

Supporting information for:

On the Nature of Ion Aggregation in EC-LiTFSI Electrolytes

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S1: Radial Distribution Function $g(r)$ for Li-TFSI and Li-EC pairs

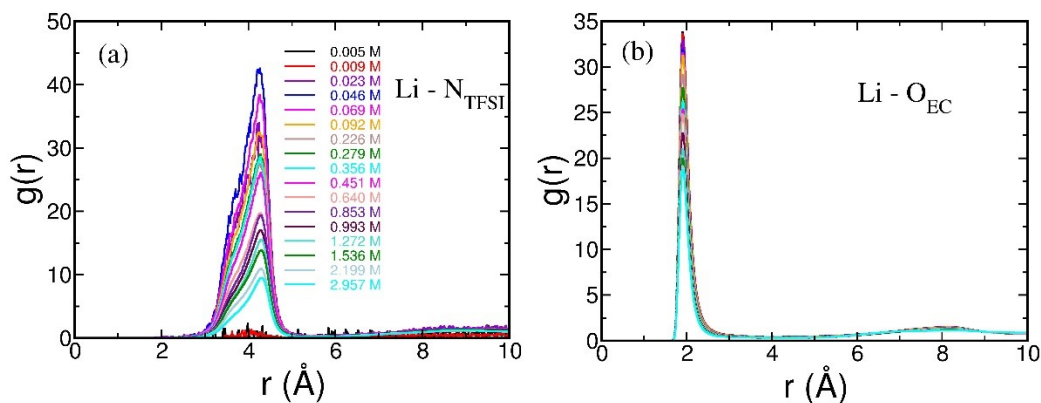


Figure S1: (a-b) Radial distribution function, $g(r)$, for Li-TFSI and Li-EC pairs.

	Li – N(TFSI)			Li – O(EC)		
c(M)	$r_{\max}$	$g(r_{\max})$	$r_{\min}$	$r_{\max}$	$g(r_{\max})$	$r_{\min}$
0.023	4.2	33.8	5.0	1.9	32.8	3.0
0.046	4.2	42.5	5.0	1.9	31.8	3.0
0.069	4.2	38.2	5.0	1.9	31.4	3.0
0.092	4.2	32.3	5.0	1.9	31.2	3.0
0.226	4.2	27.5	5.0	1.9	29.1	3.0
0.279	4.2	28.9	5.0	1.9	27.6	3.0
0.356	4.2	28.1	5.0	1.9	26.1	3.0
0.451	4.2	26.2	5.0	1.9	25.3	3.0
0.64	4.2	19.7	5.0	1.9	24.7	3.0
0.853	4.2	19.2	5.0	1.9	22.6	3.0
0.993	4.2	16.9	5.0	1.9	22.6	3.0
1.272	4.2	15.4	5.0	1.9	21	3.0
1.536	4.2	13.7	5.0	1.9	19.8	3.0
2.199	4.2	10.7	5.0	1.9	19.2	3.0
2.957	4.2	9.4	5.0	1.9	18.5	3.0

Table S1: Maximum ($r_{\max}$) and minimum ($r_{\min}$) positions of the first peak, along with the peak height $g(r_{\max})$, from the radial distribution function (RDF).

