Electronic Supplementary Information

Lithium-Ion Coordination-Induced Conformational Change of PEG Chains in Ionic-Liquid-Based Electrolytes

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Determination of desolvation number (n_d) of TFSA anions from Raman data.

For the Li^+–PEG complexation in LiTFSA/[C_2mIm][TFSA] solutions, we assumed herein the following equilibrium,

$$[Li(TFSA)_{nTFSA}]^- + EG \rightleftharpoons [Li(TFSA)_{nTFSA-nd}(EG)] + n_dTFSA$$

where EG denotes a monomer unit of PEG (i.e., ethylene glycol unit). The n_d is defined as the desolvation number of the bound TFSA per one EG, as the following equation.

$$n_d = \frac{c_f - c_f'}{c_{EG}}$$

where c_f and c_f' are the concentration for free TFSA in 1.0 M LiTFSA/[C_2mIm][TFSA] solutions with and without PEG, respectively. c_{EG} is the concentration for EG unit. The integrated intensity of the single Raman band for free TFSA in LiTFSA/[C_2mIm][TFSA]+PEG solution is represented as $I_f = J_f c_f$, where J_f is the Raman scattering coefficient for free TFSA. Total concentration of TFSA anions (c_T) in LiTFSA/[C_2mIm][TFSA] solution is given by the equation, $c_T = c_f + c_b$, where c_b is the concentration for bound TFSA. Considering the mass balance equation: $c_f' = c_T - c_b' = c_T - n_{TFSA}c_{Li}$, where n_{TFSA} and c_{Li} are the solvation number of TFSA in the first Li-ion solvation sphere and the concentration of Li salt, respectively, we can obtain the following equation,

$$\left(\frac{I_f}{J_f}\right) - (c_T - n_{TFSA}c_{Li}) = n_d c_{EG}$$

Table S1. Density d, compositions (number of ion-pairs and PEG molecules), and box length of the systems for MD simulations. a: [C_2mIm][TFSA] + PEG, b: 1.0 M LiTFSA/[C_2mIm][TFSA] + PEG, c: 1.0 M LiTFSA/[C_2mIm][TFSA].

sample	d / g cm^{-3}		LiTFSA	[C_2mIm][TFSA]	linear PEG (M_w:600)	Box length / Å
	Exp.	MD				
a	1.444	1.476	-	256	24	50.57
b	1.516	1.558	78	256	24	52.67
c	1.579	1.636	155	512	-	62.93

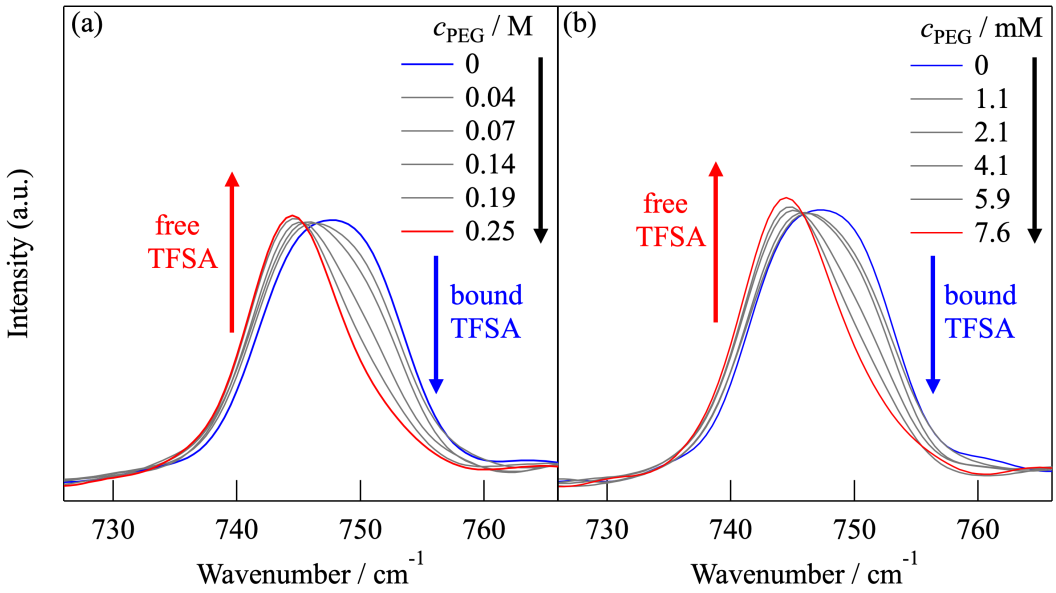

Fig. S1. Raman spectra of 1.0 M LiTFSA/[C_2mIm][TFSA] solutions with various c_{PEG} using LinearPEG of (a) M_w = 600 g mol^{-1} and (b) 20 000 g mol^{-1}.

