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Electronic Supplementary Information

Fluorinated alkyl-phosphate-based electrolytes with controlled lithium-ion coordination structure

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Modified partial charges (MD simulation).

In our previous study (LiTFSA/TFEP and LiTFSA/AN systems),[1] we examined to modify partial charges (q^+ and q^-: original values are shown in Fig. S1) by weighting a factor (f), resulting in a successful agreement of experimental and simulation-derived radial distribution functions [$G^{\mathrm{exp}}(r)$ and $G^{\mathrm{MD}}(r)$, respectivily]. The optimum value, $f = 0.6$ (i.e., 60% of the original q^+ and q^-) for the TFEP and Li-TFSA ion-pair and $f = 1.0$ for the AN. In this work (LiFSA/TFEP and LiFSA/TFEP+AN systems), we thus used (1) $f = 0.6$ for the TFEP and Li-FSA and (2) $f = 1.0$ for the AN in the current MD simulations.The $G^{\mathrm{MD}}(r)$ using the fq^+ and fq^- in Coulombic term successfully reproduced the corresponding experimental $G^{\mathrm{exp}}(r)$, as shown in Fig. 7.

Estimation of $c_{\mathrm{f\_FSA}}$ and $c_{\mathrm{b\_FSA}}$ values.

We measured separately IR spectra of [C$_2$mIm][FSA]/TFEP system (without LiFSA salt) with c_{C2mImFSA} = 0, 0.5, and 1.0 mol dm^{-3} (Fig. S2a). The peak (from 700 to 780 cm^{-1}, S-N-S symmetric stretching mode of the FSA component) increased in intensity with c_{C2mImFSA}, which could be assigned to the free FSA. The observed spectra were represented using two free FSA bands (typical result for c_{C2mImFSA} = 1.0 mol dm^{-3}, Fig. S2b), which is consistent with the current LiFSA/TFEP system described in the manuscript. The integrated intensities of the two free FSA bands, $I_{\mathrm{f\_FSA}}$ (= $I_{745} + I_{758}$) were plotted against c_{FSA} (=c_{C2mImFSA}) (Fig. S2c) and the slope corresponds to the $\varepsilon_{\mathrm{f\_FSA}}$ value according to the following relation: $I_{\mathrm{f\_FSA}} = \varepsilon_{\mathrm{f\_FSA}}\, c_{\mathrm{f\_FSA}}$.

The $\varepsilon_{\mathrm{b\_FSA}}$ value was also estimated based on the following relations: $I_{\mathrm{b\_FSA}} = \varepsilon_{\mathrm{b\_FSA}}\, c_{\mathrm{b\_FSA}}$ and $c_{\mathrm{b\_FSA}} = n_{\mathrm{FSA}}\, c_{\mathrm{Li}}$. Consequently, the ratio of molar absorption coefficients ($\varepsilon_{\mathrm{f\_FSA}}/\varepsilon_{\mathrm{b\_FSA}}$) was determined to be 1.72. Appling the $\varepsilon_{\mathrm{f\_FSA}}$ value to the LiFSA/TFEP system, we can estimate $c_{\mathrm{f\_FSA}}$ value (=$I_{\mathrm{f\_FSA}}/\varepsilon_{\mathrm{f\_FSA}}$) and $c_{\mathrm{b\_FSA}}$ (=$c_{\mathrm{T\_FSA}} - c_{\mathrm{f\_FSA}}$).

Estimation of $J_{\mathrm{f\_AN}}$ value.

To determine $J_{\mathrm{f\_AN}}$ value, we measured separately Raman spectra of TFEP+AN mixed solution (without LiFSA salt) with c_{AN} = 0, 1.0, and 2.0 mol dm^{-3} (Fig. S4a). The peak (2265 cm^{-1}, N≡C symmetric stretching mode of AN) increased linearly in intensity with c_{AN}, which could be assigned to the free AN owing to very weak intermolecular interactions between TFEP and AN. The observed spectra were represented using two free AN bands (typical result for c_{AN} = 2.0 mol dm^{-3}, Fig. S4b), which is consistent with the current LiFSA/TFEP+AN system described in the manuscript. The integrated intensities of the two free AN bands, $I_{\mathrm{f\_AN}}$ (= $I_{2261} + I_{2265}$) were plotted against c_{AN} (Fig. S4c) and the slope corresponds to the $J_{\mathrm{f\_AN}}$ value according to the following relation: $I_{\mathrm{f\_AN}} = J_{\mathrm{f\_AN}}\, c_{\mathrm{f\_AN}}$.

