Electronic Supplementary Information

Solvation-controlled lithium-ion complexes in a nonflammable solvent containing ethylene carbonate: Structural and electrochemical aspects

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Peak deconvolution (EC component) of IR spectra.

To clarify IR bands assigned to EC component in ternary (LiTFSA, TFEP, and EC) electrolyte solutions, we separately measured IR spectrum for a simple model system: LiTFSA in EC solution (1:4 by mol.), which is shown in the following figure (a). We also performed DFT calculations for the isolated EC molecule and the Li^+-EC (1:1) complex as model species of the free and bound EC [Gaussian 09,[1] B3LYP/6-311G**; geometry optimization and nomal frequency analysis]. The resulting theoretical IR bands for their optimized geometries are shown in the following figure (b) and (c), respectively.

The experimental IR spectrum (open circles) could be deconvoluted into two bands at 892.8 cm^{-1} (solid blue line) and 903.0 cm^{-1} (solid red line). The 892.8 cm^{-1} and 903.0 cm^{-1}-bands were successfully represented by the theoretical bands for the isolated EC and the Li^+-EC complex [figure (b) and (c)], demonstrating that the observed 892.8 cm^{-1} and 903.0 cm^{-1}-bands are assigned to the free and bound EC species, respectively. The fitting parameters (peak position, half-width at half-maximum, and Gauss/Lorentz ratio on a pseudo-Voigt function) determined in the LiTFSA/EC system here were applied to the curve-fitting analysis for the ternary LiTFSA/TFEP+EC system (Figure 2b in the manuscript). In the ternary system, as mentioned in the manuscript, it is too difficult to deconvolute the observed IR spectrum into single bands owing to very weaker IR intensity from EC contribution overlapped with the intense bands of TFEP components. Therefore, to separate EC and TFEP contributions from the observed total spectra, we used (1) the fitting parameters evaluated in the separate IR experiment described above and (2) solvation number, n_{EC} estimated by the current Raman spectroscopic experiment, in this peak deconvolution (i.e., least-squares curve fitting analysis), as follows.

Firstly, we measured IR spectra for binary TFEP+EC solutions (without LiTFSA salt) at x_{EC} = 0.1, 0.25, and 0.5 as standard data to determine ε_f for free EC in the solutions. The observed IR spectra could be represented by three components, free TFEP (887.0 and 907.2 cm^{-1}) and free EC (892.8 cm^{-1}). Using I_f and c_f (= c_T) for the free EC in this system, we obtained ε_f values for all the x_{EC}-solutions examined here according to $I_f = \varepsilon_f c_f$. Here, we already estimated solvation number n_{EC} by Raman spectra. By applying the ε_f and the n_{EC} values to equation $I_f/c_T = -n_{EC}\varepsilon_f (c_{Li}/c_T) + \varepsilon_f$, we could evaluate the I_f (EC) for the ternary LiTFSA/TFEP+EC system (x_{EC} = 0.1, 0.25, and 0.5) to successfully deconvolute the IR spectra into EC and TFEP contributions.

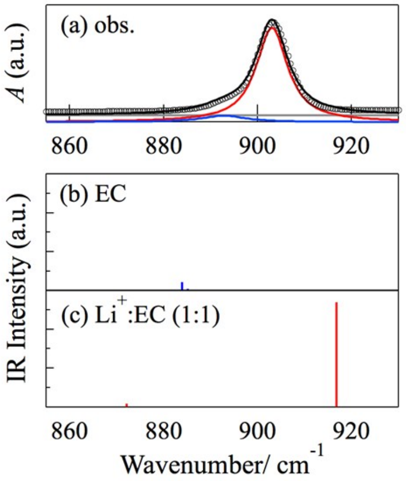

Table S1. Concentration of Li salt (c_{Li}), density (d), reflective index (n_2), and concentrations TFEP and EC (c_{TFEP} and c_{EC}) for the LiTFSA/TFEP+EC solutions (x_{EC} = 0.1, 0.25, and 0.5).