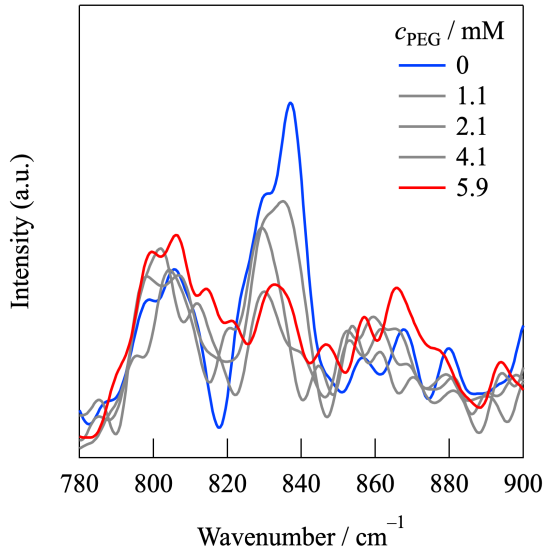

Fig. S2. Raman spectra in the range 780–900 cm^{-1} for 1.0 M LiTFSA/[C_2mIm][TFSA] solutions with various c_{PEG} (TetraPEG).

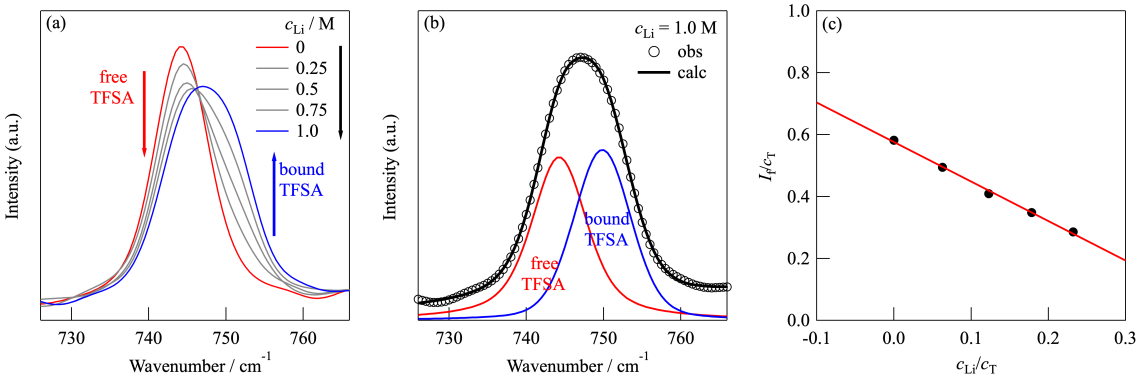

Fig. S3. (a) Raman spectra observed for the LiTFSA/[C$_2$mIm][TFSA] solutions with varying c_{Li}. (b) The typical result of deconvoluted Raman bands based on a least-squares curve fitting analysis for c_{Li} = 1.0 M solution. (c) I_f/c_T vs. c_{Li}/c_T plots.

The integrated intensity of the deconvoluted band for the free TFSA is represented as $I_f = J_f c_f$, where J_f and c_f stand for the Raman scattering coefficient and concentration, respectively, of the free TFSA. Considering the mass balance equations: $c_f = c_T - c_b = c_T - n_{TFSA}c_{Li}$, where c_T, c_b, and c_{Li} denote the concentrations of total TFSA, TFSA bound to Li^+ ions (bound TFSA), and Li^+ ions, respectively, and n_{TFSA} is the solvation number of TFSA anions around Li^+ ions, we obtain the following equation: $I_f/c_T = -n_{TFSA}J_f(c_{Li}/c_T) + J_f$. Plots of I_f/c_T against c_{Li}/c_T yield a straight line with a slope $\alpha = -n_{TFSA}J_f$ and an intercept $\beta = J_f$, and the n_{TFSA} value is thus obtained from $n = -\alpha/\beta$. The resulting value was n_{TFSA} = 2.3.

