

Supplemental Information for "Why Lithium Ions Stick to Some Anions and not Others"

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Table S1: TFSI and OTf partial charges and Lennard-Jones parameters.¹

Atom Charges and Lennard-Jones parameters

Atom	Charge(e)	ϵ (kJ/mol)	σ (nm)
F	-0.16	2.2175E-01	2.95E-01
C	0.35	2.7614E-01	3.50E-01
S	1.02	10.46E-01	3.55E-01
N	-0.66	7.1128E-01	3.25E-01
O (TFSI)	-0.53	8.7864E-01	2.96E-01
O (OTf)	-0.63	8.7864E-01	2.96E-01

Table S2: Li and EC force field parameters for both the OPLS-AA force field (ORI) and the modified force field (MOD). Values given for ORI and MOD have the same units. The Lennard-Jones parameters for Li and the partial charges for the EC atoms are altered. Atom names are the same as those shown in figure 1.

Atom	ORI Charge (e)	MOD Charge (e)	ORI ϵ (kJ/mol)	ORI σ (nm)	MOD ϵ (kJ/mol)	MOD σ (nm)
Li	1.0	1.0	2.12645e-01	7.64793e-02	1.46000e-01	7.99144e-01
O2	-0.5	-0.61294	2.96000e-01	8.78640e-01	2.96000e-01	8.78640e-01
O1	-0.45	-0.44498	3.00000e-01	7.11280e-01	3.00000e-01	7.11280e-01
C1	0.86	1.04462	3.75000e-01	4.39320e-01	3.75000e-01	4.39320e-01
C2	0.21	0.03135	3.50000e-01	2.76144e-01	3.50000e-01	2.76144e-01
H	0.03	0.098895	2.42000e-01	6.27600e-02	2.42000e-01	6.27600e-02

Lithium TFSI Single Ion Simulation Results

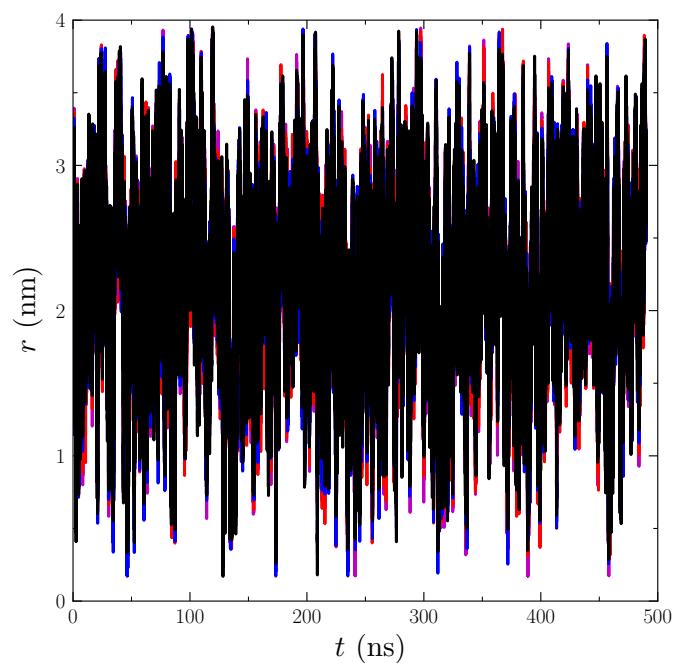


Figure S1: Distance between the lithium ion and the TFSI oxygen atoms. Each color represents a different oxygen atom on the TFSI molecule. TFSI and Li do not form a long-lived complex in contrast to OTf and Li.

