Toward a molecular understanding on conductivity of lithium-ion conducting polyanions polymer electrolytes by molecular dynamics simulation

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S1、Lithium salt synthesis method

KEtTFSI

The synthesis method was modified on the basis of literature[1]. 6.00g trifluoromethylsulfonamide, 15.32g dipotassium hydrogen phosphate, 0.16g 4-dimethylaminopyridine (DMAP) and 50ml acetonitrile were taken into a 100ml reaction tube in ice bath. 5.66g ethyl sulfonyl chloride was slowly dropped under the protection of argon in 10 minutes. The mixture was stirred at room temperature for 10h, then heated to 60 ℃ and filtered while hot. The clear liquid was spun dry to obtain white solid particles. After washed with cold ethanol for three times, the particles were recrystallized in methanol and dried under high vacuum. 6.9g colorless crystal (KEtTFSI) was obtained (yield 61.4%).

LiEtTFSI

The synthesis method refers to literature[2]. KEtTFSI was dried in high vacuum at 90℃ for 8h. 6.20g of the salt was taken into a 100ml reaction tube together with 2.25g lithium perchlorate and 30ml anhydrous acetonitrile. The mixture was stirred at 50 ℃ for 4h, and filtered under the protection of argon after cooling. The filtrate was dried once under high vacuum and gradual heated to 100 ℃ for 4h, 4.97g white particles were collected and stored in glove box (Yield 90.5%). ^{1}H NMR (DMSO-D6, 500 MHz): δ 2.94 (q, 2 H, CH_2), 1.18 (t, 3 H, CH_3). ^{13}C NMR (DMSO-D6, 126 MHz): δ 120.61 (q, 1 C, CF_3), 49.20 (s, 1 C, CH_2). 8.97 (s, 1 C, CH_3). ^{19}F NMR (DMSO-D6, 470 MHz): δ -77.54 (s, 3 F, CF_3),

$KEtSO_3$

5.0g ethyl sulfonic acid was dissolved in about 10ml deionized water to prepare solution A. 2.6g potassium hydroxide was dissolved in about 20ml deionized water to prepare solution B. Liquid A was slowly added in liquid B until the pH was 7. The mixture was spun dry at 80℃ to obtain white solid powder. The powder was recrystallized in methanol and 3.1g colorless flake crystal $KEtSO_3$ was obtained (yield 46.3%).

$LiEtSO_3$

$KEtSO_3$ was dried in high vacuum at 90℃ for 8h. 2.07g of the salt was dissolved in 20ml methanol. 1.45g lithium perchlorate was then added. The mixture was stirred at 50 ℃ for 4h, and then filtered under the protection of argon after cooling. The filtrate was dried in high vacuum and gradual heated to 100 ℃ for 8h. 1.4g white powder was collected and stored in glove box, (Yield 86.4%). ^{1}H NMR (DMSO-D6, 500 MHz): δ 2.38 (q, 2 H, CH_2), 1.06 (t, 3 H, CH_3). ^{13}C NMR (DMSO-D6, 126 MHz): δ 45.58 (s, 2 H, CH_2), 10.33 (s, 3 H, CH_3).

Trifluoromethylsulfonamide, dipotassium hydrogen phosphate, 4-dimethylaminopyridine, acetonitrile, lithium perchlorate and sulfonic acid were purchased from Energy Chemical Co. (China). Ethanol and methanol were purchased from Xilong Chemical Co. (China). All reagents are analytically pure.

Table S1. ρ_{exp}, ρ_{sim}, η_{exp} and η_{sim} of salts in G4 electrolyte with O/Li = 20 and pure G4 at 25°C.

	LiTFSI	LiEtTFSI	$LiClO_4$	$LiCF_3SO_3$	$LiCF_3COO$	Pure G4
ρ_{exp} (g/ml)	1.152	1.125	1.098	1.094	1.069	1.009
ρ_{sim} (g/ml)	1.170	1.129	1.093	1.107	1.074	1.009
η_{exp} (mPa·s)	11.40	11.10	11.25	9.77	6.27	3.33

