Supplementary Information (SI)

Anion effects on Li ion transference number and dynamic ion correlations in glyme-Li salt equimolar mixtures

Keisuke Shigenobu [1], Masayuki Shibata [2], Kaoru Dokko [1,3], Masayoshi Watanabe [3], Kenta Fujii [2,*] and Kazuhide Ueno [1,3]*

[1] Department of Chemistry and Life Science, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan.

[2] Graduate School of Sciences and Technology for Innovation, Yamaguchi University, 2-16-1 Tokiwadai, Ube, Yamaguchi 755-8611, Japan

[3] Advanced Chemical Energy Research Centre (ACERC), Institute of Advanced Sciences, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan.

CORRESPONDING AUTHORS: To whom correspondence should be addressed.

Kazuhide Ueno: Telephone/Fax: +81-45-339-3951. E-mail: ueno-kazuhide-rc@ynu.ac.jp

Kenta Fujii: Telephone/Fax: +81-836-85-9212. Email: k-fujii@yamaguchi-u.ac.jp

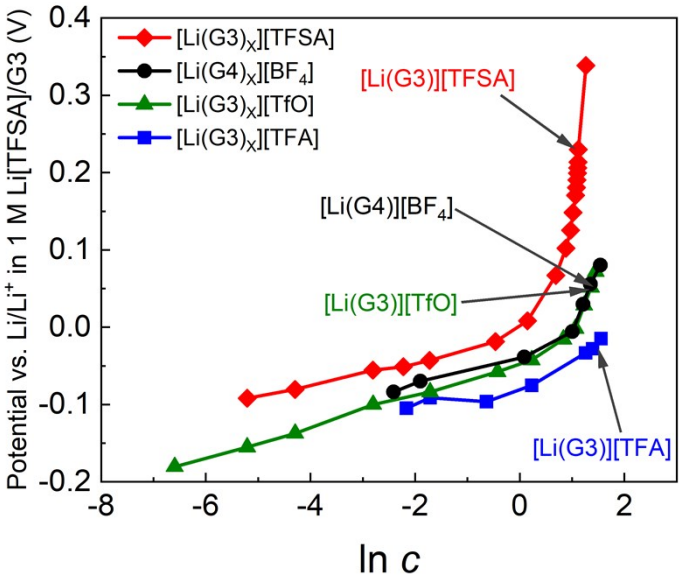

Figure S1. Plots of the Li/Li$^+$ electrode potential against natural logarithm of the Li salt concentration in mixture of LiX in glyme (G3 or G4) at 30 °C. The reference electrode was Li/Li$^+$ in 1 mol dm^{-3} Li[TFSA]/G3. Data for [Li(G3)][TFSA] were obtained from ref. 20.

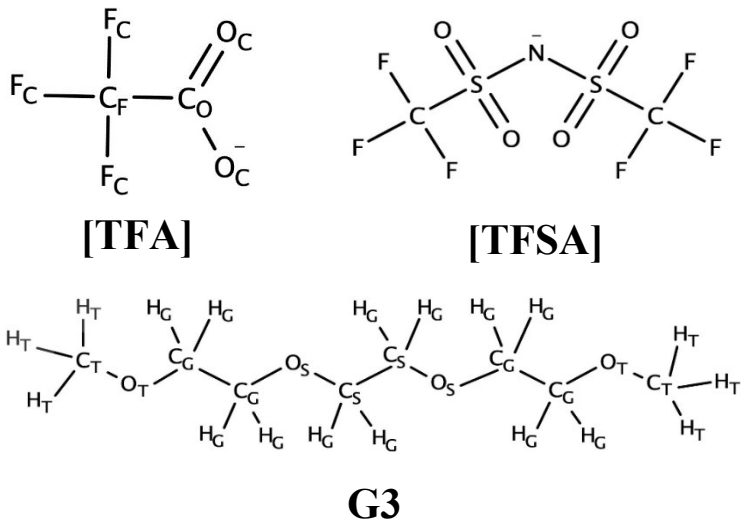

Figure S2. Atom types used for MD simulations.

