Supporting Information

A DFT Investigation on the Origins of Solvent-Dependent Polysulfide Reduction Mechanism in Rechargeable Li-S Batteries

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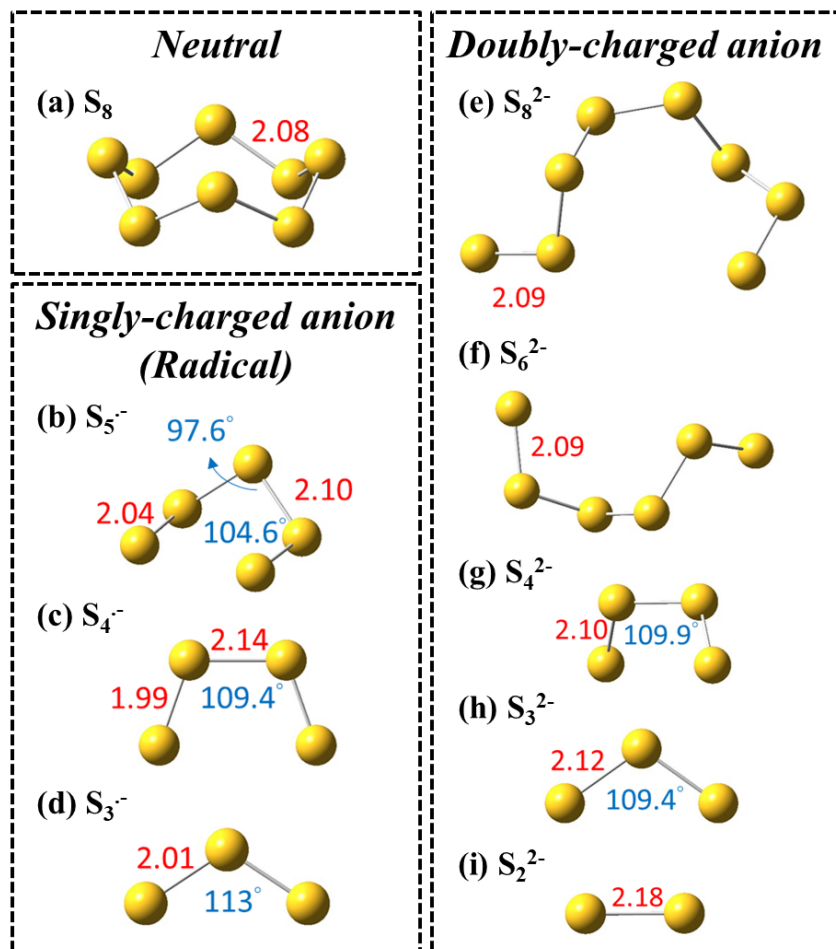Phone: (886)-2-77496219

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Figure S1. Optimized geometries of (a) neutral, (b-d) singly-charged, and (e-i) doubly-charged polysulfides in DMSO. The average bond lengths of S-S (d, in Å) and the bond angles (θ, in °) are labeled in red and blue, respectively.
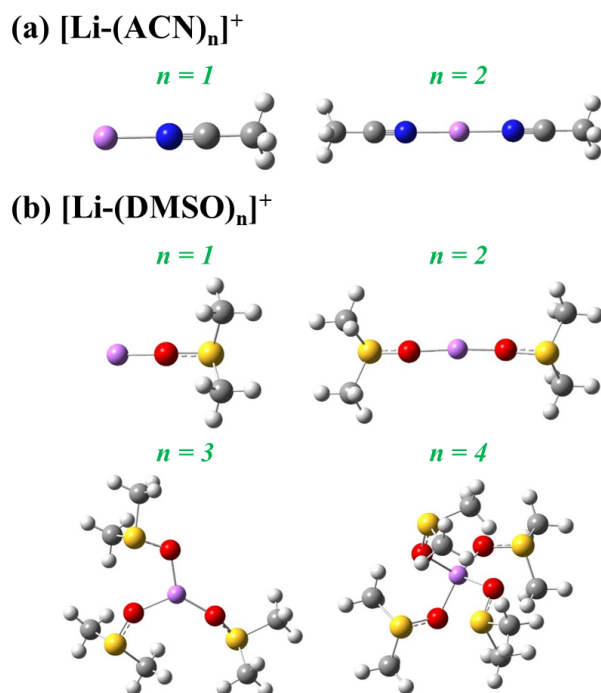
(a) [Li-(ACN)$_n$]$^+$

n = 1 *n = 2*

(b) [Li-(DMSO)$_n$]$^+$

n = 1 *n = 2*

n = 3 *n = 4*

Figure S2. Optimized geometries of (a) [Li-(ACN)$_n$]$^+$ and (b) [Li-(DMSO)$_n$]$^+$ clusters with different solvent coordination numbers (n). The colors of element S, Li, C, O, N and H are labeled in yellow, purple, gray, red, blue and white, respectively.

Table S1. Theoretical values and the reported experimental results of reduction potentials (ΔE, in V) of S$_8$, S$_8^{2-}$, and S$_3^{\bullet-}$ in different solvents.

ΔE (V)	S$_8$ + 2e$^-$ → S$_8^{2-}$		S$_8^{2-}$ + 2e$^-$ → 2S$_4^{2-}$		S$_3^{\bullet-}$ + e$^-$ → S$_3^{2-}$	
Solvent	Theo.	Exp.[a]	Theo.	Exp.[a]	Theo.	Exp.[a]
DIOX	1.07	-	0.31	-	-0.84	-
DOL:DME	2.14[b]	2.22	1.79[b]	1.98	1.19[b]	-
acetone	2.44	-	2.19	-	1.74	-
ACN	2.52	-	2.27	-	1.87	-
DMSO	2.54	2.70	2.30	2.29	1.92	2.10

[a] Reported results from ref 1. [b] We adopt the THF solvent model to simulate the mixed-solvent system DOL:DME that is actually used in the experiment.

References

[1]   Q. Zou and Y.-C. Lu *J Phys. Chem. Lett.* 7 (**2016**) 1518.