η_{sim}(mPa·s)	8.79	8.43	9.10	5.95	4.23	3.02

Table S2. σ, t and α of salts

σ (mS/cm)		**LiTFSI**	**$LiClO_4$**	**LiEtTFSI**	**$LiCF_3SO_3$**	**$LiCF_3COO$**	**$LiCH_3COO$**	**$LiEtSO_3$**
G4 (25℃)	σ_{elec_Li}	0.793	0.674	0.629	0.317	-0.225	-0.111	0.076
	σ_{elec-}	1.059	1.082	0.604	0.490	0.307	0.159	-0.055
	σ_{elec}	1.852	1.755	1.233	0.807	0.082	0.048	0.021
	σ_{exp}	2.937	1.985	1.101	0.855	0.101	0.000	0.000
	t_{elec}	0.43	0.38	0.51	0.39	\	\	\
	percentage of free Li^+	84.3%	63.0%	49.9%	19.5%	5.5%	0.0%	2.0%
G99 (80℃)	σ_{elec_Li}	0.222	0.129	0.184	0.101	0.017	-0.033	0.001
	σ_{elec-}	0.475	0.582	0.394	0.224	-0.011	0.037	-0.002
	σ_{elec}	0.697	0.711	0.579	0.325	0.006	0.004	-0.001
	σ_{exp}	1.100	0.750	0.530	0.300	0.000	0.000	0.000
	t_{elec}	0.28	0.19	0.34	0.31	\	\	\
	percentage of free Li^+	90.6%	68.4%	67.5%	20.7%	0.0%	1.8%	0.7%

dissolved in G4 (25°C) or G99 (80°C). σ_{exp} in G99 was measured in PEG-10000.

Table S3 σ, α and t of $(LiEtTFSI\text{-}PE_m)_n$ in G99 (80°C) with O/Li = 20.

σ (mS/cm)	**LiEtTFSI**	**$(LiEtTFSI)_2$**	**$(LiEtTFSI)_4$**	**$(LiEtTFSI)_{11}$**	**$(LiEtTFSI\text{-}PE_2)_{11}$**	**$(LiEtTFSI\text{-}PE_4)_{11}$**	**$(LiEtTFSI\text{-}PE_8)_{11}$**

σ_{elec}_Li	0.184	0.063	0.000	0.000	0.040	0.059	0.046
σ_{elec-}	0.394	0.146	0.050	0.025	0.030	0.052	0.025
t_{elec}	0.32	0.30	\	\	0.57	0.53	0.65
percentage of free Li+	68%	59%	27%	19%	56%	59%	61%

Table S4 σ, α and t of (LiEtTFSI-PE_m)$_n$ in G4 (25°C) with O/Li = 20.

σ (mS/cm)	**LiEtTFSI**	**$(LiEtTFSI)_2$**	**$(LiEtTFSI)_4$**	**$(LiEtTFSI)_{11}$**	**$(LiEtTFSI-PE_2)_{11}$**	**$(LiEtTFSI-PE_4)_{11}$**	**$(LiEtTFSI-PE_8)_{11}$**
σ_{elec}_Li	0.619	0.096	0.035	0.000	0.232	0.345	0.180
σ_{elec-}	0.734	0.351	0.129	0.167	0.335	0.270	0.146
t_{elec}	0.46	0.22	0.21	\	0.41	0.56	0.55
percentage of free Li+	50%	41%	30%	11%	25%	41%	46%

Table S5. HOMO, LUMO and ESP_{min} value of each model single ion conductor anion. theoretical level: B3LYP-D3/6-311+G(d,p)

anions	HOMO(eV)	LUMO(eV)	ESP_{min}(kcal/mol)
$EtSO_3^-$	-2.01	3.14	-134.4
$Et(SO_2)NCF_3^-$	-3.10	2.85	-126.1
$Et(SO_2)N(SO_2)Ph^-$	-3.39	2.04	-120.2
$Et(SO_2)N(SO_2)CF_3^-$	-3.57	2.48	-115.8
$Et(SO_2)N(SO_2)CN^-$	-4.11	2.53	-112.6
$Et(SO_2)N(SO_2)NO_2^-$	-3.98	1.40	-111.6
$Et(SO_2)N(SOCF_3)N(SO_2)CF_3^-$	-4.67	2.28	-103.7
$Et(SO_2)N(SOCF_3N)_2$ $(SO_2)CF_3^-$	-4.99	1.88	-93.5
$CF_3SO_3^-$	-2.93	3.78	-120.2
TFSI	-4.37	3.05	-114.3
ClO_4^-	-3.06	4.39	-121.6