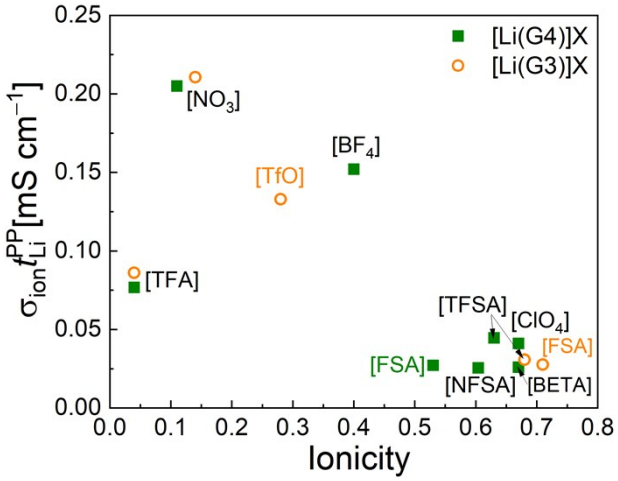

Figure S3. Plots of the product of t_{Li}^{PP} and ionic conductivity (σ_{ion}) versus ionicity for [Li(glyme)]X.

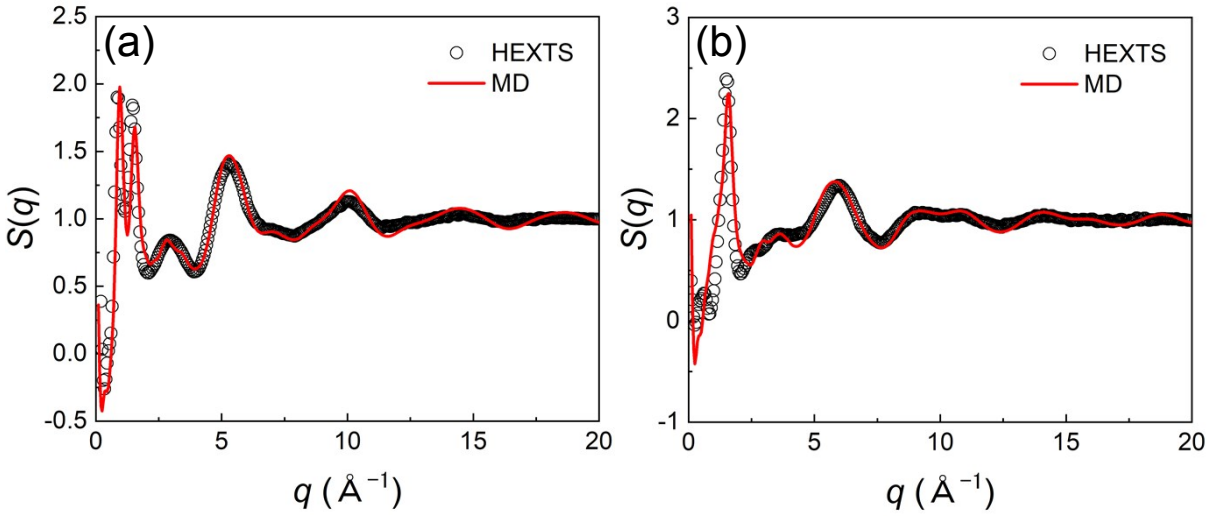

Figure S4. Structure factors in the form $S(q)$obtained by HEXTS measurements (open circles) and MD simulations (solid red lines) for (a) [Li(G3)][TFSA] and (b) [Li(G3)][TFA].

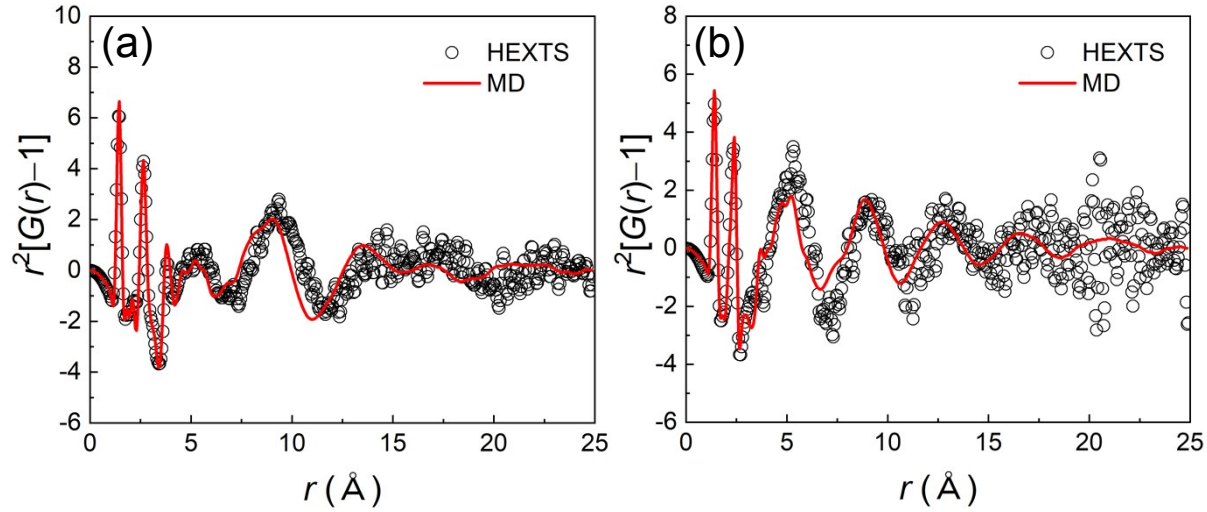

Figure S5. X-ray radial distribution functions in the $r^2[G(r)-1]$ form derived from HEXTS experiments (open circles) and MD simulations (solid red lines) for (a) [Li(G3)][TFSA] and (b) [Li(G3)][TFA].

