# Energetics of Li<sup>+</sup> Coordination with Asymmetric Anions in Ionic Liquids by Density Functional Theory

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#### **Supplementary Information**

#### Sample Input File for Gaussian Optimization and Frequency Calculations

%chk=LiCTFSI.chk # opt freq=raman b3lyp/6-311g(d,p) geom=connectivity

Li CTFSI opt freq

01			
Ν	1.41686100	0.36969900	0.79977800
S	0.07565600	0.70808000	0.11601800
0	-0.74510300	1.63314200	0.95550700
0	0.05833900	1.25089600	-1.28722700
С	-0.99586900	-0.84760300	-0.01875500
F	-2.17981600	-0.50889200	-0.54714100
F	-1.18727600	-1.36979000	1.18492400
F	-0.39840500	-1.73344700	-0.80630600
С	2.39728600	-0.26742700	0.16032500
Ν	3.30327800	-0.81297100	-0.31437200
Li	-1.09212300	2.63355300	-0.64436200
1 2 1.5 9	1.5		
232.04	1.5		
3 11 1.0			
4 11 1.0			
561.07	1.0 8 1.0		
6			
7			
8			

10

9 10 3.0

11

#### Differential Energy Analysis

**Table S1**. Differential Analysis of Li-solvates with [CTFSI] systems. Energies are truncated to 2 decimal points. Green represent systems in which the change in energy from the initial to the final state are negative, indicating a thermodynamically favored transition, while red represents thermodynamically unfavorable transitions. The  $\Delta E$  (eV) represent the difference in energy for initial system and the final Li-solvate. Integral energies are those listed next to the Li<sup>+</sup> + n[CTFSI]<sup>-</sup> systems (i.e.  $\Delta E$  between Li<sup>+</sup> + 2[CTFSI]<sup>-</sup> and Li[CTFSI]2<sup>-</sup>) and the differential energies are listed next to the Li[CTFSI]<sup>-</sup> normal Li[CTFSI]2<sup>-</sup>). There is no distinction between differential and integral for the first system containing only one [CTFSI].

	Energy (Hartree)	
Li <sup>+</sup>	-7.2849	ΔE (eV)
[CTFSI] <sup>-</sup>	-1034.0697	
Li[CTFSI]	-1041.5651	-5.73
	Energy (Hartree)	
Li[CTFSI]2 <sup>-</sup>	-2075.7279	ΔE (eV)
Li⁺ + 2[CTFSI]⁻	-2075.4242	-8.26
Li[CTFSI] + [CTFSI] <sup>-</sup>	-2075.6348	-2.53
	Energy (Hartree)	
Li[CTFSI]₃²⁻	-3109.7740	ΔE (eV)
Li⁺ + 3[CTFSI] <sup>-</sup>	-3109.4939	-7.62
Li[CTFSI]2 + [CTFSI]	-3109.7976	0.64
	Energy (Hartree)	
Li[CTFSI]4 <sup>3-</sup>	-4143.7334	ΔE (eV)
Li <sup>+</sup> + 4[CTFSI] <sup>-</sup>	-4143.5636	-4.62
Li[CTFSI]3 <sup>2-</sup> + [CTFSI] <sup>-</sup>	-4143.8436	3.00

**Table S2.** Differential Analysis of Li-solvate with [FTFSI] systems. Energies are truncated to 2 decimal points. Green represent systems in which the change in energy from the initial state to the final state that are negative, indicating a thermodynamically favored transition, while red represents thermodynamically unfavorable transitions The  $\Delta E$  (eV) represent the difference in energy for initial system and the final Li-solvate. Integral energies are those listed next to the Li<sup>+</sup> + n[FTFSI]<sup>-</sup> systems (i.e.  $\Delta E$  between Li<sup>+</sup> + 2[FTFSI]<sup>-</sup> and Li[FTFSI]<sub>2</sub><sup>-</sup>) and the differential energies are listed next to the Li[FTFSI]<sub>n</sub><sup>-(n-1)</sup> + [FTFSI]<sup>-</sup> systems (i.e.  $\Delta E$  between Li[FTFSI] + [FTFSI]<sup>-</sup> and Li[FTFSI]<sub>2</sub><sup>-</sup>). There is no distinction between differential and integral energies for the first system containing only one [FTFSI].

