Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

ELECTRONIC SUPPLEMENTARY INFORMATION

Lithium polysulfide conformer analysis in ether-based solvents for Li-S batteries

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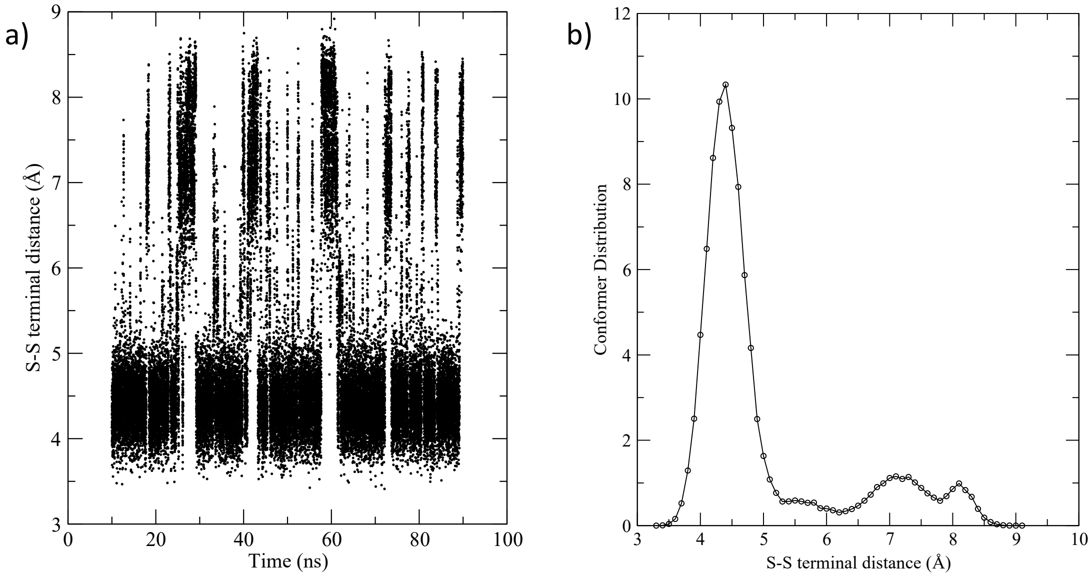

Figure S1. **(a)** Intramolecular S-S terminal distance variation through time obtained by the *gmx mindist* program and **(b)** the corresponding distribution curve obtained by the *gmx analyze* program.

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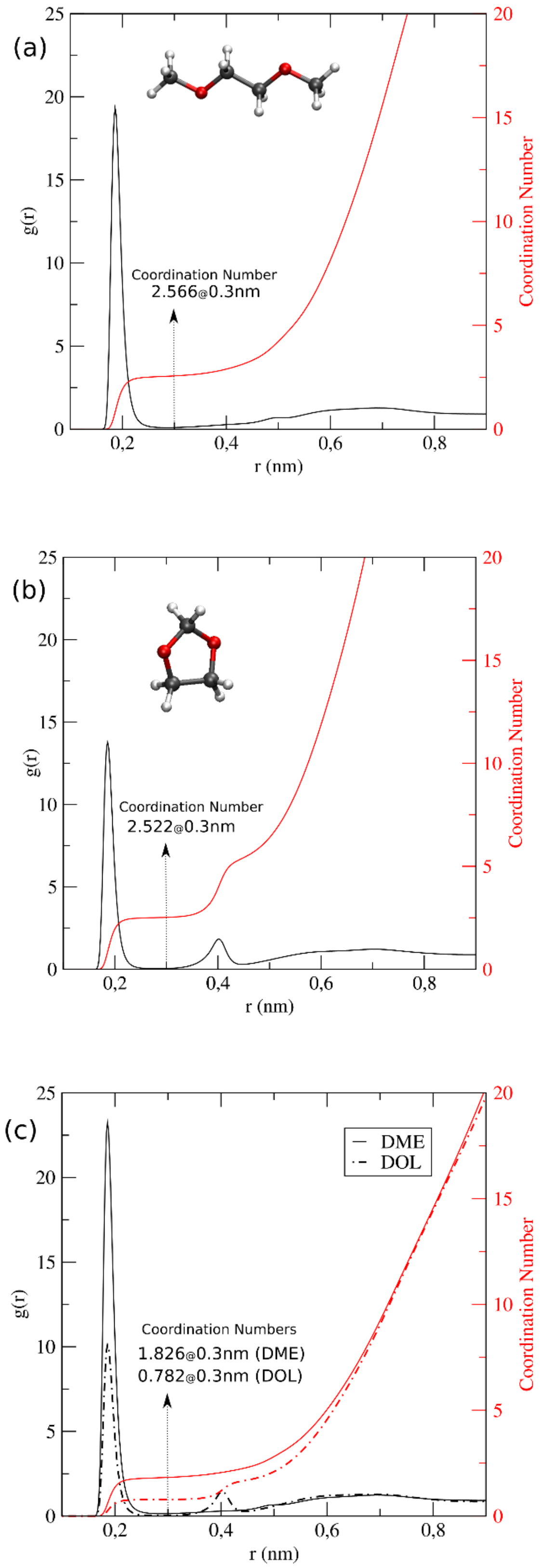