The $J_{\mathrm{b\_AN}}$ value was also estimated based on the following relations: $I_{\mathrm{b\_AN}} = J_{\mathrm{b\_AN}}\, c_{\mathrm{b\_AN}}$ and $c_{\mathrm{b\_AN}} = n_{\mathrm{AN}}\, c_{\mathrm{Li}}$. Consequently, the ratio of Raman scattering coefficients ($J_{\mathrm{f\_AN}}/J_{\mathrm{b\_AN}}$) was determined to be 0.57.

Table S1. Molar ratio (salt:solvent), concentrations of LiFSA salt (c_{Li}), TFEP (c_{TFEP}), and AN (c_{AN}), density (d), refractive index (n_2) for binary LiFSA/TFEP and ternary LiFSA/TFEP+AN solutions.

binary LiFSA/TFEP system				
LiFSA : TFEP	c_{Li} / mol dm^{-3}	c_{TFEP} / mol dm^{-3}	d / g cm^{-3}	n_2
-	0	4.60	1.450	1.329
1 : 22.7	0.20	4.53	1.596	1.329
1 : 11.2	0.40	4.46	1.611	1.329
1 : 7.32	0.60	4.39	1.625	1.329
1 : 5.38	0.80	4.30	1.633	1.332
1 : 4.24	1.00	4.24	1.648	1.332

ternary LiFSA/TFEP+AN system					
LiFSA : TFEP:AN	c_{Li} /mol dm^{-3}	c_{TFEP} /mol dm^{-3}	c_{AN} /mol dm^{-3}	d / g cm^{-3}	n_2
1 : 3.96 : 1.02	1.00	3.96	1.02	1.599	1.334
1 : 3.70 : 2.04	1.00	3.70	2.04	1.552	1.336

Table S2. c_{Li}, c_{AN}, d and compositions (number of ion-pairs and solvents) for the MD simulations (1.0 mol dm^{-3} LiFSA/TFEP solutions with AN, Li:AN (by mol.) = 1:0 and 1:2).

c_{Li} / mol dm^{-3}	c_{AN} / mol dm^{-3}	d / g cm^{-3}		Li-FSA	TFEP	AN
		Exp.[a]	MD[b]			
1.0	-	1.648	1.678	133	567	-
1.0	2.0	1.552	1.578	145	538	317

[a] Value obtained from the present MD simulations. [b] Experimental values.

Table S3. Ionic conductivities of $c_{\mathrm{Li}} = 1.0$ mol dm^{-3} solutions at 298K.

Sample	σ /mS·cm^{-1} (at 298K)
LiTFSA/EC+DMC [2, 3]	51.0
LiTFSA/AN [4]	38.0 (at 303K)
LiTFSA/H_2O [2]	36.8
LiTFSA/DMF [2, 5]	15.1
$LiPF_6$/EC+DMC [2, 3]	12.1
LiFSA/TFEP (Li:AN = 1:0)	1.1
LiFSA/TFEP (Li:AN = 1:1)	1.6
LiFSA/TFEP (Li:AN = 1:2)	3.5

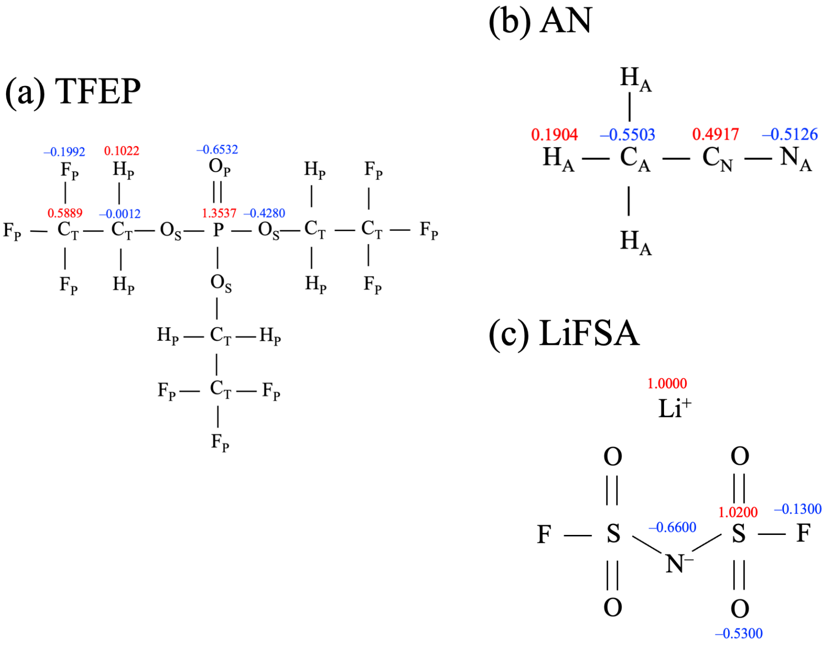

Fig. S1. The original partial charge values of (a) TFEP, (b) AN,[6] and (c) LiFSA[7]. The values of TFEP were calculated based on ChelpG method (MP2/cc-pVTZ(-f) calculation)[1].