	Energy (Hartree)	
Li <sup>+</sup>	-7.2849	∆E (eV)
[FTFSI] <sup>-</sup>	-1589.7242	
Li[FTFSI]	-1597.2413	-6.32
	Energy (Hartree)	
Li[FTFSI]2 <sup>-</sup>	-3187.0434	∆E (eV)
Li <sup>+</sup> + 2[FTFSI] <sup>-</sup>	-3186.7333	-8.44
Li[FTFSI] + [FTFSI] <sup>-</sup>	-3186.9654	-2.12
	Energy (Hartree)	
Li[FTFSI]3 <sup>2-</sup>	-4776.7163	∆E (eV)
Li <sup>+</sup> + 3[FTFSI] <sup>-</sup>	-4776.4574	-7.05
Li[FTFSI]2 <sup>-</sup> + [FTFSI] <sup>-</sup>	-4776.7675	1.39



**Figure S1.** Calculated Raman frequency of cis-[TFSI] (black) and Li<sup>+</sup>-[TFSI] (green). The Single [TFSI] coordinated with Li<sup>+</sup> structure is shown in **Figure 5**. Frequencies are scaled by a factor of 0.964. A blue shift is observed for the symmetric stretch of S-N-S with Li<sup>+</sup> coordination. A red shift is observed for the symmetric stretch of S=O with Li<sup>+</sup> coordination.



**Figure S2.** Calculated Raman frequency of [DCA] (black) and Li<sup>+</sup>-[DCA] (green). The Single [DCA] coordinated with Li<sup>+</sup> structure is shown in **Figure 6**. Frequencies are scaled by a factor of 0.964. A blue shift is observed for both the symmetric and asymmetric stretches of C-N-C with Li<sup>+</sup> coordination.



**Figure S3.** Calculated Raman frequency of [CTFSI] (black) and Li<sup>+</sup>-[CTFSI] (green). Frequencies are scaled by a factor of 0.964. The symmetric stretch of C $\equiv$ N is from the structure shown in **Figure 3a**; it shows a blue shift compared to [DCA] in **Figure S2**. The symmetric stretches of S=O and S-N-C<sub>CN</sub> are from the structure shown in **Figure 3b**. While the S-N-C<sub>CN</sub> stretch shows a blue shift, the S=O stretch experiences a red shift with Li<sup>+</sup> coordination; similar to [TFSI] in **Figure S1**.

## **Calculated Dissociation Energies**

**Table S3.** Calculated dissociation energies  $(E_D)$  in units of eV for all of the Li-solvate structures investigated in this study.

Anion	Number of Anions	Coordination	Li Coordination Environment	E <sub>D</sub> (eV)
[DCA]	1	1	i+-N(≡C)	6 044
	2	2	$Li^{+}N(\equiv C)$	8 719
	3	3	$Li^+ N(\equiv C)$	7.975
	4	4	Li+-N(≡C)	4.696
[CFSI]	1	1	Li⁺-N(≡C)	5.676
	2	2	Li⁺-N(̇̀≡C)́	8.215
	3	3	Li⁺-N(̇̀≡C)́	7.590
	4	4	Li⁺-N(≡C)́	4.582
[CTFSI]	1	1	Li⁺-N(≡C)́	5.729
	1	2	Li <sup>+</sup> -S(=O), bi	5.687
	2	2	Li <sup>+</sup> -O(=S), mono	8.241
			Li <sup>+</sup> -N(≡C)	
	2	3	Li+-S(=O), bi	8.014
			Li⁺-N(≡C)	
	2	4	Li+-S(=O), bi	7.756
	2	2	Li⁺-N(≡C)	8.263
	3	3	Li⁺-N(≡C)	7.458
			Li <sup>+</sup> -O(=S), mono	
	3	3	Li⁺-N(≡C)	7.621
	4	4	Li⁺-N(≡C)	4.621
[TFSI]:[DCA]	2	3	Li+-S(=O), bi Li+-N(≡C)	8.621
	3	3	Li+-S(=O), mono Li⁺-N(≡C)	7.627
	3	3	Li⁺-N(≡C) (2 DCA)	7.678
	3	3	Li <sup>+</sup> -O(=S), mono (2 TFSI)	7.213
	3	4	Li + S(=0) bi (TESI)	7 422
	U	-	$Li^+-O(=S)$ mono (TESI)	1.422
			Li <sup>+</sup> -N(≡C) (DCA)	
[TFSI]:[FSI]	2	4	Li+-S(=O), bi	8,461
	3	3	Li+-S(=O), mono (2 FSI)	7.205
	3	4	Li <sup>+</sup> -O(=S), bi (TFSI)	6.907
			Li <sup>+</sup> -O(=S), mono (TFSI,FSI)	
[FSI]	1	2	Li <sup>+</sup> -O(=S), bi	6.253
	1	2	Li <sup>+</sup> -O(=S), bi (one sulfonyl)	5.149
	2	4	Li+-O(=S), bi	8.403
	3	3	Li <sup>+</sup> -O(=S), mono	6.838
[TFSI]	1	2	Li+-O(=S), bi	6.406
-	1	2	Li <sup>+</sup> -O(=S), bi (one sulfonyl group)	5.644
	2	4	Li+-O(=S), bi	8.523
	2	4	Li <sup>+</sup> -O(=S), bi (mixed)	8.593
	3	4	Li+-O(=S), bi	7.274
			Li+-O(=S), mono	
[FTFSI]	1	2	Li+-O(=S), bi	6.318