$x_{\mathrm{EC}} = 0.1$

c_{Li} / mol kg^{-1}	d / g cm^{-3}	c_{Li} / mol dm^{-3}	n_2	c_{TFEP} / mol dm^{-3}	c_{EC} / mol dm^{-3}
0.000	1.5735	0.000	1.324	4.447	0.495
0.200	1.6021	0.303	1.329	4.282	0.476
0.400	1.6228	0.583	1.332	4.040	0.449
0.599	1.6402	0.840	1.336	3.833	0.426
0.800	1.6550	1.076	1.337	3.649	0.406

$x_{\mathrm{EC}} = 0.25$

c_{Li} / mol kg^{-1}	d / g cm^{-3}	c_{Li} / mol dm^{-3}	n_2	c_{TFEP} / mol dm^{-3}	c_{EC} / mol dm^{-3}
0.000	1.5678	0.000	1.330	4.198	1.401
0.200	1.5915	0.301	1.334	4.030	1.345
0.400	1.6112	0.578	1.337	3.870	1.292
0.599	1.6288	0.832	1.340	3.721	1.242
0.800	1.6432	1.069	1.343	3.578	1.194

$x_{\mathrm{EC}} = 0.5$

c_{Li} / mol kg^{-1}	d / g cm^{-3}	c_{Li} / mol dm^{-3}	n_2	c_{TFEP} / mol dm^{-3}	c_{EC} / mol dm^{-3}
0.000	1.5371	0.000	1.346	3.552	3.576
0.200	1.5400	0.292	1.349	3.365	3.388
0.399	1.5759	0.564	1.351	3.267	3.289
0.600	1.5978	0.818	1.353	3.150	3.171
0.800	1.6121	1.049	1.354	3.029	3.049

Table S2. Li salt concentration (c_{Li}), integrated intensity ratio of bound TFSA/free TFSA (I_b/I_f), and the concentration ratio of bound TFSA/total TFSA (c_b/c_T). To estimate concentrations of free and bound TFSA species, we performed the following estimation using the observed intensity and Raman scattering coefficient. In our previous work, we reported that the ratio of the Raman scattering coefficients, J_f/J_b, is approximately constant (~ 0.9) in some electrolytes containing LiTFSA salt.[2] We used this value ($J_f/J_b = 0.9$) to estimate the concentrations of free and bound TFSA (c_f and c_b, respectively) through $c_T = c_f + c_b$ and $(I_b/I_f)\,(J_f/J_b) = c_b/c_f$.

$x_{\mathrm{EC}} = 0.1$

c_{Li} / mol dm^{-3}	I_b/I_f	c_b/c_T
0.0	-	-
0.3	1.41	0.56
0.6	1.73	0.60
0.8	2.29	0.67
1.0	2.02	0.65
		Avg. 0.64

$x_{\mathrm{EC}} = 0.25$

c_{Li} / mol dm^{-3}	I_b/I_f	c_b/c_T
0.0	-	-
0.3	1.24	0.53
0.6	1.15	0.51
0.8	1.33	0.54
1.0	1.61	0.59
		Avg. 0.54

$x_{\mathrm{EC}} = 0.5$

c_{Li} / mol dm^{-3}	I_b/I_f	c_b/c_T
0.0	-	-
0.3	0.81	0.42
0.6	0.65	0.37
0.8	0.85	0.43
1.0	0.92	0.45
		Avg. 0.42

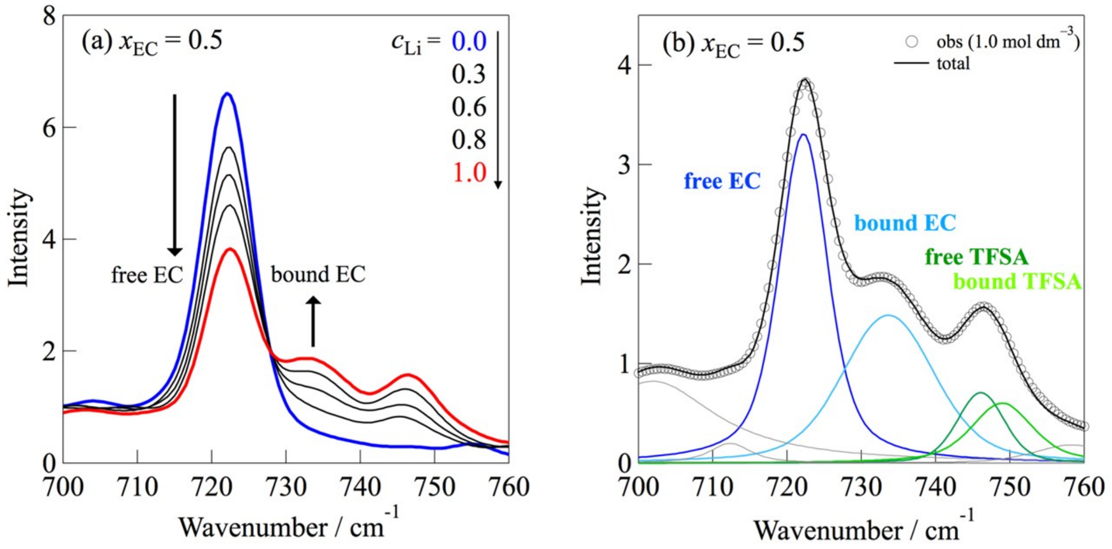

Figure S1. (a) Raman spectra observed for the LiTFSA in TFEP+EC mixtures (x_{EC} = 0.5) with varying c_{Li}, (b) a typical curve-fitting result for the c_{Li} = 1.0 mol dm^{-3} solution.