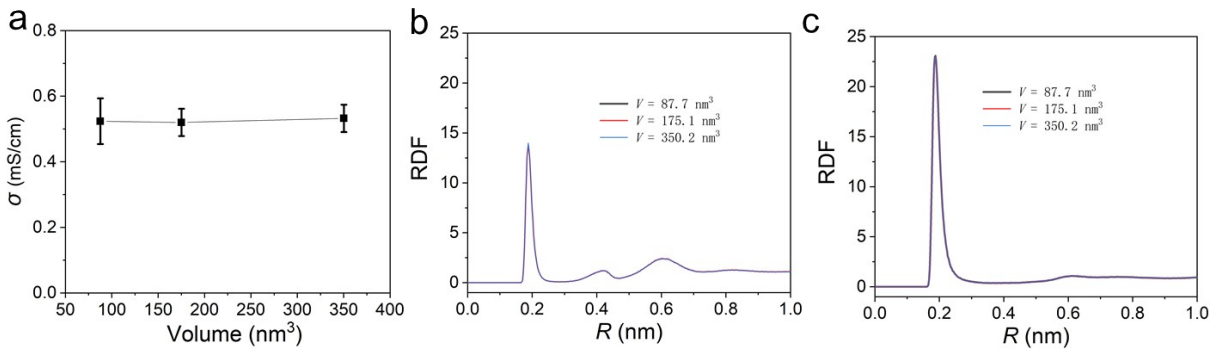

Fig. S1 MD simulation results of different box sizes for LiEtTFSI in G99 with O/Li = 20. (a) conductivities. (b) RDF of Li^+ with O atoms of $EtTFSI^-$. (c) RDF of Li^+ with O atoms of G99.

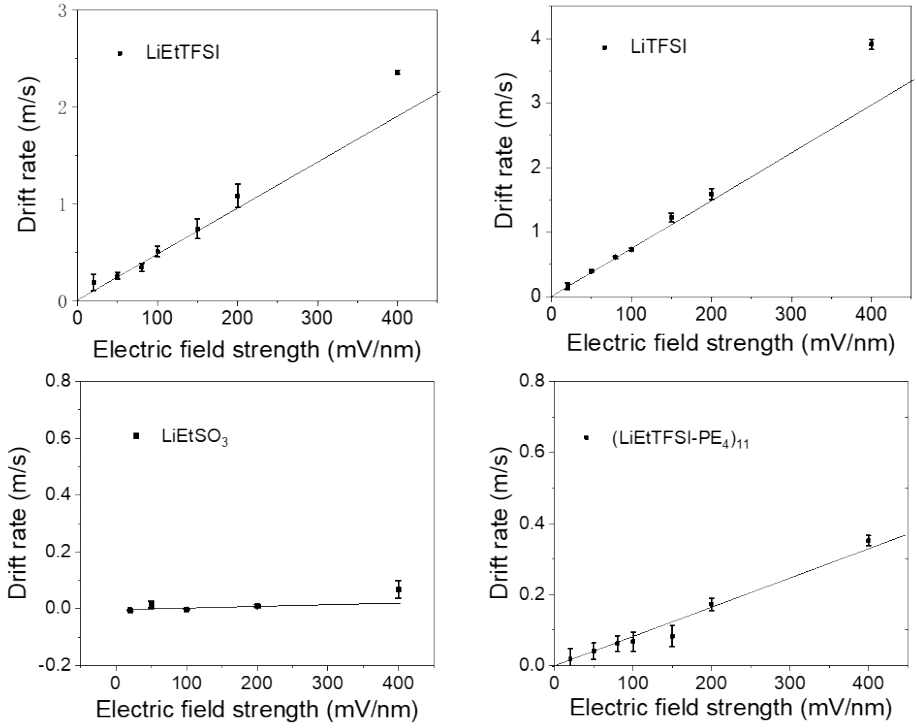

Fig. S2 Relationships between average carrier drift rate with different electric field strength. (in G99 electrolyte with O/Li = 20 at 80 °C).

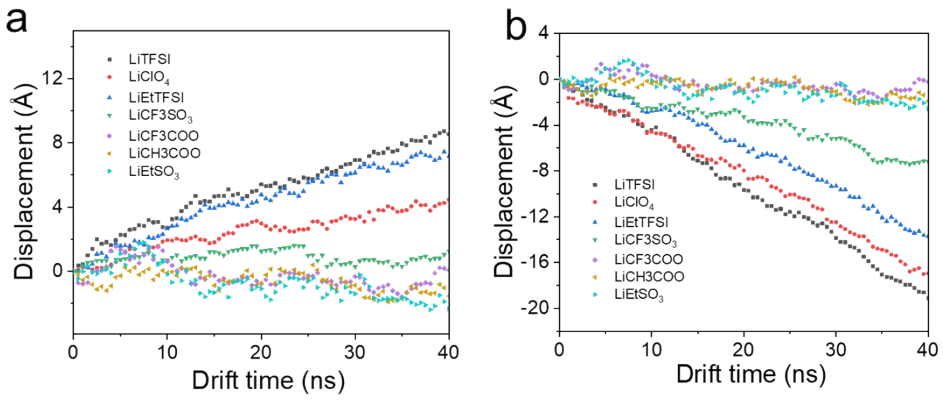

Fig. S3 The drift displacement curve of (a) Li^+ and (b) anion in G99 electrolyte with O/Li = 20 at 80 ˚C. *E* = 0.10 V/nm