Force field validation: Solvation structure of dilute Li⁺ in ethylene carbonate

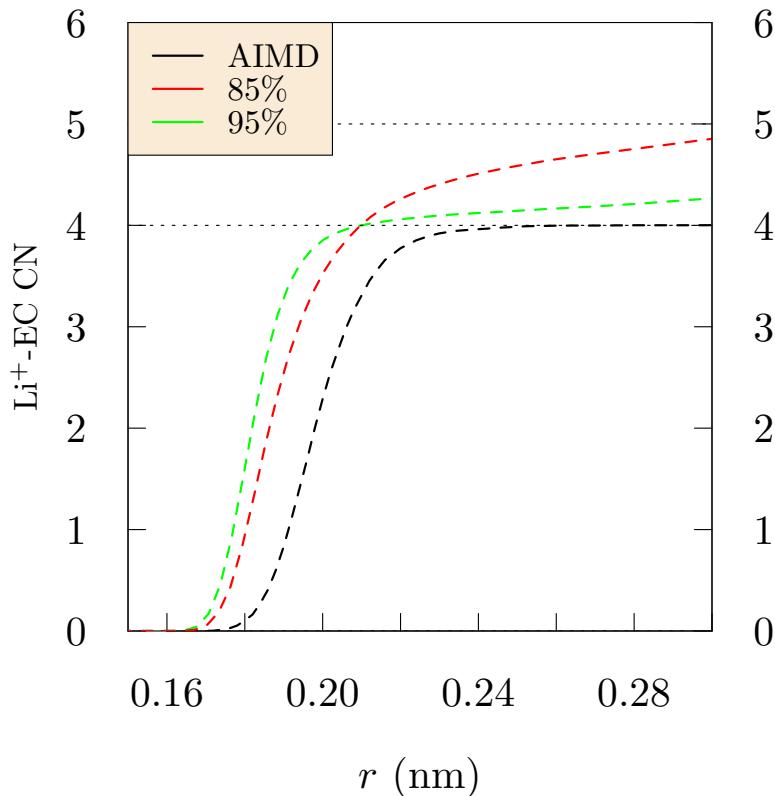


Figure S2: A single Li⁺ ion was simulated in a box of 128 EC at 313K with scaled charges models (85% and 95%) for the neutral EC molecule. We choose the 95% scaled charge model in all our calculations. The calculated coordination number (4.1) is in good agreement with ab initio MD (AIMD) calculations. Here, 100 ps of AIMD were performed with 1 Li⁺ and 61 EC molecules at 313K with the Nose-Hoover thermostat² using CP2K.³ The PBE density functional⁴ was utilized with GTH⁵ pseudopotentials in the Gaussian and plane wave schemes.⁶ Molecularly optimized DZVP-GTH⁷ basis sets were obtained from the CP2K website.