Figure S2. Radial distribution function g(r) (black curves, left y-axis) and coordination numbers (red curves, right y-axis) of the Li-O pairs for different electrolyte compositions, corresponding to Li_2S_6 0.5 M in **(a)** pure DME, **(b)** pure DOL and **(c)** DOL:DME equimolar.

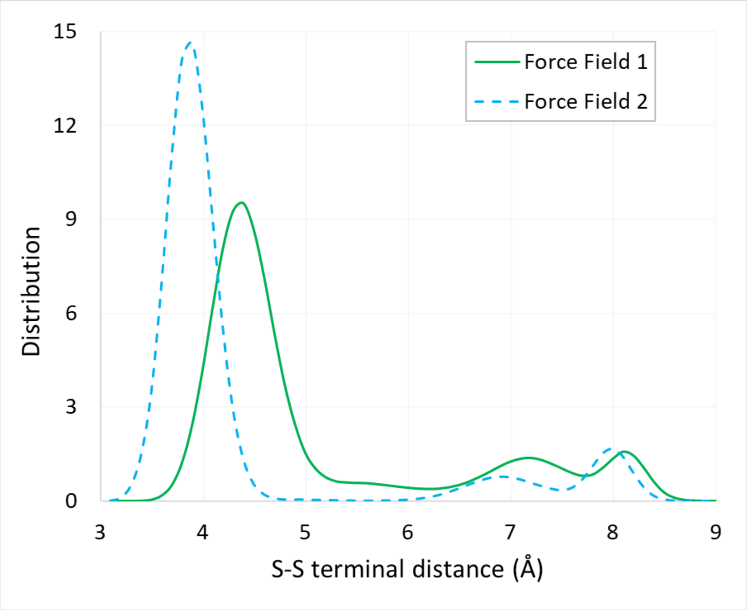

Figure S3. Distribution curves of the S-S terminal intramolecular distance for Li_2S_6 1M in DOL:DME equimolar, using two different force field parameters. The differences between LJ parameters are shown in the Tables below.

Table S1. Li^+ and S Parameters of Force Field 1 (reference[1])

Parameter	**Li^+**	**S (internal)**	**S (terminal)**
σ (nm)	0.1506	0.3590	0.3590
ε (kJ/mol)	0.6905	1.4393	1.4393
q (a.u.)	0.72	-0.1247	-0.4706

Table S1. Li^+ and S Parameters of Force Field 2 (reference [2])

Parameter	**Li^+**	**S (internal)**	**S (terminal)**
σ (nm)	0.1460	0.3563	0.3563
ε (kJ/mol)	0.7991	1.046	1.046
q (a.u.)	1	-0.1732	-0.6366