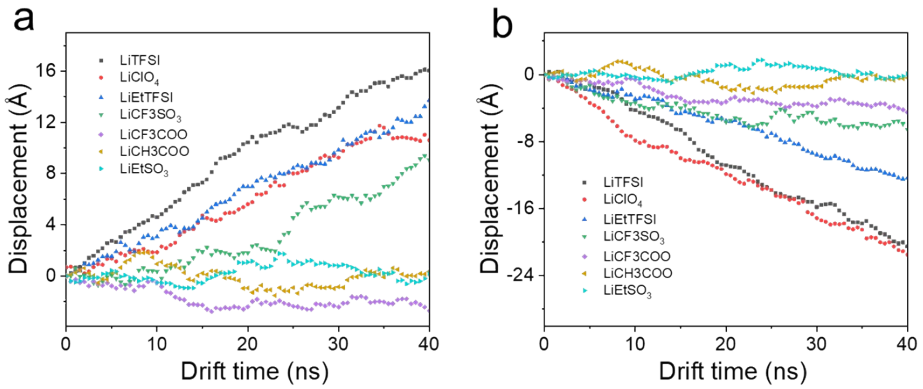

Fig. S4 The drift displacement curve of (a) Li^+ and (b) anion in G4 electrolyte with O/Li = 20 at 80 ˚C. *E* = 0.05 V/nm

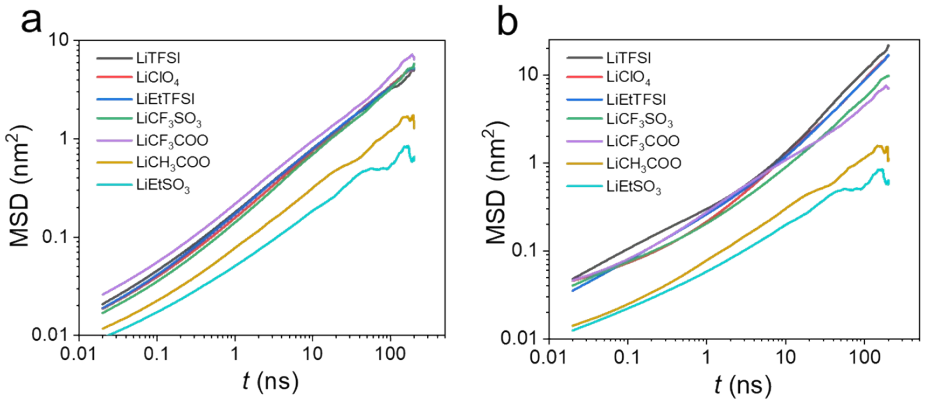

Fig. S5 The MSD of (a) Li^+ and (b) anions for different salts in G99 electrolyte with O/Li = 20 at 80 ˚C

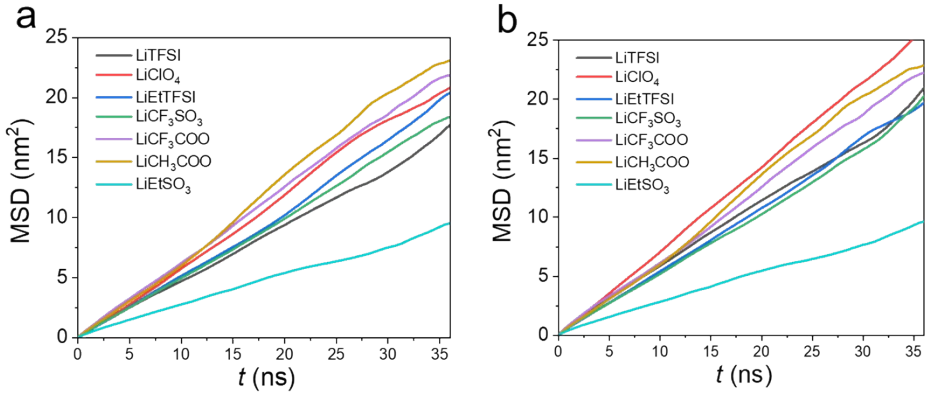

Fig. S6 The MSD of (a) Li^+ and (b) anions for different salts in G4 electrolyte with O/Li = 20 at 25 ˚C

