Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information:

Li$^+$ Solvation in Glyme-Li Salt Solvate Ionic Liquids

Kazuhide Ueno,[a] Ryoichi Tatara,[a] Seiji Tsuzuki,[b] Sohi Saito,[c] Hiroyuki Doi,[c] Kazuki Yoshida,[a] Toshihiko Mandai,[a] Masaru Matsugami,[d] Yasuhiro Umebayashi,[c] Kaoru Dokko,[a] Masayoshi Watanabe[a]*

[a] Department of Chemistry and Biotechnology, Yokohama National University,79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

[b] Research Initiative of Computational Sciences (RICS), Nanosystem Research Institute, National Institute of Advanced Industrial Science and Techno logy (AIST), 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

[c] Graduate School of Science and Technology, Niigata University, 8050 Ikarashi, 2-no-cho, Nishi-ku, Niigata City, 950-2181, Japan

[d] Faculty of Liberal Studies, Kumamoto National College of Technology, 2659-2 Suya, Koshi, Kumamoto 861–1102, Japan

AUTHOR EMAIL ADDRESS:mwatanab@ynu.ac.jp

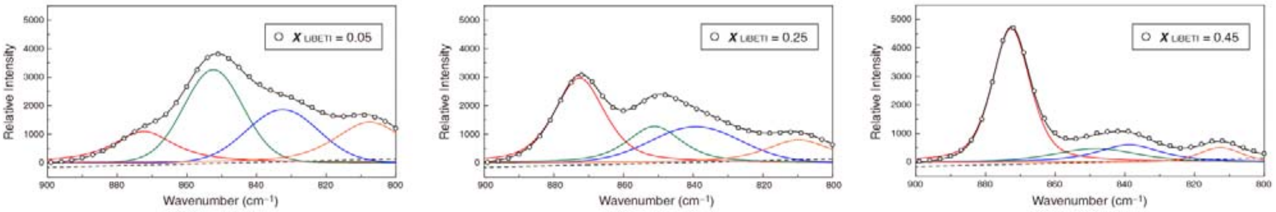

Figure S1. Typical results on the deconvolutions of Raman spectra into four bands at around 810, 835, 850, and 873 cm^{-1}, by the Gaussian-Lorentzian function.

