M SBPBF4/DMC with 0.4 M LiBF4	120	300	1644	68.21	1.163	1.159	0.6	1.6
1 M SBPBF4/DMC with 1 M LiBF4	190	190	1900	68.96	1.166	1.155	1.0	1.0
neat EMIBF4	–	512	–	51.80	1.218	1.29	–	–

*Bottom phase of 1.0 M SBPBF4/DMC with 0.4 M LiBF4, corresponding to 1.6 M SBPBF4/DMC with 0.6 M LiBF4
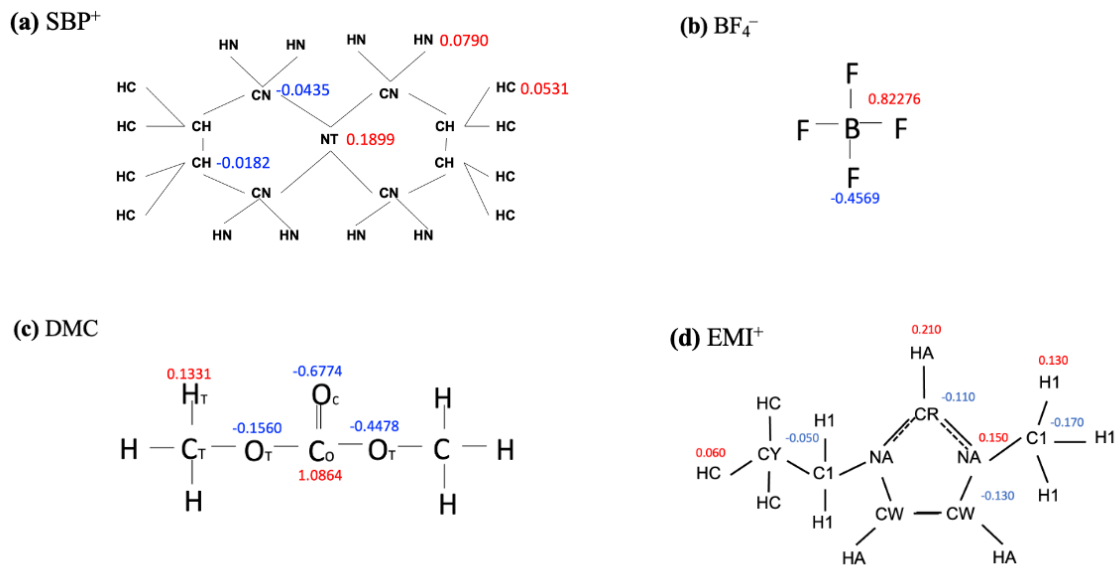
Figure S1. Partial charges of (a) SBP$^+$, (b) BF$_4^-$, (c) DMC, and (d) EMI$^+$ calculated DFT calculations [ChelpG method: MP2/cc-pVTZ(-f)//HF/6-31G(d)].
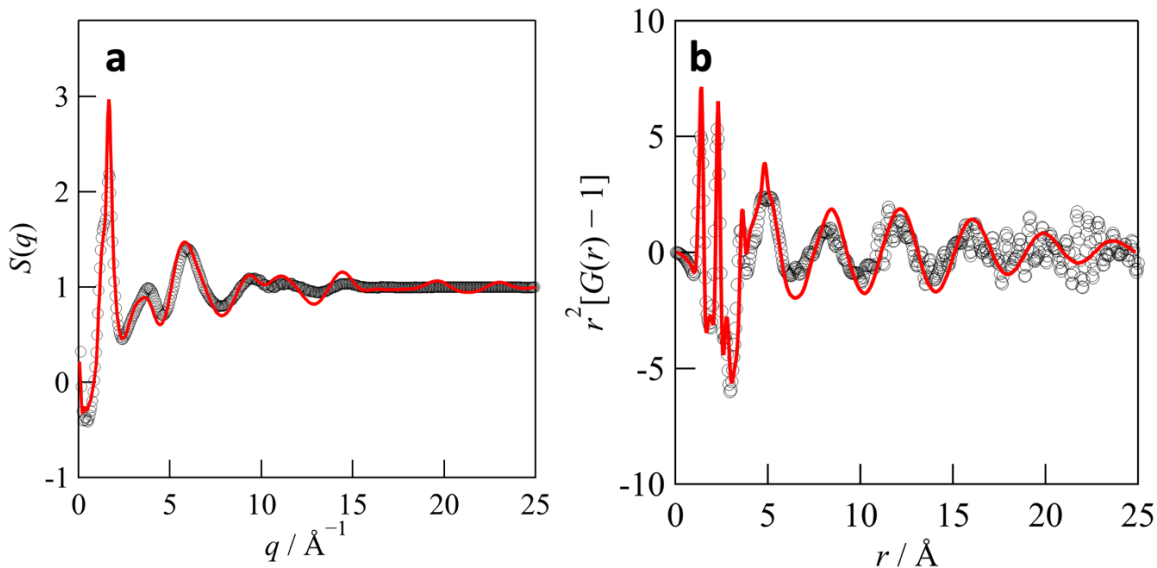
Figure S2. (a) $S(q)$ and (b) $r^2[G(r) - 1]$ obtained by HEXTS measurements (open black circles) and MD simulations (solid red lines) for 1.0 M LiBF$_4$/DMC.