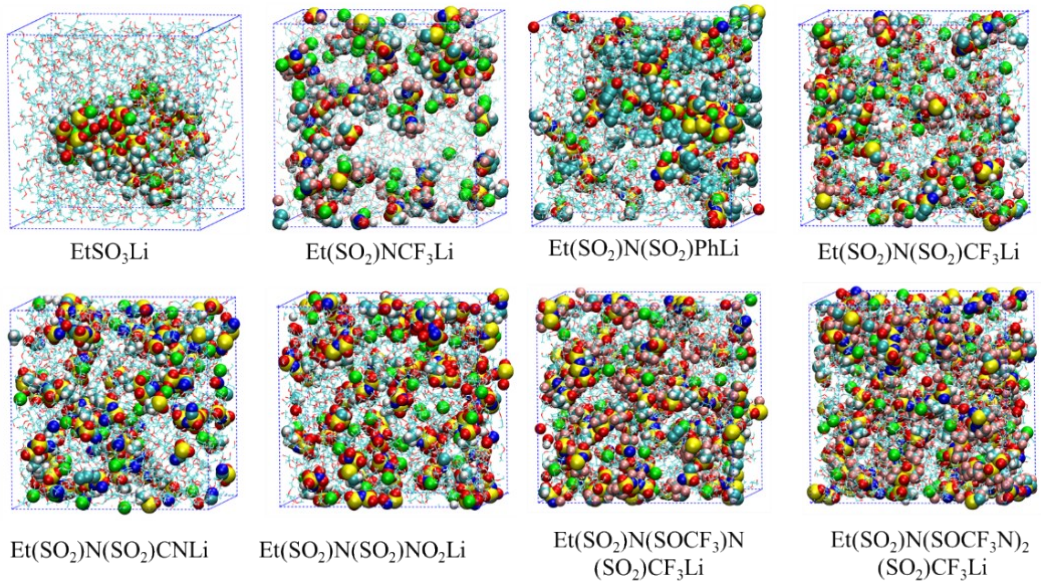

Fig. S7 The simulation boxes of different salts in G99 electrolyte with O/Li = 20 at 80 ˚C

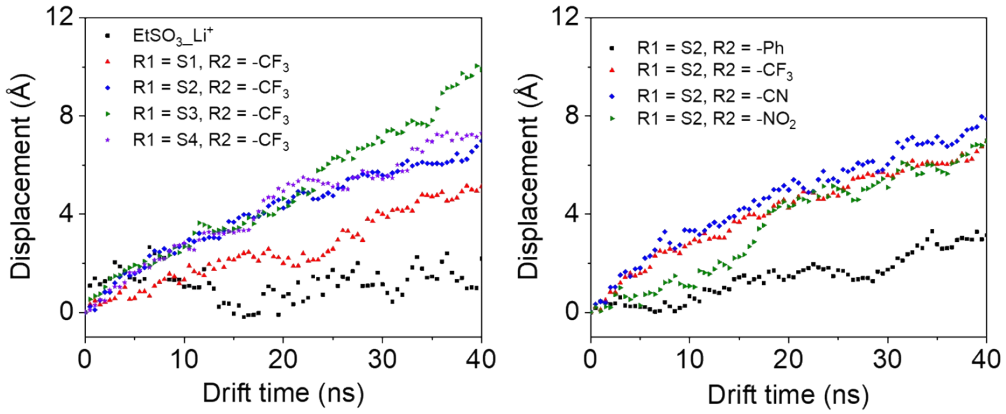

Fig. S8 Relationships between drift displacement of Li^+ in G99 electrolyte with O/Li = 20 at 80 ˚C. E = 0.10 V/nm

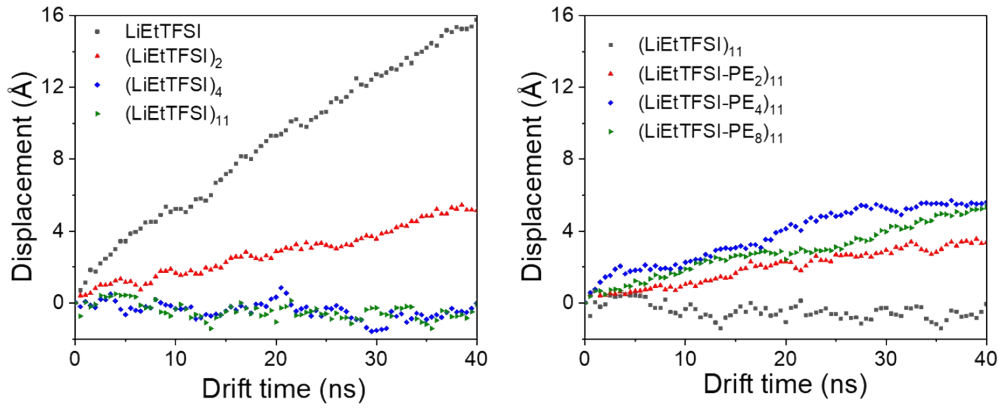

Fig. S9 Relationships between drift displacement of Li^+ in G99 electrolyte with O/Li = 20 at 80 ˚C. E = 0.20 V/nm