S2: Coordination Number (CN) for Li-TFSI and Li-EC pairs

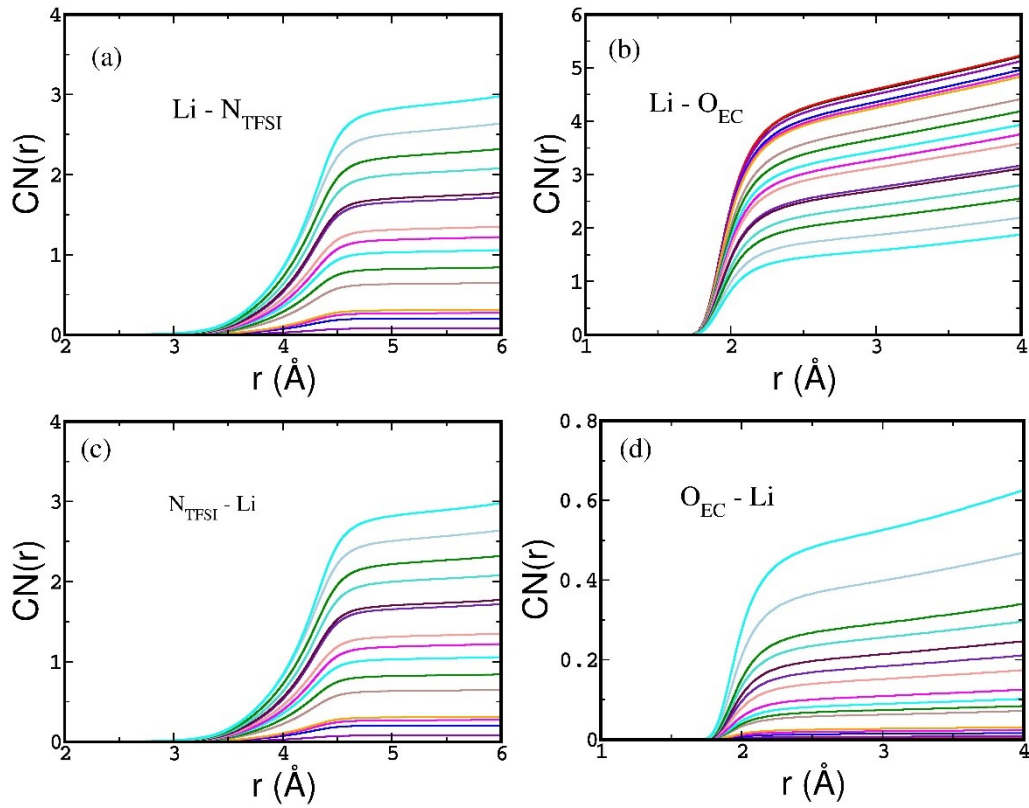


Figure S2: (a-b) Coordination number, $CN(r)$, for Li-TFSI and Li-EC pairs. (c-d) Coordination number, $CN(r)$, for TFSI-Li and EC-Li pairs.

S3: Ion aggregation probability distribution function $P(n)$ for Li-TFSI and Li-EC pairs

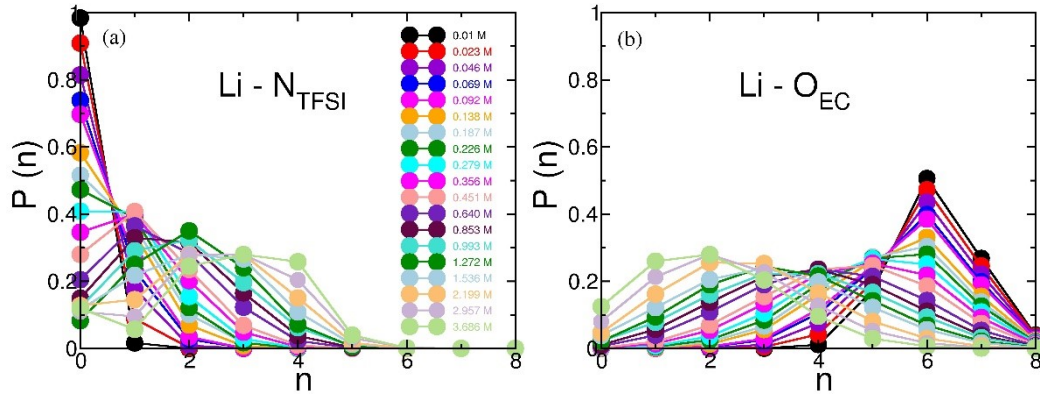


Figure S3: (a-b) Ion aggregation probability distribution function, $P(n)$ vs. n for Li-N(TFSI) and Li-O(EC) pairs at different salt concentrations.

c (M)	$CN_{Li-TFSI}$ at $r_{cut} = 5 \text{ \AA}$	$P(0)$	$P(1)$	$P(2)$	$P(3)$	$P(4)$	$P(5)$	$P(6)$
0.005	0.000	0.97	0.03	0.00	0.00	0.00	0.00	0.00
0.009	0.001	0.98	0.02	0.00	0.00	0.00	0.00	0.00
0.023	0.078	0.91	0.09	0.00	0.00	0.00	0.00	0.00
0.046	0.201	0.81	0.18	0.01	0.00	0.00	0.00	0.00

0.069	0.268	0.74	0.23	0.03	0.00	0.00	0.00	0.00
0.092	0.305	0.70	0.27	0.03	0.00	0.00	0.00	0.00
0.138	0.560	0.58	0.34	0.07	0.01	0.00	0.00	0.00
0.187	0.594	0.52	0.36	0.10	0.02	0.00	0.00	0.00
0.226	0.633	0.47	0.39	0.12	0.02	0.00	0.00	0.00
0.279	0.820	0.41	0.41	0.15	0.03	0.00	0.00	0.00
0.356	1.029	0.35	0.40	0.20	0.05	0.00	0.00	0.00
0.451	1.186	0.28	0.41	0.23	0.07	0.01	0.00	0.00
0.640	1.312	0.20	0.36	0.28	0.12	0.02	0.00	0.00
0.853	1.655	0.15	0.33	0.32	0.17	0.04	0.00	0.00
0.993	1.703	0.12	0.29	0.32	0.20	0.06	0.01	0.00
1.272	1.998	0.08	0.25	0.35	0.24	0.07	0.01	0.00
1.536	2.218	0.12	0.22	0.28	0.27	0.11	0.01	0.00
2.199	2.508	0.13	0.15	0.28	0.28	0.15	0.02	0.00
2.957	2.820	0.11	0.10	0.28	0.28	0.20	0.03	0.00
3.686	3.021	0.12	0.06	0.24	0.28	0.26	0.04	0.00
4.259	3.128	0.36	0.04	0.19	0.19	0.19	0.04	0.00
6.467	3.671	0.52	0.01	0.03	0.19	0.19	0.07	0.00