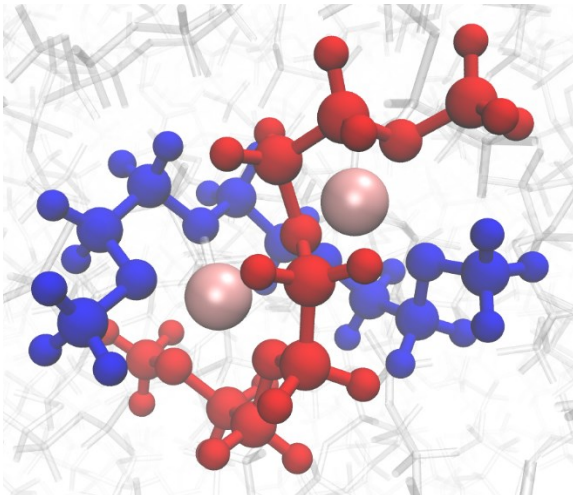

Figure S6. Snapshot of the coordination structure of $[Li_2(G3)_2]^{2+}$ found in [Li(G3)][TFSA] obtained from MD simulations. Pink: Li^+ and Blue and Red: G3.

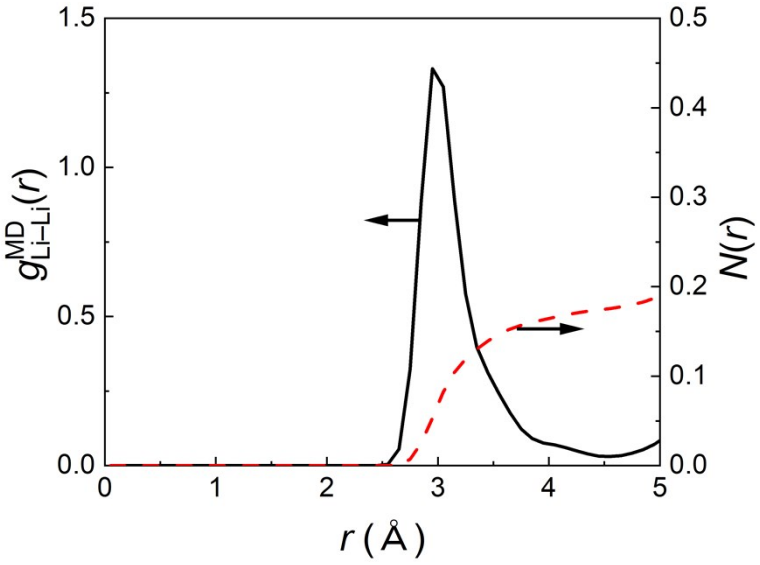

Figure S7. Li^+–Li^+ pair correlation function [$g^{MD}_{Li-Li}(r)$: left axis and solid black line] and the integrated profile [cumulative coordination number $N(r)$: right axis, dashed red line] for [Li(G3)][TFSA].

Numerical data

Table S1. Densities, compositions (numbers of ion-pairs and solvents) and box lengths of the systems for the MD simulations.

Sample	Density [g cm^{-3}]		Li-anion	G3	Box length [Å]
	MD[a]	Exp.[b]			
[Li(G3)][TFSA]	1.5157	1.430	790	790	73.9
[Li(G3)][TFA]	1.2744	1.2091	790	790	67.6

[a] Density values obtained from the MD simulations.

[b] Experimental density values.

Table S2. Force field parameters used for molecular dynamics simulations (Atom types is shown in **Figure S2**).

Partial charges and Lennard-Jones potential parameters: Partial charges of $[TFA]^-$ were calculated based on the ChelpG method [MP2/cc-pVTZ(-f)//HF/6-31G(d) levels of theory]. Lennard-Jones potential parameters σ and ε of C_O and O_C atoms were obtained from ref. 33 SI and those of F_C and C_F atoms were obtained from ref. 34. All of the parameters regarding $[TFSA]^-$ and G3 were obtained from ref. 31 and ref. 35, respectively.