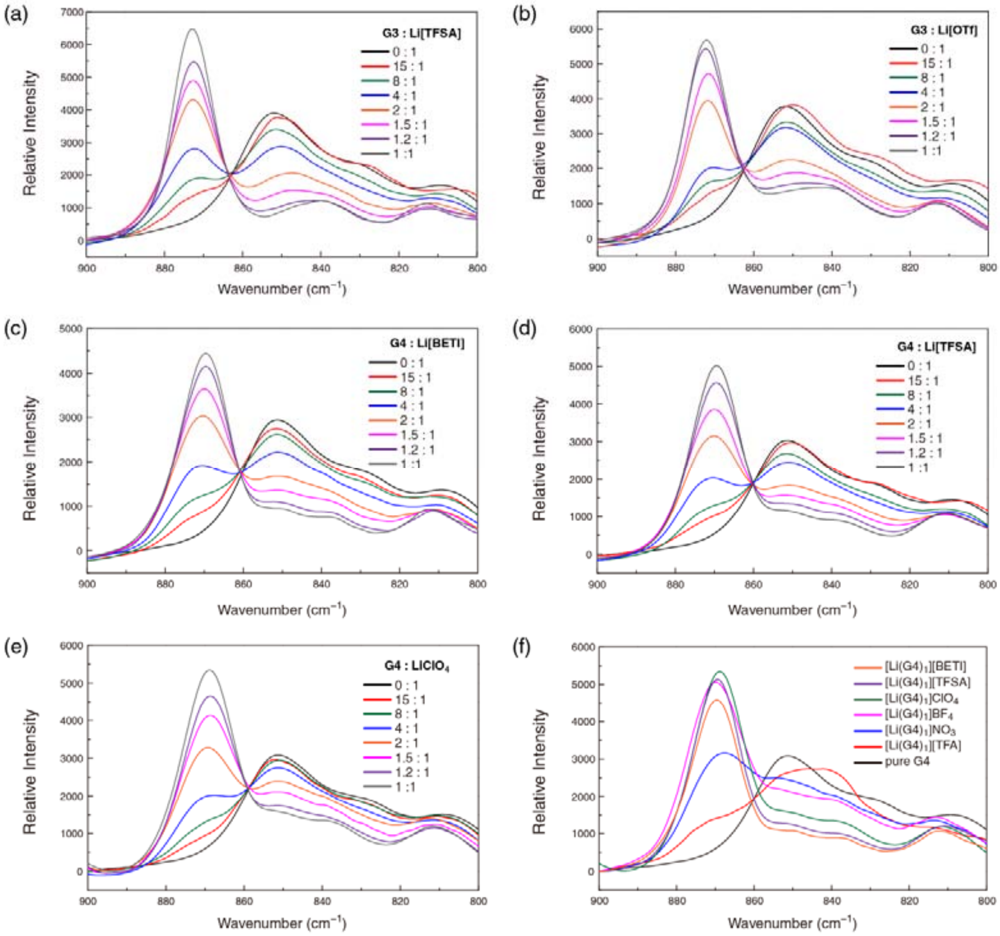

Figure S2. Normalized Raman spectra of (a) G3-Li[TFSA] mixtures, (b) G3-Li[OTf] mixtures, (c) G4-Li[BETI] mixtures, (d) G4-Li[TFSA] mixtures, (e) G4-LiClO$_4$ mixtures, and (f) [Li(G4)$_1$]X.

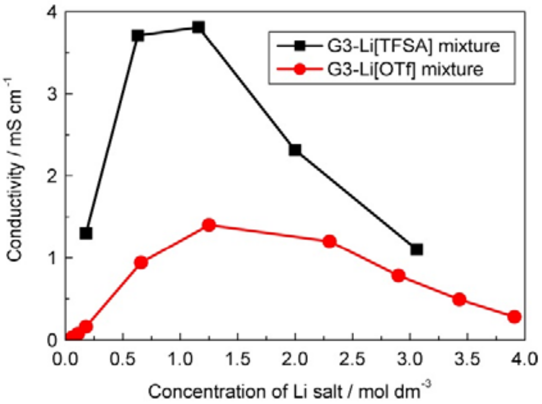

Figure S3. Ionic conductivity plotted against Li salt concentration in the G3-Li[TFSA] and the G3-Li[OTf] mixtures at 30 °C.

Electrode potentials of Li/Li$^+$.

The electrode potential E_2 was calculated by the following procedure, with c_f values obtained from Raman spectroscopic analysis (Table S1).

Table S1. Estimated value of concentration of free G3 in $[Li(G3)_n][TFSA]$ at 30 °C by Raman study.

	c_f (mol%)	c_f (mol dm^{-3})
$[Li(G3)_1][TFSA]$	2.3	0.071
$[Li(G3)_{1.2}][TFSA]$	17	0.58
$[Li(G3)_{1.5}][TFSA]$	22	0.78
$[Li(G3)_2][TFSA]$	35	1.4
$[Li(G3)_4][TFSA]$	65	3.0

The potential $E_2^{0\prime}$ of the reference electrode, Li/Li$^+$ in 1 mol dm^{-3} Li[TFSA]/G3 (=$[Li(G3)_{4.8}][TFSA]$) can be written as:

$$\begin{aligned} &E_2^0{}' = E_2^0 + \frac{2.303RT}{F}\log\frac{1}{3.8} = 0 \\ &\Leftrightarrow E_2^0 = E_2^0{}' + \frac{2.303RT}{F}\log 3.8 \end{aligned} \qquad \text{(S1)}$$

Substituting Eq. S1 in Eq. 7, we get:

$$E_2 = E_2^{0}{'} + \frac{2.303RT}{F}\log 3.8 + \frac{2.303RT}{F}\log\frac{a_{[\mathrm{Li(glyme)}]^+}}{a_{\mathrm{glyme}}} \qquad \text{(S2)}$$

where $E_2^{0\prime}$ is 0, because it represents the reference electrode potential. Thus, we can calculate E_2 by substituting $a_{[\mathrm{Li(glyme)}]+} = c_{\mathrm{Li}}$ and $a_{\mathrm{glyme}} = c_{\mathrm{G}} - c_{\mathrm{Li}}$ in the dilute solutions ($c_{\mathrm{Li}} \leq$ 1mol dm^{-3} for G3-Li[TFSA] mixtures), and $a_{[\mathrm{Li(glyme)}]+} = c_{\mathrm{Li}}$, $a_{\mathrm{glyme}} = c_{\mathrm{f}}$ in the concentrated regime ($c_{\mathrm{Li}} >$ 1mol dm^{-3}) in **Figure 9**.