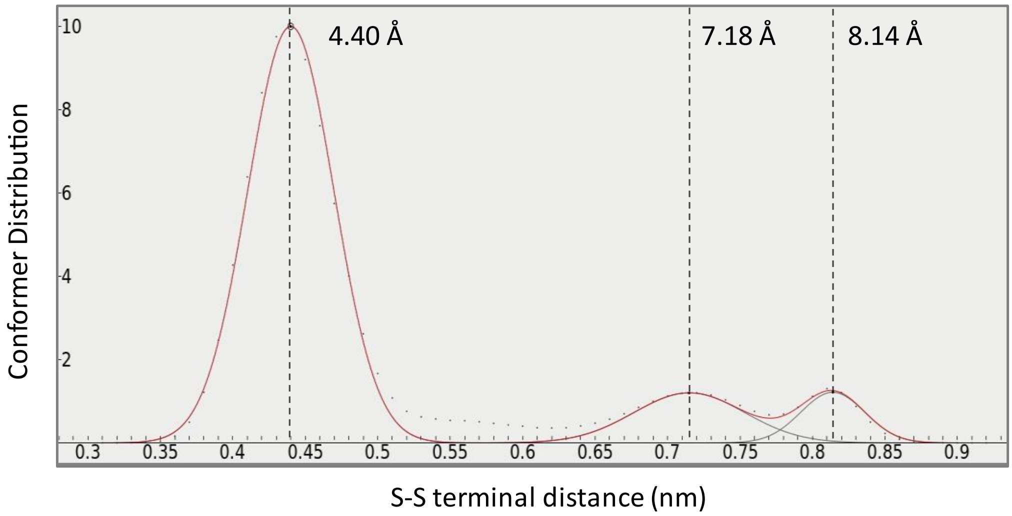

Figure S4. Fitted gaussian curves (in grey) on the three main peaks; the red curve is the sum of the three gaussians, the grey dots are the data points of the average distribution curve (0.5 M Li_2S_6, red curve of Fig 1a of the main article).