	2	4	Li+-O(=S), bi	8.438
	3	4	Li+-O(=S), bi	7.045
			Li <sup>+</sup> -O(=S), mono	
	3	3	Li <sup>+</sup> -O(=S), mono	6.851
	3	3	Li <sup>+</sup> -O(=S), mono	6.811
	3	3	Li <sup>+</sup> -O(=S), mono	6.815
[PFTFSI]	1	2	Li+-O(=S), bi	6.369
	2	4	Li+-O(=S), bi	8.464
[HFTFSI]	1	2	Li+-O(=S), bi	6.333
	2	4	Li+-O(=S), bi	8.440
[NFFSI]	1	2	Li+-O(=S), bi	6.271
	2	4	Li+-O(=S), bi	8.398
[NFTFSI]	1	2	Li+-O(=S), bi	6.317
	2	4	Li+-O(=S), bi	8.419

### Comparison of Solvation Energies between [CTFSI] and [CFSI]







Structures of [FSI], [TFSI], [NFFSI], and [NFTFSI] and their Li<sup>+</sup> solvates

**Figure S5**. Representative structures for [FSI], [FTFSI], and [FSI]/[TFSI] anions coordinated with Li<sup>+</sup>. The atom color code: red=oxygen, blue=nitrogen, yellow=sulfur, gray=carbon, purple=lithium, and light blue=fluorine.



**Figure S6**. Representative structures [NFTFSI] and [NFFSI] anions coordinated with Li<sup>+</sup>. Red=oxygen, blue=nitrogen, yellow=sulfur, gray=carbon, purple=lithium, and light blue=fluorine.

#### Ab initio thermodynamic analysis derivation:

We transform the free energy (*G*) from a fixed number of coordinating ligands ( $N_{TFSI}^*$  and  $N_{DCA}^*$ ) to a fixed chemical potential ( $\mu_{TFSI}^*$  and  $\mu_{DCA}^*$ ) to determine the influence of ligand concentration on the stability of different coordinated clusters (Equation S1).

$$G^{(0)}(T, P, N_{Li^+}, N_{TFSI}^*, N_{DCA}^*) \to G^{(2)}(T, P, N_{Li^+}, \mu_{TFSI}^*, \mu_{DCA}^*)$$
(S1)

The transformed free energy  $G^{(2)}$  is described by Equation S2, which includes the chemical potentials of the coordinating ligands.

$$G^{(2)}(T, P, N_{Li^{+}}, \mu_{TFSI}^{*}, \mu_{DCA}^{*}) = G^{(0)}(T, P, N_{Li^{+}}, N_{TFSI}^{*}, N_{DCA}^{*}) -(\mu_{TFSI}^{*})(N_{TFSI}^{*}) - (\mu_{DCA}^{*})(N_{DCA}^{*})$$
(S2)

where  $N_{Li}$  is the number of Li atoms, T is the temperature, and P is the pressure.

We calculate the relative free energy ( $\Delta G$ ) by taking the free energy difference between a modified structure (containing Li<sup>+</sup> and coordinating ligands) and the reference structure (Li+). The reference structure composition is  $N_{Li^+} = 1$ ,  $N_{TFSI}^* = 0$ , and  $N_{DCA}^* = 0$ , and therefore define the free energy for this structure as  $G^{(0)}(T, P)$ . The modified structure contains different Li coordination resulting in variable  $N_{TFSI}^*$  and  $N_{DCA}^*$  species included in the analysis. The final free energy expression is given by Equation S3.

$$\Delta G^{(2)}(T, P, N_{Li^+}, \mu^*_{TFSI}, \mu^*_{DCA}) = [G^{(0)}(T, P, N_{Li^+} = 1, N^*_{TFSI}, N^*_{DCA}) - G^{(0)}(T, P)] -(\mu^*_{TFSI})(N^*_{TFSI}) - (\mu^*_{DCA})(N^*_{DCA})$$
(S3)

We approximate both  $G^{(0)}(T, P, N^*_{TFSI}, N^*_{DCA})$  and  $G^{(0)}(T, P)$  by the electronic energies of the modified and reference electronic energies calculated by DFT.