PMF along Li⁺-N coordinate for LiTFSI

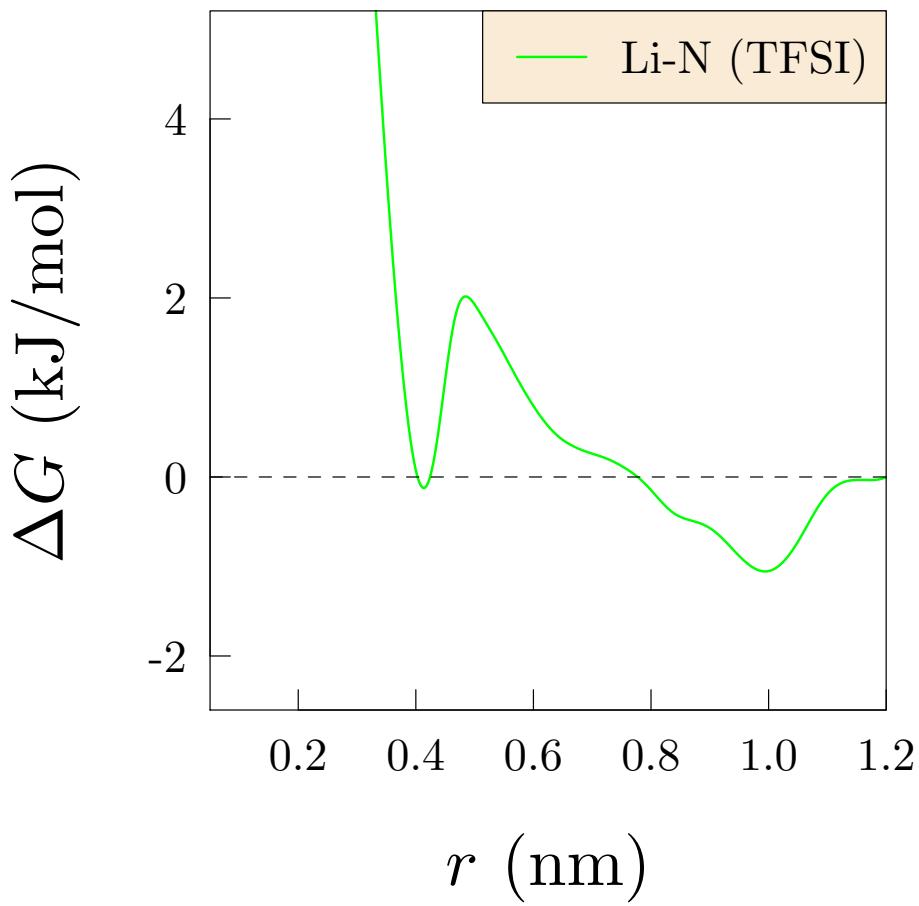


Figure S3: The PMF along the Li⁺-N coordinate for LiTFSI. The first minimum for Li⁺-N occurs at ≈ 0.4 nm compared to ≈ 0.18 nm for Li⁺-O coordinate (Figure 4b of manuscript). This indicates that Li⁺ binds to O atoms of TFSI rather than the N.

$g(r)$ for Li⁺-EC

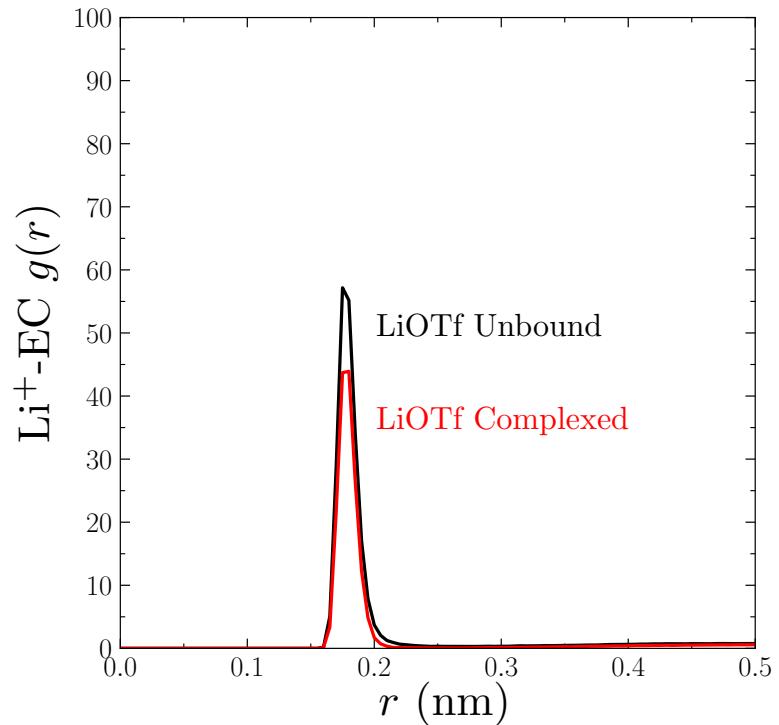


Figure S4: The radial distribution function, $g(r)$ for Li⁺ and the EC carbonyl oxygen atom. The unbound state has a larger peak than the complexed state resulting in the decrease of coordination number from 4 to 3 in Figure 6 of the main text.

References

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