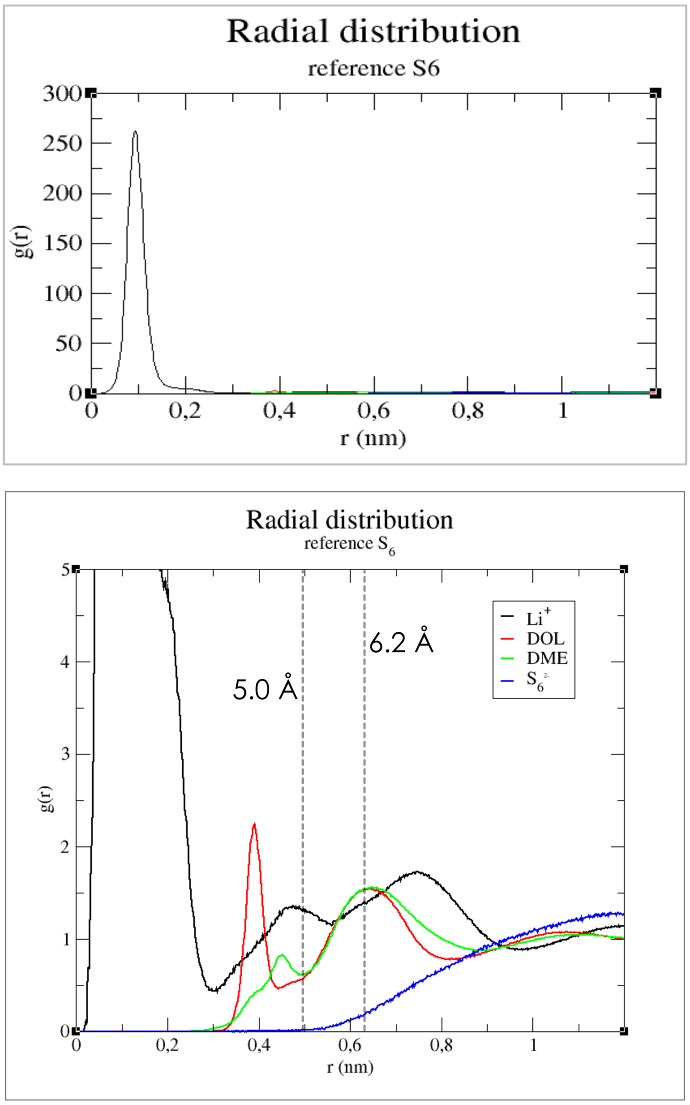

Figure S5. Radial distribution function between S_6^{2-} centre of mass and the corresponding ones of the electrolyte species reported in the figure legend. The cutoff tested are indicated by vertical dashed lines: using 5.0 Å was initially tested since it contains all the first minima of the rdf, frequently used to determine first coordination shell; however, the extracted clusters showed empty spaces around hexasulfide. Hence, a higher cutoff of 6.2 Å, falling on the second maximum of solvent molecules, was chosen as the cutoff.

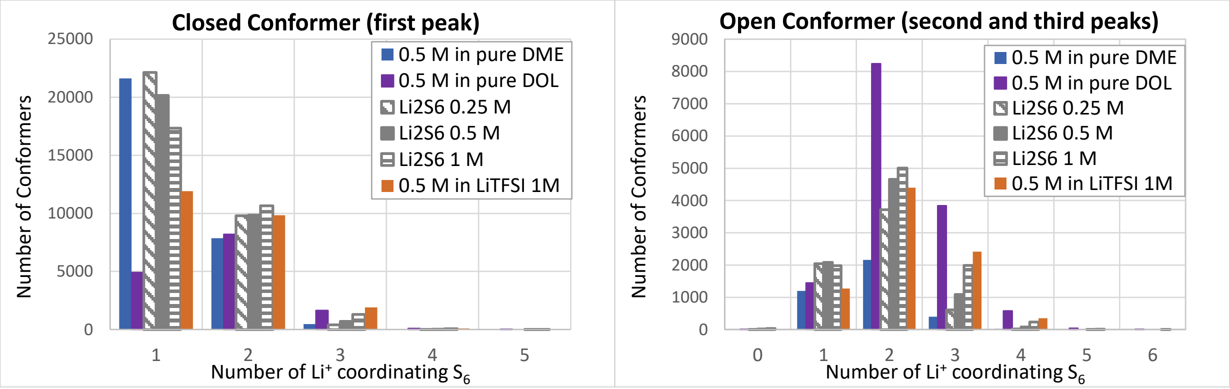

Figure S6. Histograms showing the Li$^+$ coordination number for the closed conformer (left, first peak of Figure 1 of the article) and the open conformer (right, second and third peaks of Figure 1 of the article).

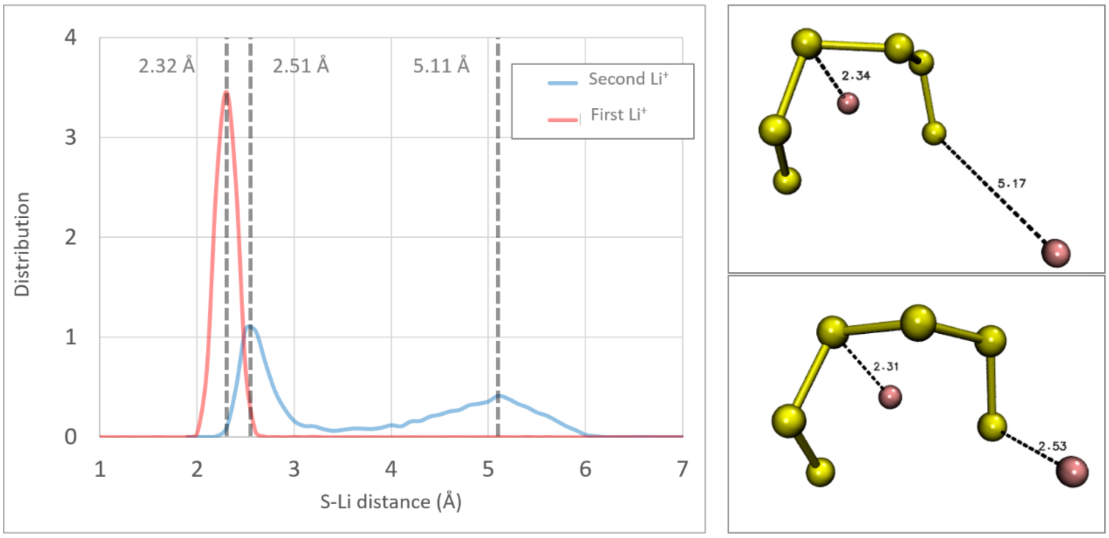

Figure S7. The distribution curves on the left indicate the minimum distance probability between Li^+ and any of the S atoms for the closed conformer with 2 Li^+ cations within 6.2 Å of the hexasulfide centre of mass. The representative conformers are shown on the right.