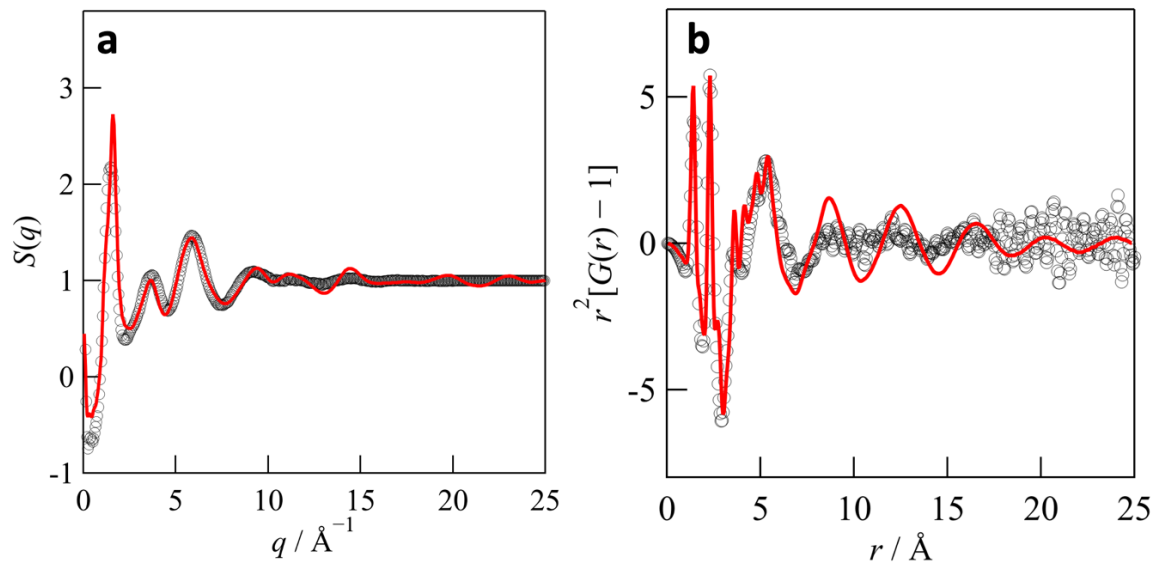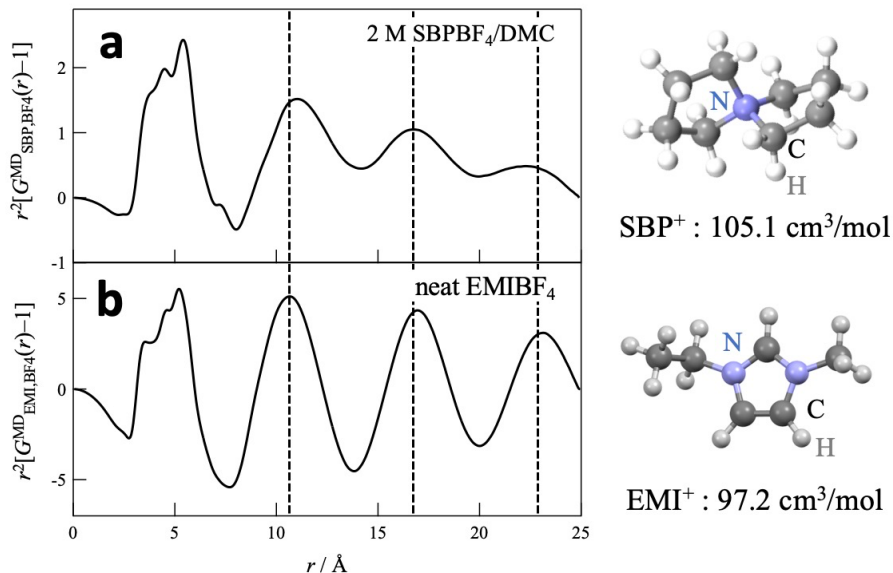
Figure S3. (a) $S(q)$ and (b) $r^2[G(r) - 1]$ obtained by HEXTS measurements (open black circles) and MD simulations (solid red lines) for 2.0 M SBPBF$_4$/DMC.