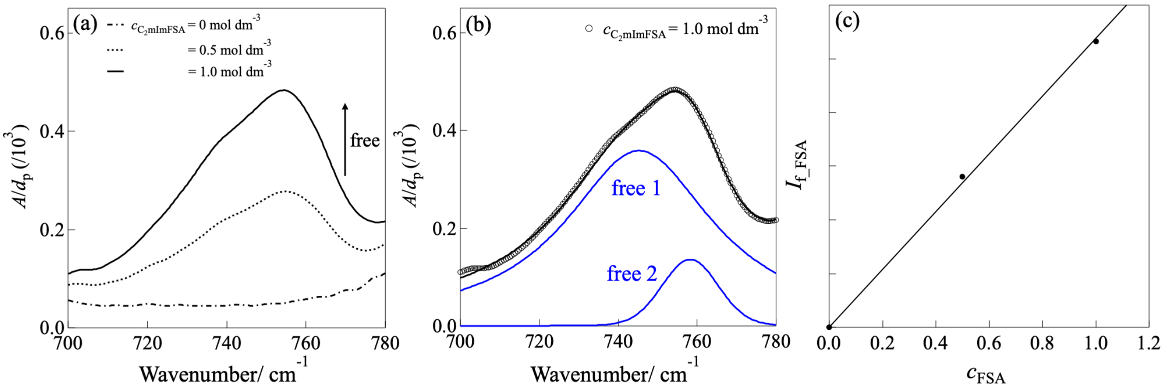

Fig. S2. (a) FT-IR spectra for the TFEP solution with varying $c_{C2mImFSA}$, (b) A curve-fitting result for the $c_{C2mImFSA}$ = 1.0 mol dm^{-3} solution, and (c) The integrated intensities of the two free FSA bands, I_{f_FSA} (= I_{745} + I_{758}) plotted against FSA concentration (c_{FSA}).

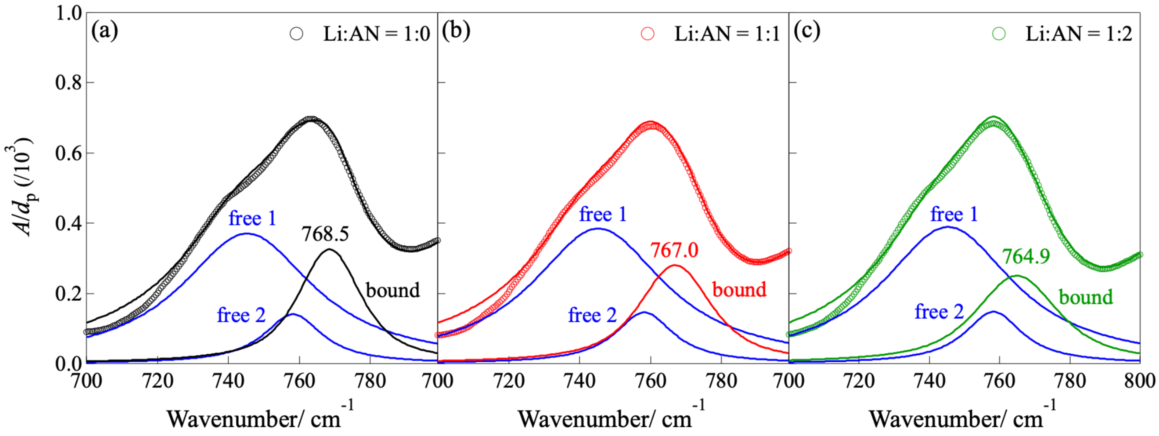

Fig. S3. Curve fitting results of the IR spectra observed for the 1.0 mol dm^{-3} LiFSA/TFEP solutions with added AN: (a) Li:AN (by mol.) = 1:0, (b) 1:1, and (c) 1:2.