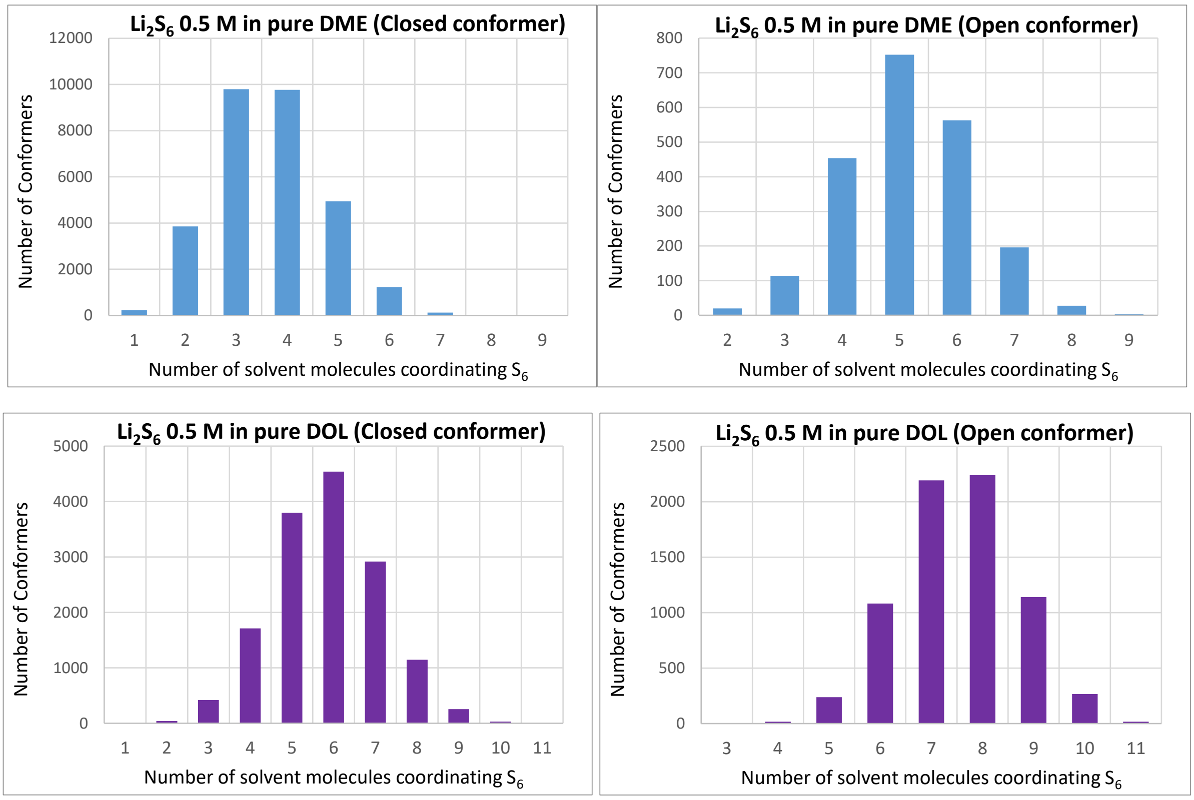

Figure S8. Histograms showing the number of conformers surrounded by solvent molecules, for the systems Li_2S_6 0.5 M in pure DME (upper panels) and in pure DOL (lower panels), for the closed conformer (left panels) and open conformer (right panels).