To calculate the chemical potentials of  $\mu_{TFSI}^*$  and  $\mu_{DCA}^*$ , we assume that coordinated [*DCA*] and [*TFSI*] anion species are in equilibrium with a reservoir of [*DCA*] and [*TFSI*] species, thereby relating the chemical potential of the coordinated anion species to the bulk reservoir (e.g.,  $\mu_{[TFSI]}^* = \mu_{[TFSI]}(T, x_{TFSI})$ ). The chemical potential terms,  $\mu_{[TFSI]}^*$  and  $\mu_{[DCA]}^*$ , are a function of both temperature and the mole fraction ( $\mu_{[TFSI]}^*$ ) of the anionic species. The anionic ligand chemical potential terms are now a function of both temperature (*T*) and mole fraction ( $x_i$ ) of the anionic species (*i*) as described by:

$$\mu_{TFSI}^* = \mu_{TFSI}^o + RTln(\gamma_{TFSI}x_{TFSI})$$

$$\mu_{DCA}^* = \mu_{DCA}^o + RTln(\gamma_{DCA}x_{DCA})$$
(S4)

Using the library of structures, that include the [DCA] and [TFSI] species, we vary the mole fractions of  $x_{TFSI}$  and  $x_{DCA}$  from 0.00 to 0.30 based on experimental observations into the composition of anionic liquids. The highest mole fractions of [TFSI] and [DCA] in

solution are approximately 0.25. At present, we do not consider the Li<sup>+</sup> mole fraction within the solution. The other components in solution would include Li<sup>+</sup> and the IL cation.



**Figure S7**. Activity coefficient ( $\gamma_{DCA}$  and  $\gamma_{TFSI}$ ) sensitivity analysis for *ab initio* thermodynamic analysis. Phase diagram for Li+ are computed as function of the mole fractions of [DCA] and [TFSI]. Color key: The purple region (1) = (Li<sup>+</sup>-[TFSI]<sub>2</sub>)<sup>-1</sup> and the orange region (2) = (Li<sup>+</sup>-[DCA]<sub>2</sub>)<sup>-1</sup>.

**Figure S7** shows the influence of activity coefficient sensitivity during *ab initio* thermodynamic analysis. Both [DCA] and [TFSI] activity coefficients ( $\gamma_{DCA}$  and  $\gamma_{TFSI}$ ) are varied from 0.5 to 2.0. Under all explored conditions activity coefficients, the phase diagrams show the (Li<sup>+</sup>-[DCA]<sub>2</sub>)<sup>-1</sup> dominates over (Li<sup>+</sup>-[TFSI]<sub>2</sub>)<sup>-1</sup> under the explored conditions. The sensitivity analysis further validates our assumption that activity coefficients of one can provide big picture conclusions about this system.

When comparing between anions with similar solvation (i.e. [CTFSI] and [CFSI] coordinating via the cyano group and [DCA]), a similar trend was noticed, where longer bonding distances resulted in lower dissociation energies, up until a CN of 4, where the dense packing of anions resulted in longer bonding distances for [DCA] even though it had higher dissociation energies.

**Table S4.** Calculated dissociation energies ( $E_D$ ) in units of eV in comparison to average bond length in unites of Å for all of the Li-solvate structures investigated in this study.

	[CTFSI]		[DCA]		[CFSI]	
# of Coordinating Anions	Average Li⁺-N bond length (Å)	E <sub>D</sub> (eV)	Average Li⁺-N bond length (Å)	E <sub>D</sub> (eV)	Average Li <sup>+</sup> -N bond length (Å)	E <sub>D</sub> (eV)
1	1.7650	5.729	1.7589	6.044	1.7672	5.676
2	1.8643	8.263	1.8557	8.719	1.8656	8.215
3	1.9792	7.621	1.9781	7.975	1.9784	7.590
4	2.1143	4.621	2.1369	4.696	2.1167	4.582