Table S2: Coordination Number (CN) and ion aggregation probability distribution function P(n) for Li - TFSI

c (M)	CN_ Li-EC at $r_{\text{cut}} = 3 \text{ \AA}$	P(0)	P(1)	P(2)	P(3)	P(4)	P(5)	P(6)	P(7)	P(8)
0.005	4.579	0.00	0.00	0.00	0.00	0.02	0.18	0.50	0.26	0.04
0.009	4.603	0.00	0.00	0.00	0.00	0.01	0.17	0.51	0.27	0.04
0.023	4.505	0.00	0.00	0.00	0.00	0.04	0.20	0.47	0.25	0.04
0.046	4.363	0.00	0.00	0.00	0.01	0.07	0.22	0.44	0.22	0.03
0.069	4.297	0.00	0.00	0.00	0.02	0.10	0.24	0.40	0.20	0.03

0.092	4.249	0.00	0.00	0.01	0.03	0.12	0.24	0.38	0.19	0.03
0.138	3.960	0.00	0.00	0.01	0.06	0.16	0.26	0.33	0.16	0.02
0.187	3.871	0.00	0.00	0.02	0.07	0.18	0.27	0.30	0.14	0.02
0.226	3.876	0.00	0.00	0.03	0.08	0.19	0.27	0.28	0.13	0.02
0.279	3.668	0.00	0.01	0.04	0.10	0.21	0.27	0.25	0.11	0.02
0.356	3.439	0.00	0.01	0.05	0.13	0.22	0.25	0.22	0.09	0.01
0.451	3.277	0.00	0.02	0.07	0.15	0.24	0.25	0.19	0.07	0.01
0.640	3.132	0.01	0.04	0.11	0.19	0.24	0.21	0.14	0.05	0.01
0.853	2.756	0.01	0.06	0.14	0.21	0.24	0.19	0.11	0.04	0.01
0.993	2.703	0.02	0.08	0.16	0.22	0.22	0.17	0.09	0.03	0.00
1.272	2.418	0.02	0.09	0.19	0.24	0.22	0.14	0.07	0.02	0.00
1.536	2.192	0.04	0.12	0.20	0.24	0.20	0.12	0.06	0.02	0.00
2.199	1.867	0.05	0.16	0.26	0.25	0.17	0.08	0.03	0.01	0.00
2.957	1.578	0.08	0.21	0.28	0.23	0.13	0.05	0.02	0.00	0.00
3.686	1.312	0.12	0.26	0.28	0.20	0.10	0.03	0.01	0.00	0.00
4.259	1.191	0.38	0.19	0.19	0.16	0.07	0.02	0.00	0.00	0.00
6.467	0.279	0.73	0.19	0.08	0.01	0.00	0.00	0.00	0.00	0.00

Table S3: Coordination Number (CN) and ion aggregation probability distribution P(n) for Li – EC

S4: Lennard-Jones parameters and partial charges for TFSI

Atom type	Sigma (nm)	Epsilon (kJ/mol)
F1	0.295	0.22175
CBT	0.35	0.27614
SBT	0.355	1.046
OBT	0.296	0.87864
NBT	0.325	0.71128

Table S4: Lennard-Jones parameters for TFSI

Atom type	Charges
NBT	-0.528
SBT	0.816

SBT	0.816
OBT	-0.424
CBT	0.28
OBT	-0.424
OBT	-0.424
OBT	-0.424
F1	-0.128
F1	-0.128
F1	-0.128
CBT	0.28
F1	-0.128
F1	-0.128
F1	-0.128