Although we assume $a_{\mathrm{Li+}}$ (= $a_{[\mathrm{Li(glyme)}]+}$)= c_{Li} for the sake of simplicity, the activities can indeed be represented as $a_{\mathrm{Li+}}$ (= $a_{[\mathrm{Li(glyme)}]+}$) = $c_{\mathrm{Li}}\gamma_{\mathrm{Li}}$ with the activity coefficient of Li$^+$ (γ_{Li}). If the activity coefficient is taken into consideration, the Nernst equation of the electrode reaction; Li$^+$ + e$^-$ ⇄ Li, can be modified as:

$$\begin{aligned} E_1 &= E_1^0 + \frac{2.303RT}{F}\log a_{\mathrm{Li}^+} \\ &= E_1^0 + \frac{2.303RT}{F}\log \gamma_{\mathrm{Li}} + \frac{2.303RT}{F}\log c_{\mathrm{Li}} \end{aligned} \qquad \text{(S3)}$$

The electrode potential ($E^0{}_1{}'$) in the reference solution of c_{Li} = 1 mol dm^{-3} with the activity coefficient ($\gamma_{\mathrm{Li,\,1M}}$) can be written as:

$$\begin{aligned} &E_1^{0}{'} = E_1^{\,0} + \frac{2.303RT}{F}\log \gamma_{\mathrm{Li,1M}} (=0) \\ &\Leftrightarrow E_1^{\,0} = E_1^{0}{'} - \frac{2.303RT}{F}\log \gamma_{\mathrm{Li,1M}} \end{aligned} \qquad \text{(S4).}$$

Substituting Eq. S4 in Eq. S3, we obtain:

$$E_1 = E_1^{0}{'} + \frac{2.303RT}{F}\log\frac{\gamma_{\mathrm{Li}}}{\gamma_{\mathrm{Li,1M}}} + \frac{2.303RT}{F}\log c_{\mathrm{Li}} \qquad \text{(S5)}$$

In Eq. S5, the first term ($E^0{}_1{}'$) is 0 because Li/Li$^+$ in 1 mol dm^{-3} Li[TFSA]/G3 is the reference electrode, the second term represents the error caused by the variation of activity coefficient with Li$^+$ concentration, and the third term is a calculable value. Thus, the difference between experimental and calculated values of the electrode potential originated from the second term. **Figure S4** indicates that the activity coefficient (γ_{Li}) was a little higher than that of the 1 mol dm^{-3} in the lower concentration region (< 1 mol dm^{-3}). In the highly concentrated regime, the drastic increase in the electrode potential can also be described by the second term with the activity coefficients in Eq. S5.

In the case of [Li(G3)][TFSA], for example, the experimental data for Li/Li$^+$ electrode potential is 0.230 V, whereas the calculated value is 0.029 V based on Eq. 6, $E = 2.303RT \log c_{\mathrm{Li}}/F$ (**Figure S4**). If the interpretation of the difference between the experimental and calculated values (0.201 V) was imposed to the second term in Eq. S5, γ_{Li} must be 2176 times higher than $\gamma_{\mathrm{Li,\,1M}}$. However, physical meaning of the significantly high γ_{Li} is obscure. Instead, we attempted to explain the drastic potential change by considering the activity of the free glymes without imposing the compensation of the activity coefficients.