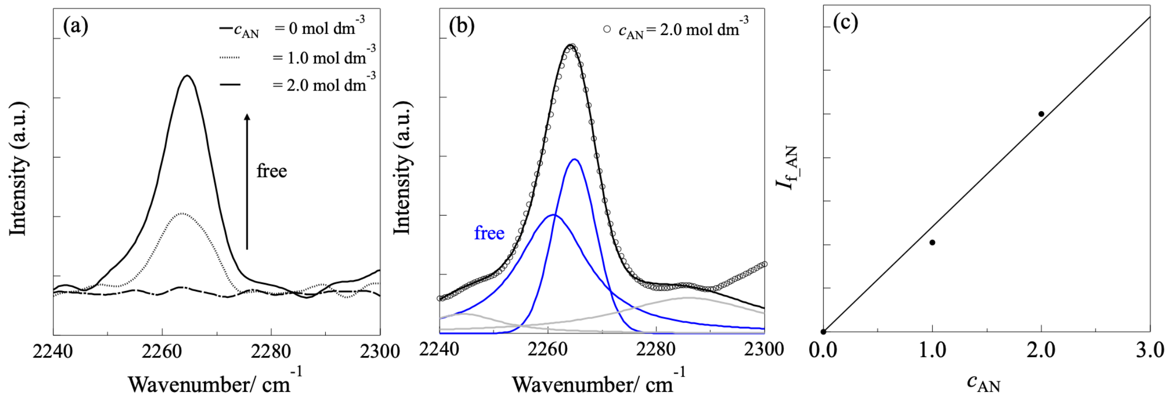

Fig. S4. (a) Raman spectra for the TFEP+AN mixed solutions (without LiFSA salt) with c_{AN} = 0, 1.0, and 2.0 mol dm^{-3}, (b) A curve-fitting result for 1.0 mol dm^{-3} LiFSA/TFEP with c_{AN} = 2.0 mol dm^{-3} and (c) The integrated intensities of the two free AN bands, I_{f_AN} (= I_{2261} + I_{2265}) plotted against c_{AN}.

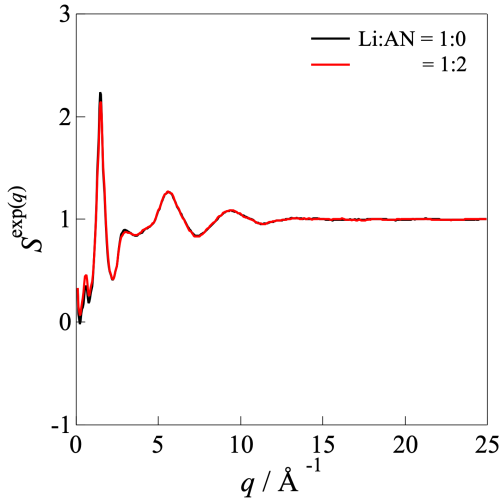

Fig. S5. $S^{\exp}(q)$ profiles obtained from HEXTS measurements for 1.0 mol dm^{-3} LiFSA/TFEP +AN solutions (Li:AN = 1:0 and 1:2).

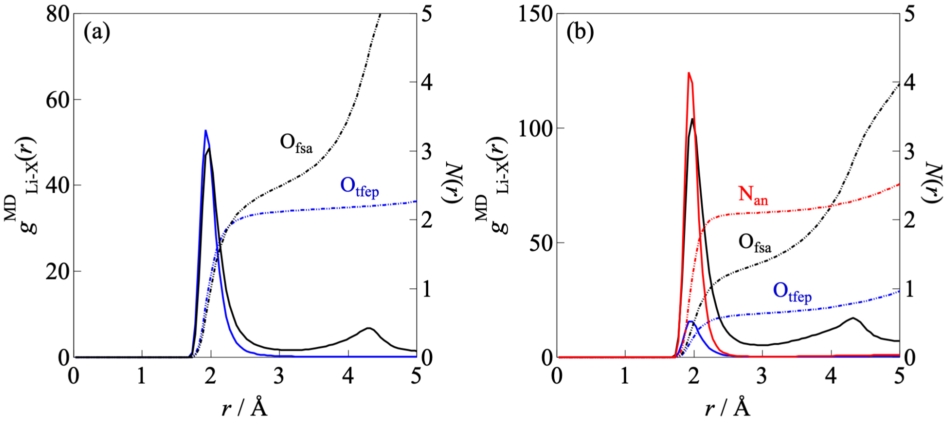

Fig. S6. Atom-atom pair correlation functions [$g^{\mathrm{MD}}_{\text{Li-X}}(r)$: left axis, solid lines] for the O atoms of TFEP (blue), the O atoms of FSA (black) and the N atoms of AN (red) around the Li ions and their integrated profiles [coordination number $N(r)$: right axis, dashed lines] for (a) 1.0 mol dm^{-3} LiFSA/TFEP solution and (b) that with AN (Li:AN = 1:2).

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