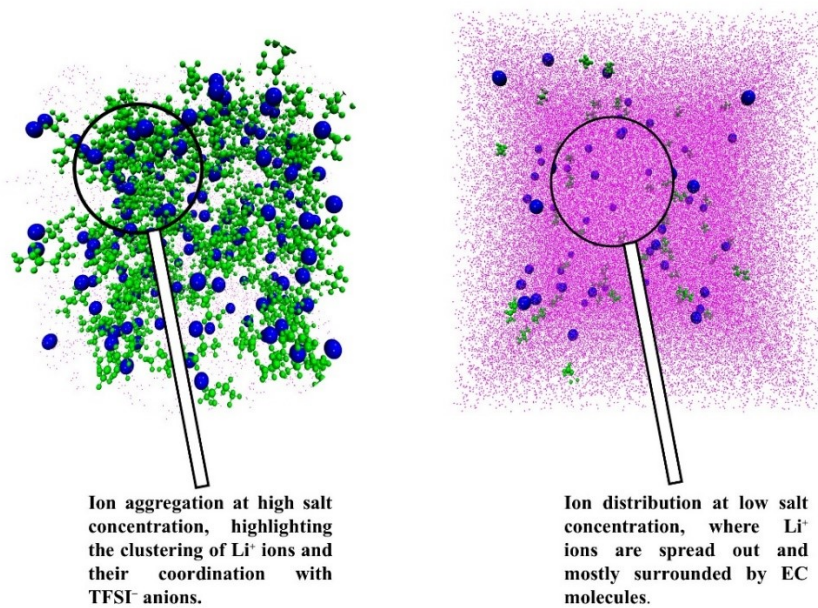
Table S5: Partial charges for TFSI

S5: Diffusion Coefficient of Ethylene Carbonate (EC) at Different Salt Concentrations

Salt concentration	Range	Power	slope	D _{EC} (cm ² /s)
0.451 M	80-250	0.99616	0.0030308	5.05E-06
0.64 M	80-250	1.0139	0.0028133	4.69E-06
2.957 M	100-250	1.0772	0.00023856	3.98E-07

Table S6: Diffusion Coefficient of Ethylene Carbonate

S6: Visual Diagram of Ion Aggregation at High Salt and Ion Distribution at Low Salt in EC-LiTFSI



S7: Comparison of Ion Aggregation Probabilities for Li-TFSI: Long vs. Multiple Independent Trajectories

LiTFSI (0.68 M) – 300 ns Trajectory							
Concen. (M)	p(0)	p(1)	p(2)	p(3)	p(4)	p(5)	p(6)
0.68 (300 ns)	0.2045	0.3646	0.2832	0.1228	0.0225	0.0016	0.0004
Li-TFSI (0.68 M) – 5 Trajectories of 40 ns Each							
Concen. (M)	p(0)	p(1)	p(2)	p(3)	p(4)	p(5)	p(6)
0.68 (Run 1)	0.2024	0.3407	0.3005	0.1279	0.0263	0.0019	0.0000
0.68 (Run 2)	0.2071	0.3718	0.2809	0.1144	0.0234	0.0015	0.0006
0.68 (Run 3)	0.1937	0.3571	0.2841	0.1357	0.0230	0.0036	0.0025
0.68 (Run 4)	0.2130	0.3715	0.2815	0.1196	0.0142	0.0000	0.0000
0.68 (Run 5)	0.2108	0.3787	0.2705	0.1111	0.0258	0.0027	0.0000
Average	0.2054	0.3640	0.2835	0.1217	0.0225	0.0019	0.0006

Table S7: Ion Aggregation Probabilities for LiTFSI (0.68 M) from 300 ns and 5 independent 40 ns Trajectories.

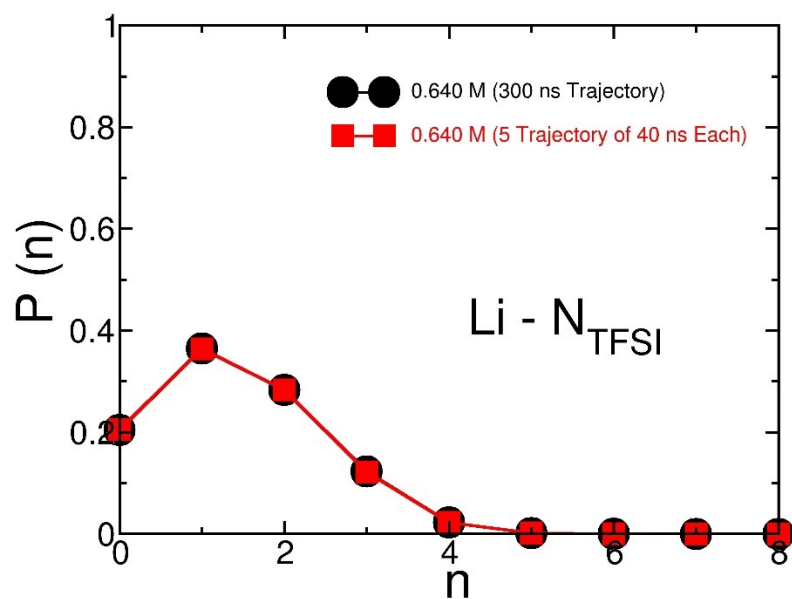


Figure S4: Ion aggregation probabilities for LiTFSI (0.68 M) from a 300 ns trajectory and the average of five independent 40 ns trajectories