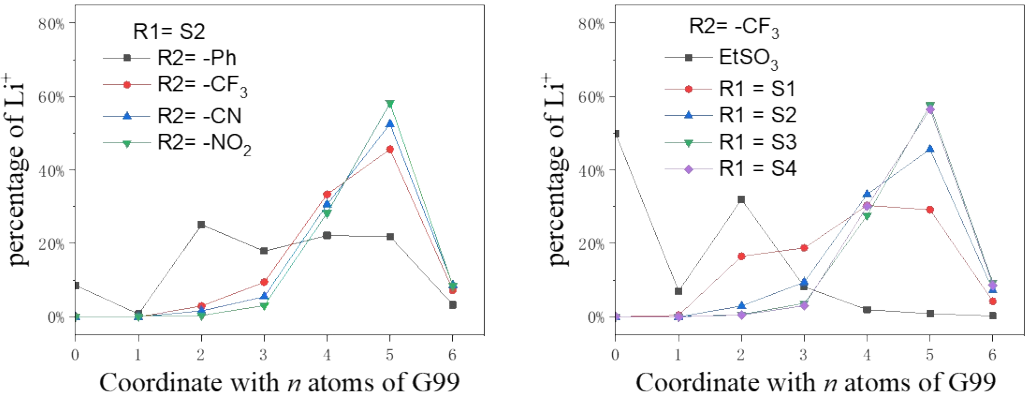

Fig. S10 Percentage of Li^+ coordinate with *N* atoms of G99 in LiR1R2 electrolytes

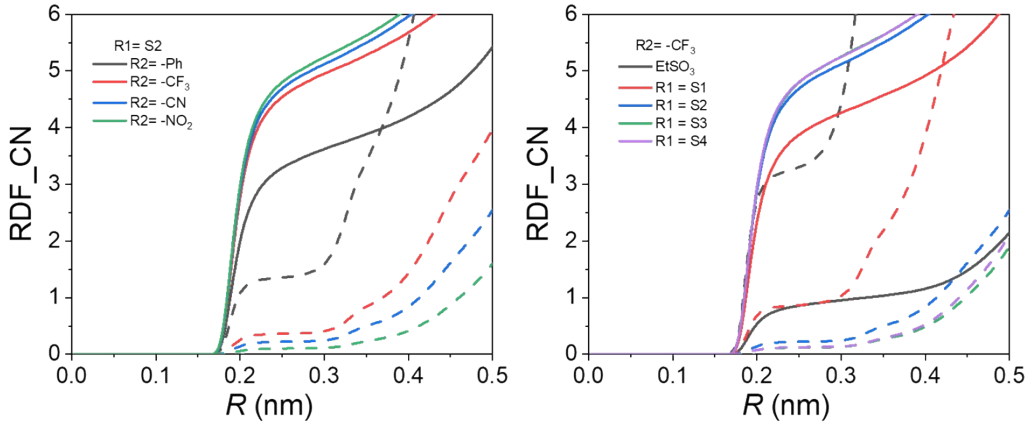

Fig. S11 Coordination number calculated by integrating RDF in LiR1R2 electrolytes. Solid line is the O atoms of G99 coordinated with a Li ion; dashed line is the anion coordinated with a Li ion

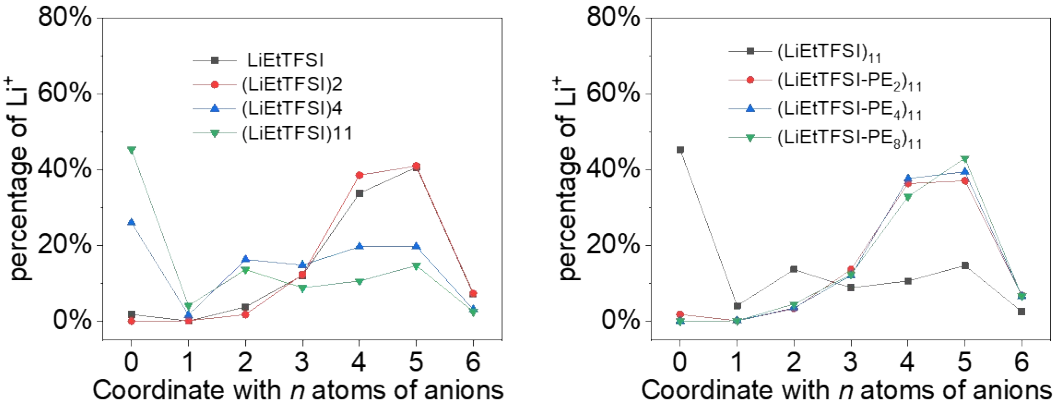

Fig. S12 Percentage of Li^+ coordinate with *N* atoms of G99 in $(LiEtTFSI\text{-}PE_m)_n$ electrolytes