	Atom	Partial charge	Lennard-Jones potential	
			σ [Å]	ε [kcal mol^{-1}]
[TFA]$^-$	C_O	0.8033	3.75	0.105
	O_C	–0.7701	2.96	0.210
	F_C	–0.2750	2.95	0.053
	C_F	0.5619	3.5	0.066
[TFSA]$^-$	F	–0.16	2.95	0.053
	C	0.35	3.5	0.066
	O	–0.53	2.96	0.210
	S	1.02	3.55	0.250
	N	–0.66	3.25	0.170
G3	H_T	0.03	2.5	0.030
	H_G	0.06	2.5	0.030
	C_T	0.11	3.5	0.066
	C_G	0.15	3.5	0.066
	C_S	0.18	3.5	0.066
	O_T	–0.45	2.9	0.140
	O_S	–0.59	2.9	0.14

Bond stretching parameters: The parameters of $[TFA]^-$ regarding $F_C–C_F$ bond stretching were obtained from ref. 34 and those of $C_F–C_O$ and $O_C–C_O$ bond stretching and G3 were collected from ref. 32. In regard to $[TFSA]^-$, we have used the parameters appeared in ref. 31.

	Bond	K_S [kcal mol^{-1} Å^{-2}]	r [Å]
$[TFA]^-$	$F_C–C_F$	367.0	1.332
	$C_F–C_O$	317.0	1.522
	$O_C–C_O$	656	1.25
$[TFSA]^-$	C–F	441.7	1.323
	C–S	232.9	1.818
	S–O	636.8	1.437
	N–S	374.7	1.57
G3	$H_T–C_T$	340	1.09
	$C_T–O_T$	320	1.41
	$O_T–C_G$	320	1.41
	$H_G–C_G$	340	1.09
	$C_G–C_G$	310	1.526
	$C_G–O_S$	320	1.41
	$O_S–C_S$	320	1.41
	$H_G–C_S$	340	1.09
	$C_S–C_S$	310	1.526

Angle bending parameters: The parameters of $[TFA]^-$ regarding $F_C–C_F–F_C$ and $F_C–C_F–C_O$ angle bending were obtained from ref. 34 and those of $C_F–C_O–O_C$ and $O_C–C_O–O_C$ angle bending and G3 were collected from ref. 32. In regard to $[TFSA]^-$, we have used the parameters appeared in ref. 31.

	Angle	K_θ [kcal mol^{-1} rad^{-2}]	θ [deg]
$[TFA]^-$	$F_C–C_F–F_C$	77.0	109.1
	$F_C–C_F–C_O$	50.0	109.5
	$C_F–C_O–O_C$	70.0	117
	$O_C–C_O–O_C$	80	126
$[TFSA]^-$	F–C–F	93.3	107.1
	S–C–F	82.9	111.7
	O–S–O	115.7	118.5
	C–S–O	103.9	102.6
	O–S–N	94.2	113.6
	C–S–N	91.3	103.5
	S–N–S	80.1	125.6
G3	$H_T–C_T–H_T$	35.0	109.5
	$H_T–C_T–O_T$	50.0	109.5
	$C_T–O_T–C_G$	60.0	109.5
	$O_T–C_G–H_G$	50.0	109.5
	$O_T–C_G–C_G$	50.0	109.5
	$H_G–C_G–H_G$	35.0	109.5
	$H_G–C_G–C_G$	50.0	109.5
	$C_G–C_G–O_S$	50.0	109.5
	$H_G–C_G–O_S$	50.0	109.5
	$C_G–O_S–C_S$	60.0	109.5
	$O_S–C_S–H_G$	50.0	109.5

	O_S–C_S–C_S	50.0	109.5
	H_G–C_S–C_S	50.0	109.5
	H_G–C_S–H_G	35.0	109.5

Torsional parameters: The parameters of $[TFA]^-$ and G3 were obtained from ref. 33 SI and those of $[TFSA]^-$ were collected from ref. 31.