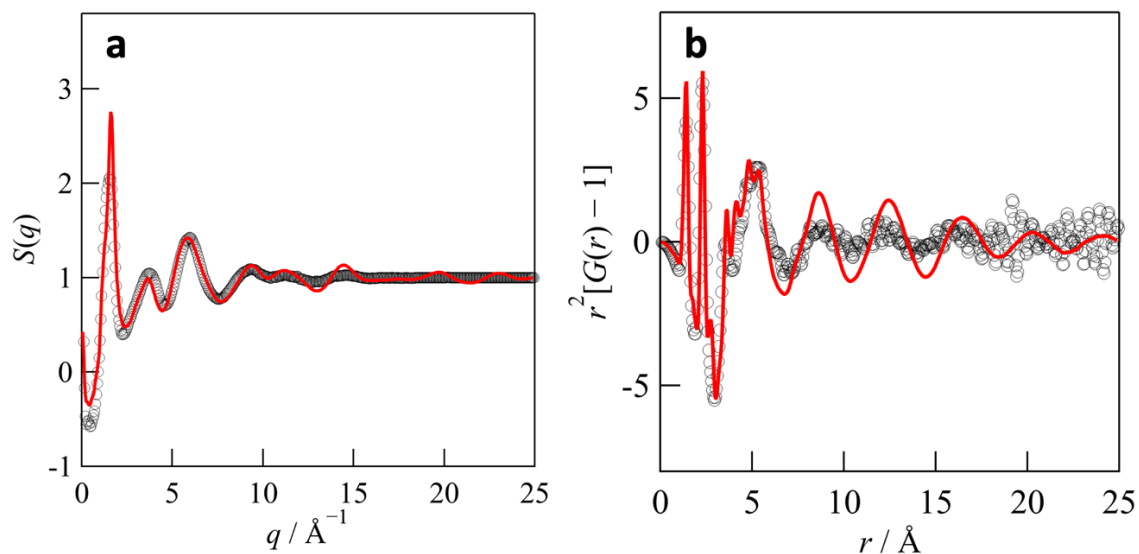
Figure S4. (a) $S(q)$ and (b) $r^2[G(r) - 1]$ obtained by HEXTS measurements (open black circles) and MD simulations (solid red lines) for 1.6 M SBPBF$_4$/DMC with 0.6 M LiBF$_4$, corresponding to the bottom phase of 1.0 M SBPBF$_4$/DMC solution with 0.4 M LiBF$_4$.

Figure S5. The $r^2[G^{MD}(r) - 1]$ functions for cation-anion correlations in (a) 2 M SBPBF$_4$/DMC (SBP$^+$–BF$_4^-$ correlation) and (b) neat EMIBF$_4$ (EMI$^+$–BF$_4^-$ correlation). Note that SBP$^+$ and EMI$^+$ cations have similar molar volumes, 105.1 cm^3 mol^{-1} and 97.2 cm^3 mol^{-1}, respectively. It has been established that in popular ionic liquids, cations and anions electrostatically interact with each other to form a highly ionic ordered structure, resulting in clear periodic correlations in $G(r)$ function,[7, 8] as shown in Fig. S5b (EMIBF$_4$ ionic liquid, in this work). Similar periodic correlations were observed in the 2 M SBPBF$_4$/DMC system (Fig. S5a), indicating loosely structured SBP$^+$–BF$_4^-$ aggregates in the DMC solution. We expect that the formation of ionic aggregates is the molecular origin of the specific phase separation in the SBPBF$_4$/DMC system.

References

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