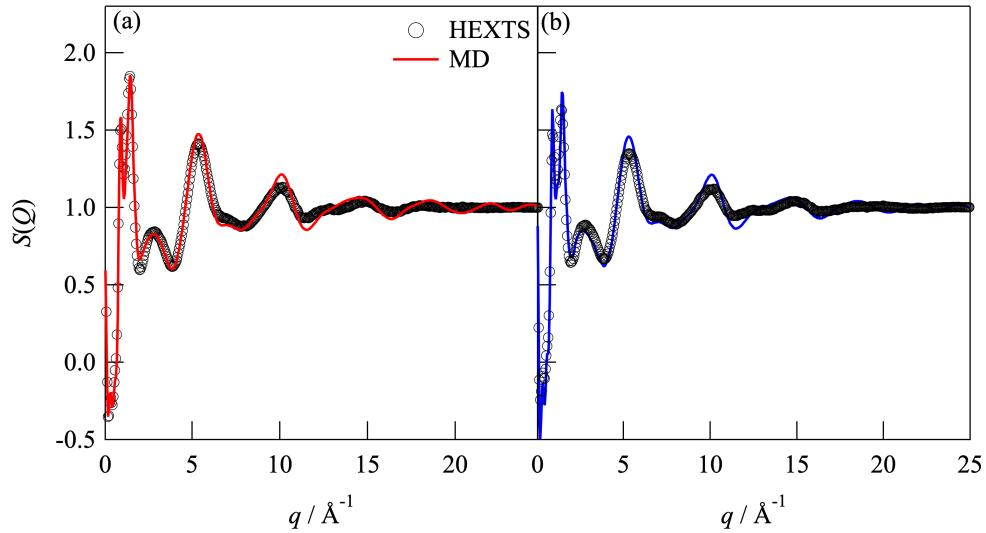

Fig. S4. $S(q)$s obtained from HEXTS experiments (open circles) and MD simulations (solid lines) for the (a) c_{Li} = 0 M and (b) c_{Li} = 1.0 M LiTFSA/[C$_2$mIm][TFSA] solutions containing PEG. [C$_2$mIm][TFSA] : PEG = 10.7:1 (by mol).

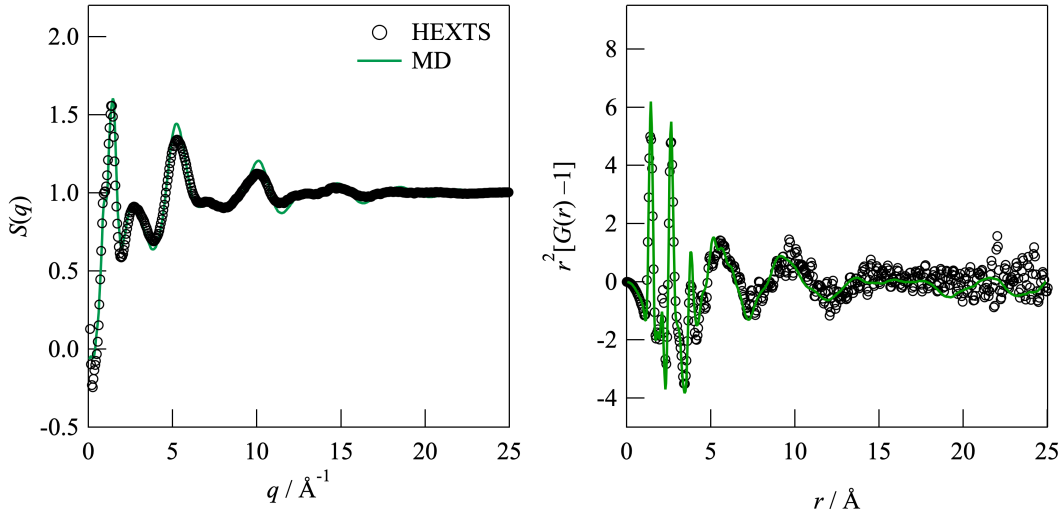

Fig. S5. $S(q)$ and $G(r)$ functions obtained from (open circles) and MD simulations (solid lines) for 1.0 M LiTFSA/[C_2mIm][TFSA] solution.

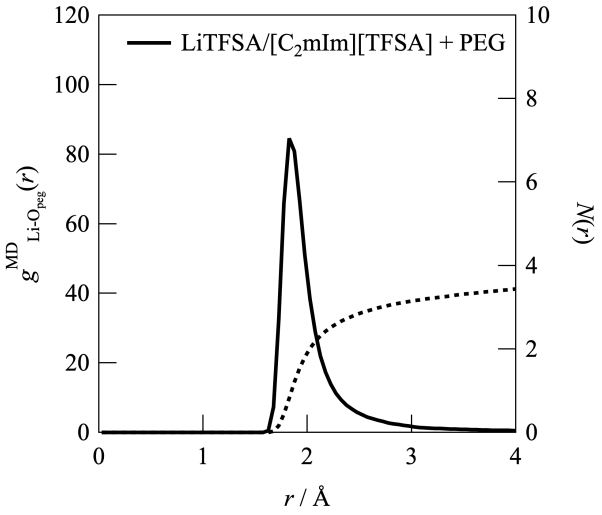

Fig. S6. Atom-atom pair correlation functions [$g^{MD}_{Li\text{-}Opeg}(r)$: solid line (left-axis)] for the O atoms of PEG around the Li ions, and their integrated profiles [$N(r)$: dashed lines (right-axis)] for 1.0 M LiTFSA/[C_2mIm][TFSA] solution containing PEG ([C_2mIm][TFSA]:PEG = 10.7:1 (by mol)).