	Dihedral	V_1 [kcal mol^{-1}]	V_2 [kcal mol^{-1}]	V_3 [kcal mol^{-1}]
$[TFA]^-$	F_C–C_F–C_O–O_C	0.000	0.000	0.000
$[TFSA]^-$	O–S–C–F	0.000	0.000	0.347
	N–S–C–F	0.000	0.000	0.316
	O–S–N–S	0.000	0.000	−0.004
	S–N–S–C	7.833	−2.489	−0.763
G3	H_T–C_T–O_T–C_G	0.000	0.000	0.760
	C_T–O_T–C_G–H_G	0.000	0.000	0.760
	C_T–O_T–C_G–C_G	0.650	−0.250	0.670
	O_T–C_G–C_G–H_G	0.000	0.000	0.468
	O_T–C_G–C_G–O_S	1.740	−0.157	0.279
	H_G–C_G–C_G–H_G	0.000	0.000	0.318
	H_G–C_G–C_G–O_S	0.000	0.000	0.468
	C_G–C_G–O_S–C_S	0.650	−0.250	0.670
	C_G–O_S–C_S–C_S	0.650	−0.250	0.670
	C_G–O_S–C_S–H_G	0.000	0.000	0.760
	H_G–C_G–O_S–C_S	0.000	0.000	0.760
	O_S–C_S–C_S–H_G	0.000	0.000	0.468
	O_S–C_S–C_S–O_S	1.740	−0.157	0.279
	H_G–C_S–C_S–H_G	0.000	0.000	0.318
	H_G–C_S–C_S–O_S	0.000	0.000	0.468

Table S3. Experimentally obtained parameters for the calculation of Onsager transport coefficients. [Li(G3)][TFSA] was obtained from ref. 20 and σ_{ion}, D_{Li}, and D_{anion} of [Li(G4)][BF_4] and [Li(G3)][TFA] were obtained from ref. 21.

Sample	σ_{ion} [mS cm^{-1}]	t_{Li}^{PP}	D_{Li} [10^{-7} cm^2 s^{-1}]	D_{anion} [10^{-7} cm^2 s^{-1}]	D_{salt} [10^{-7} cm^2 s^{-1}]	$\frac{d\Delta\varphi}{dln(c)}$
[Li(G3)][TFSA]	1.1	0.028	0.77	0.54	0.53	0.78
[Li(G3)][TfO]	0.30	0.44	0.42	0.33	1.6	0.20
[Li(G3)][TFA]	0.096	0.90	0.87	0.73	3.6	0.06
[Li(G4)][BF_4]	0.50	0.30	0.44	0.43	0.69	0.16

Table S4. Normalized transport coefficients of all the electrolytes at 30 °C. Data for [Li(G3)][TFSA] were obtained from ref. 20.

Sample	$\sigma_{+}^{self}/\sigma_{ion}$	$\sigma_{-}^{self}/\sigma_{ion}$	$\sigma_{++}^{distinct}/\sigma_{ion}$	$\sigma_{--}^{distinct}/\sigma_{ion}$	σ_{+-}/σ_{ion}
[Li(G3)][TFSA]	0.79	0.56	−0.65	−0.45	–0.21
[Li(G3)][TfO]	2.02	1.59	−1.37	−0.14	0.55
[Li(G3)][TFA]	13.47	11.30	53.70	60.30	68.89
[Li(G4)][BF_4]	1.26	1.23	−0.94	−0.41	0.06

Table S5. The possible Li–Li coordination distances between labelled each Li atom obtained from the crystal structure of Li[TFA] and G4 mixture. (Crystal structure and labelled Li atoms were shown in **Figure S8**).

Possible Li–Li coordination		Distance [Å]
1	2	3.139
1	3	5.007
1	4	8.438
1	5	9.998
1	6	15.684
2	3	3.857
2	4	7.504
2	5	8.321
2	6	13.912
3	4	3.876
3	5	4.994
3	6	10.678
4	5	3.162
4	6	7.954
5	6	5.69

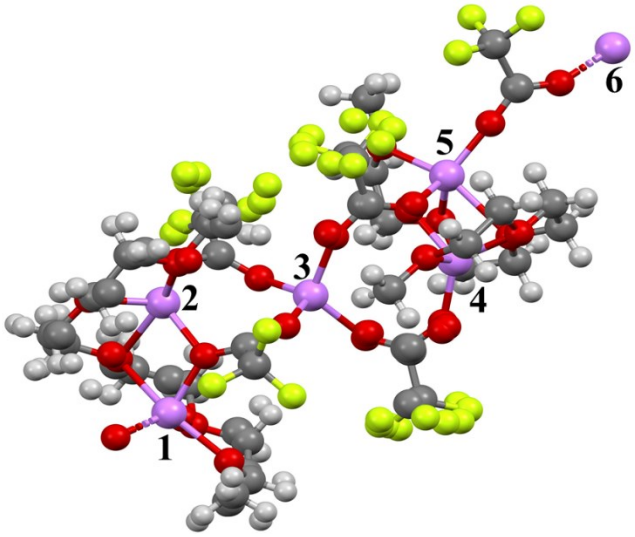

Figure S8. Crystal structure of Li[TFA] and G4 mixture and labelled Li atoms (Purple). The structure was obtained from ref. 60.