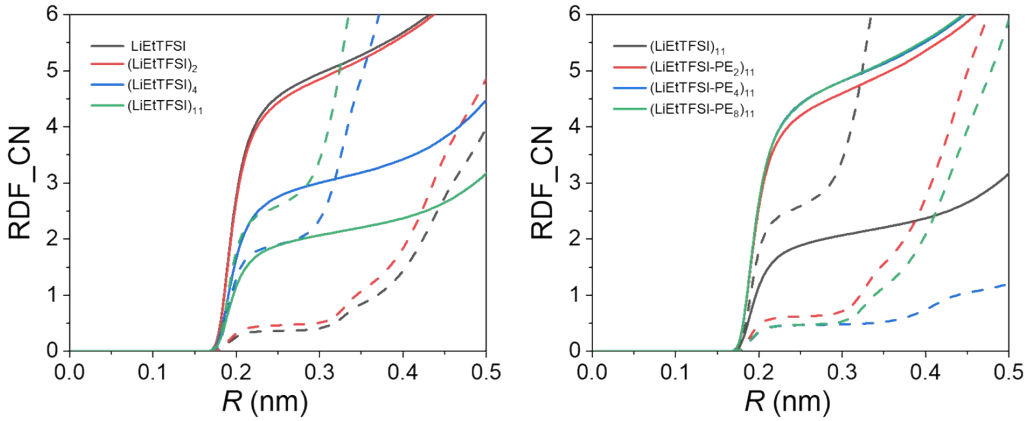

Fig. S13 Coordination number calculated by integrating RDF in (LiEtTFSI-PE$_m$)$_n$. Solid line is the O atoms of G99 coordinated with a Li ion; dashed line is the atoms of anion coordinated with a Li ion

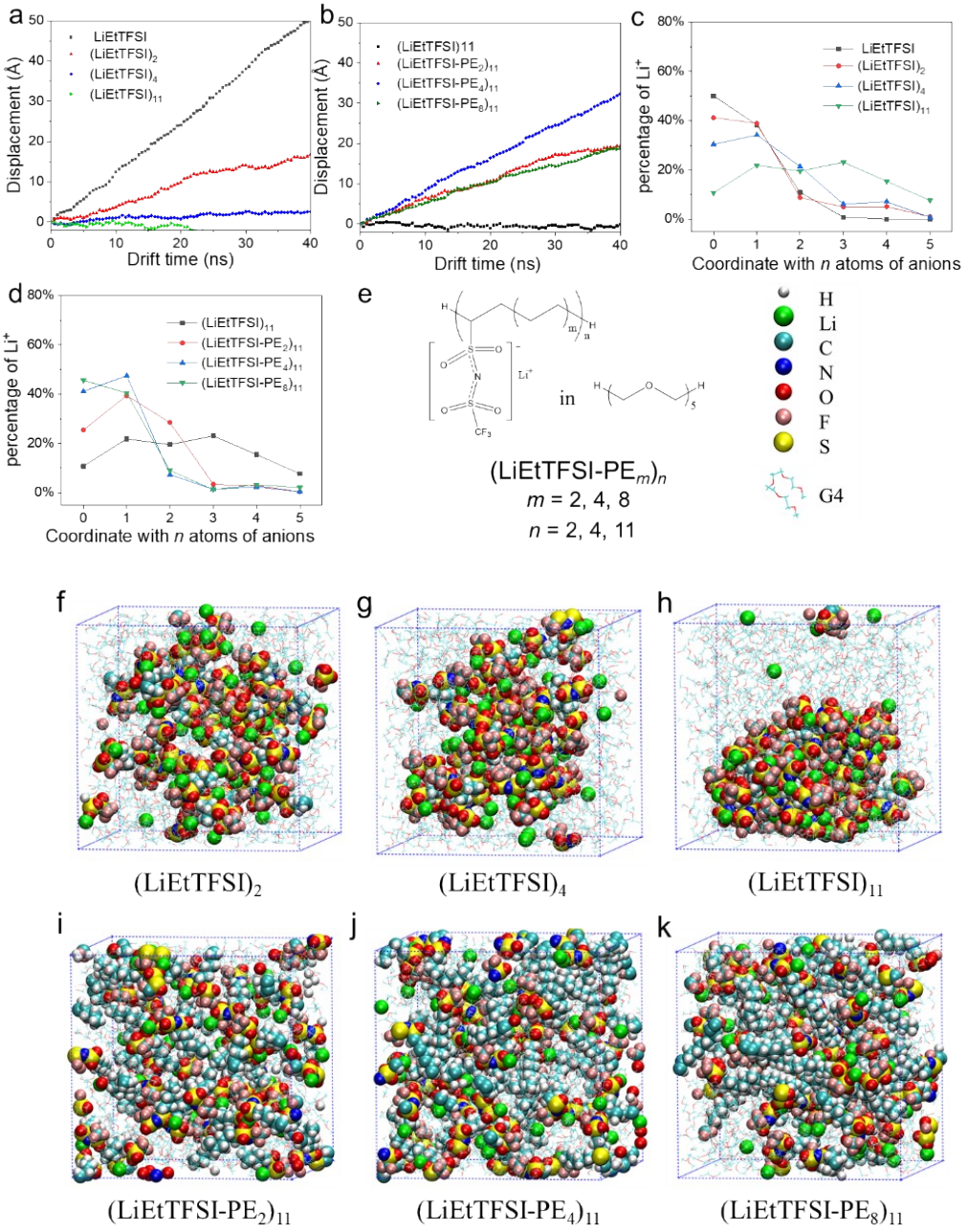

Fig. S14. The simulation results of $(LiEtTFSI\text{-}PE_m)_n$ in G4 electrolyte with O/Li = 20 at 25°C. (a-b) relationships between drift displacement and drift time under electric field E = 0.2 V/nm. (c-d) percentage of Li^+ coordinate with N atoms of anions. (e) structural formula of the electrolyte. (f-k) snapshots of simulation boxes.