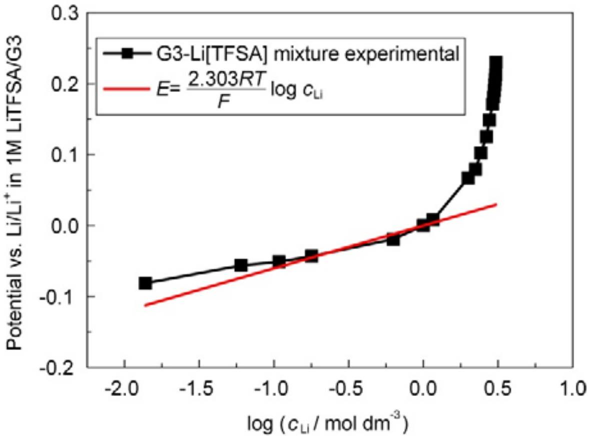

Figure S4. Plots of the experimental and calculated (based on Nernst Equation) value of Li/Li$^+$ electrode potential against common logarithm of the Li salt concentration in [Li(G3)$_n$][TFSA] at 30 °C. Reference electrode was Li/Li$^+$ in 1 mol dm^{-3} Li[TFSA]/G3.

For the modified electrode reaction accompanied by de-solvation process, $[\mathrm{Li(glyme)}]^+ + e^- \rightleftarrows \mathrm{Li} + \mathrm{glyme}$, Nernst equation with the activity coefficients of [Li(glyme)]$^+$ ($\gamma_{[\mathrm{Li(glyme)}]+}$) and glyme ($\gamma_{\mathrm{glyme}}$) can be modified as follows:

$$
\begin{aligned}
E_2 &= E_2^0 + \frac{2.303RT}{F}\log\frac{a_{[\mathrm{Li(glyme)}]^+}}{a_{\mathrm{glyme}}} \\
&= E_2^0 + \frac{2.303RT}{F}\log\frac{\gamma_{[\mathrm{Li(glyme)}]^+}}{\gamma_{\mathrm{glyme}}} + \frac{2.303RT}{F}\log\frac{c_{[\mathrm{Li(glyme)}]^+}}{c_{\mathrm{f}}}
\end{aligned} \tag{S6}
$$

The electrode potentials ($E^0{}_2'$) in the reference solution with $c_{[\mathrm{Li(G3)1]}}{}^{+} = 1$ mol dm^{-3}, and $c_{\mathrm{glyme}} = 3.8$ mol dm^{-3} are;

$$
\begin{aligned}
&E_2^0{}' = E_2{}^0 + \frac{2.303RT}{F}\log\frac{\gamma_{[\mathrm{Li(G3)}]^+,1\mathrm{M}}}{\gamma_{\mathrm{G3_{free}},3.8\mathrm{M}}} - \frac{2.303RT}{F}\log 3.8 (=0) \\
&\Leftrightarrow E_2{}^0 = E_2^0{}' - \frac{2.303RT}{F}\log\frac{\gamma_{[\mathrm{Li(G3)}]^+,1\mathrm{M}}}{\gamma_{\mathrm{G3_{free}},3.8\mathrm{M}}} + \frac{2.303RT}{F}\log 3.8
\end{aligned} \tag{S7}
$$

Substituting Eq. S7 in Eq. S6, we obtain:

$$
E_2 = E_2^0{}' + \frac{2.303RT}{F}\log\frac{\gamma_{[\mathrm{Li(glyme)}]^+}}{\gamma_{[\mathrm{Li(G3)}]^+,1\mathrm{M}}} + \frac{2.303RT}{F}\log\frac{\gamma_{\mathrm{G3_{free}},3.8\mathrm{M}}}{\gamma_{\mathrm{glyme}}} + \frac{2.303RT}{F}\log 3.8 + \frac{2.303RT}{F}\log\frac{c_{[\mathrm{Li(glyme)}]^+}}{c_{\mathrm{f}}}
$$

(S8)

In Eq. S8, the first term is 0 because Li/Li$^+$ in 1 mol dm^{-3} Li[TFSA]/G3 is reference electrode, the second and third terms represent the error caused by the change in the activity coefficients of the complex cation and the free glymes against Li$^+$ concentration, the fourth term is constant, and the fifth term is a calculable value. The drastic increase in the potential at high concentrations can be explained by the fifth term as c_{G3free} in the denominator. However, the difference between experimental and calculated values in **Figure 9** could originate from the second and third terms, as well as Eq. S5.