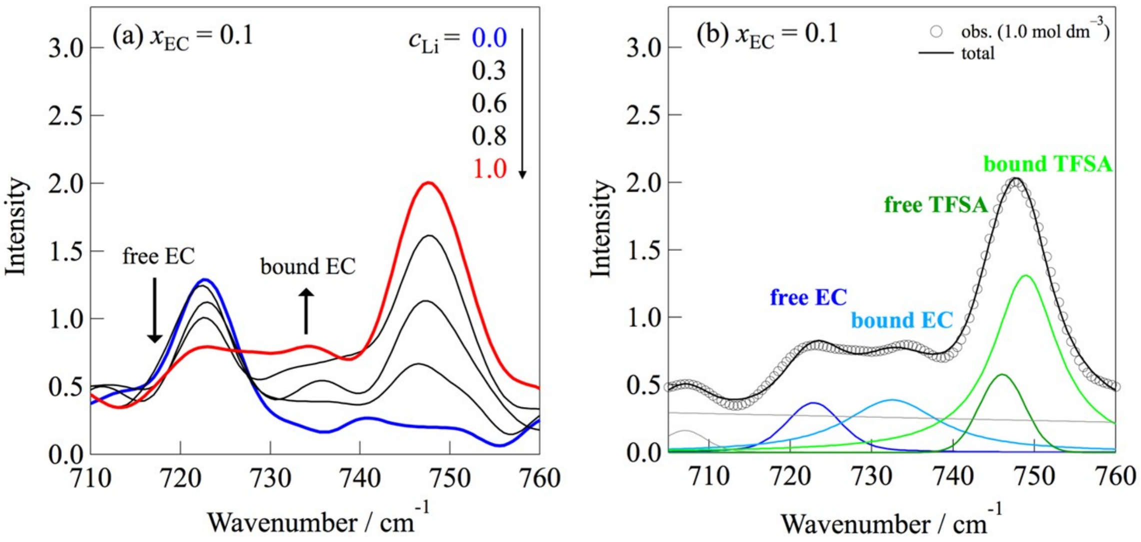

Figure S2. (a) Raman spectra observed for the LiTFSA in TFEP+EC mixtures (x_{EC} = 0.1) with varying c_{Li}, (b) a typical curve-fitting result for the c_{Li} = 1.0 mol dm^{-3} solution.

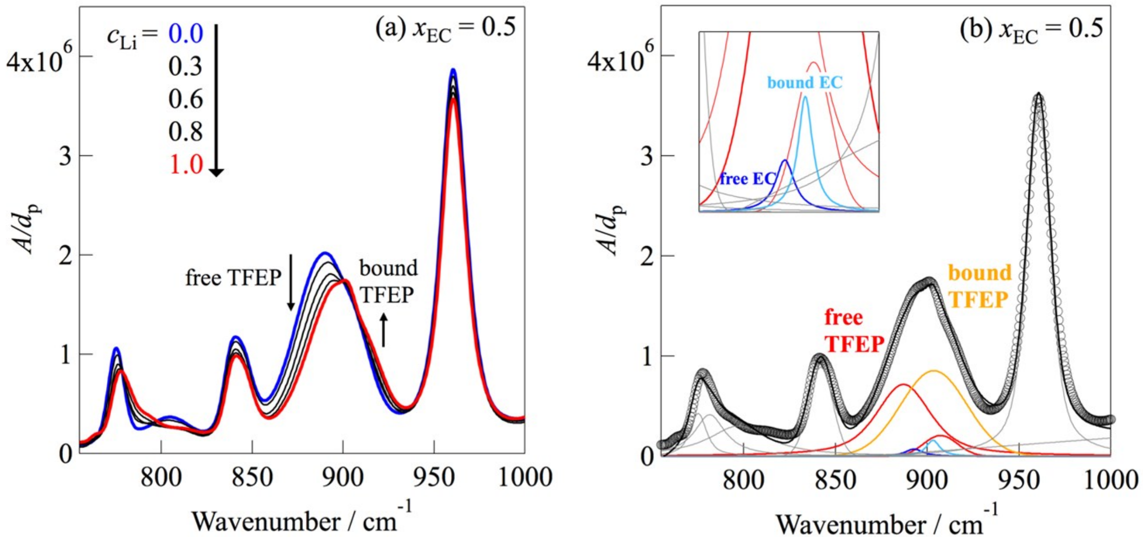

Figure S3. (a) IR spectra observed for the LiTFSA in TFEP+EC mixtures (x_{EC} = 0.5) with varying c_{Li}, (b) a typical curve-fitting result for the c_{Li} = 1.0 mol dm^{-3} solution.