Table S6 σ, α and u of (LiEtTFSI-PE$_m$)$_n$ in G4 (25°C) or G99 (80°C) with O/Li = 20.

G4 (25°C)	***n* = 1 *m* = 0**	**n = 2 m = 0**	**n = 4 m = 0**	**n = 11 m = 0**	**n = 11 m = 2**	**n = 11 m = 4**	**n = 11 m = 8**
σ (mS/cm)	0.619	0.096	0.035	0	0.232	0.345	0.18
α	50.1%	41.2%	30.4%	10.7%	25.4%	41.1%	45.6%
u (10^{-6} cm^2/Vs)	12.88	2.37	1.17	0.00	9.98	9.77	5.13

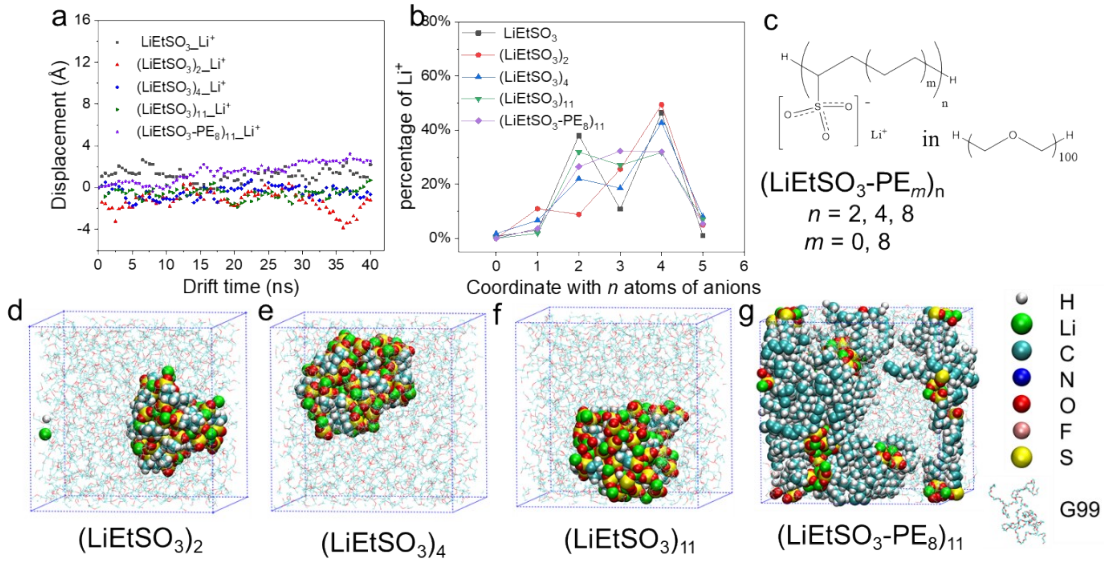

Fig. S15 The simulation results of (LiEtSO$_3$-PE$_m$)$_n$ in G99 electrolyte with O/Li = 20 at 80°C. (a) relationships between drift displacement and drift time under electric field E = 0.2 V/nm. (b) percentage of Li^+ coordinate with N atoms of anions. (c) structural formula of the electrolyte. (d-g) snapshots of electrolyte by MD simulation.

Table S7 σ, and u of (LiEtSO$_3$-PE$_m$)$_n$ in G99 (80°C) with O/Li = 20.

G100 (80°C)	***n* = 1 *m* = 0**	***n* = 2 *m* = 0**	***n* = 4 *m* = 0**	***n* = 11 *m* = 0**	***n* = 11 *m* = 8**
σ (mS/cm)	0.001	0.000	0.006	0.001	0.032
u **(10^{-6} cm^2/Vs)**	0.7%	0.0%	1.8%	0.0%	0.0%

Reference

1. R. Meziane, J.-P. Bonnet, M. Courty, K. Djellab and M. Armand, *Electrochim. Acta*, 2011, **57**, 14-19.
2. H.-B. Han, Y.-X. Zhou, K. Liu, J. Nie, X.-J. Huang, M. Armand and Z.-B. Zhou, *Chem. Lett.*, 2010, **39**, 472-474.