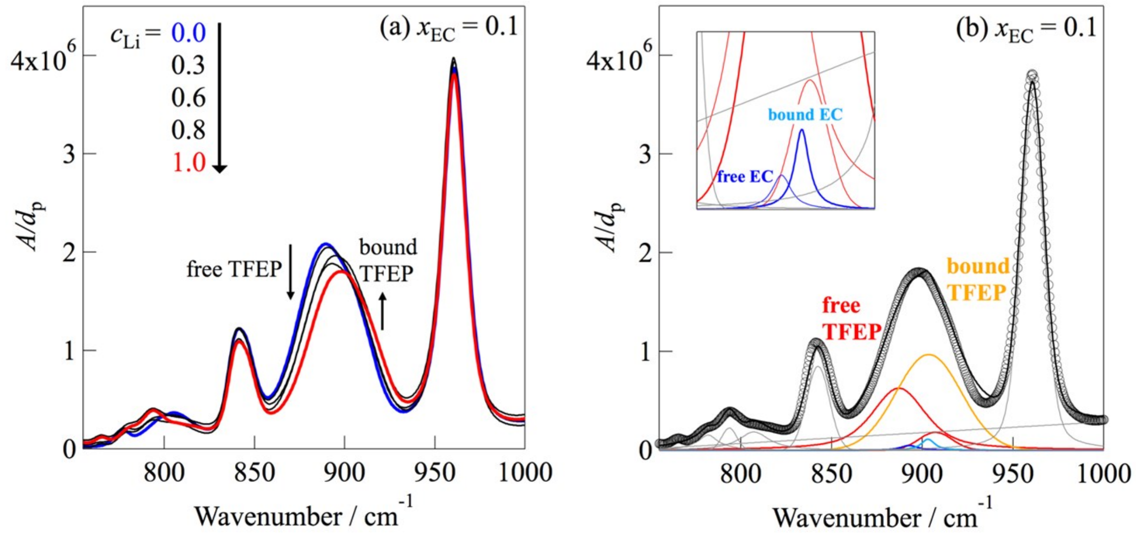

Figure S4. (a) IR spectra observed for the LiTFSA in TFEP+EC mixture (x_{EC} = 0.1) with varying c_{Li}, (b) a typical curve-fitting result for the c_{Li} = 1.0 mol dm^{-3} solution.

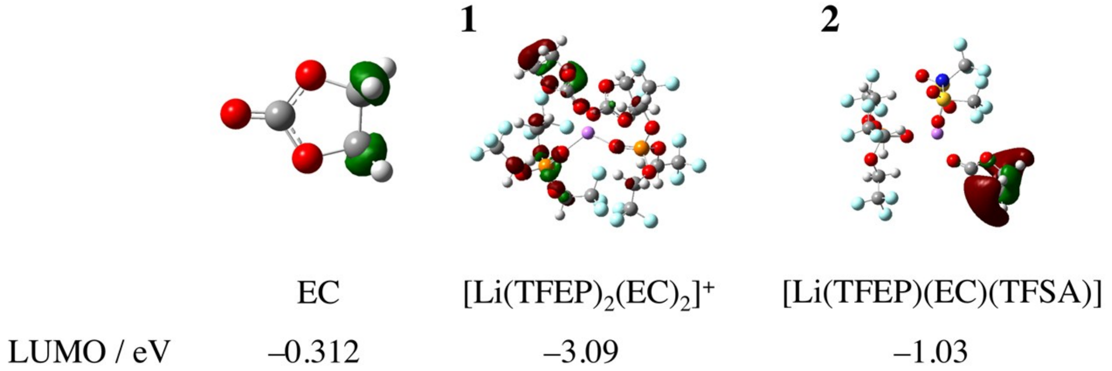

Figure S5. The LUMO energy levels of the isolated EC and possible Li-ion complexes (1: $[Li(TFEP)_2(EC)_2]^+$ and 2: [Li(TFEP)(EC)(TFSA)]) calculated from their optimized geometries by DFT calculations (B3LYP/6-311G** level).

References.

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson et. al., *Wallingford, CT.*, 2009, **19**, 227-238.
2. R. Sai, K. Ueno, K. Fujii, Y. Nakano, N. Shigaki and H. Tsutsumi, *Phys. Chem. Chem. Phys.*, 2017, **19**, 5185-5194.