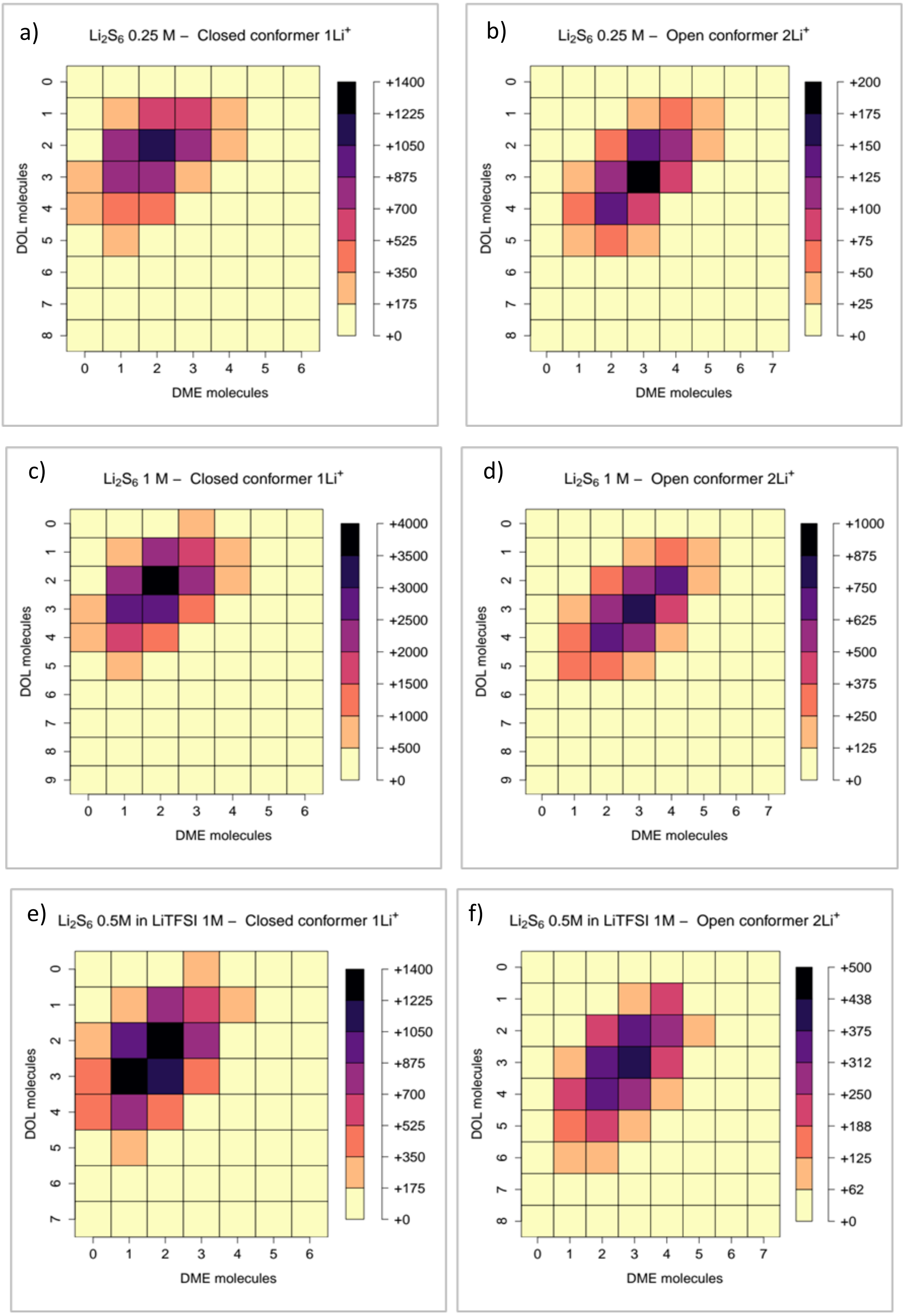

Figure S9. Heatmaps showing the amount of DOL and DME molecules around the hexasulfide for the electrolyte compositions of 0.25 M Li_2S_6,(**a** and **b**) 1 M Li_2S_6 (**c** and **d**) and 0.5 M Li_2S_6 + 1 M LiTFSI (**e** and **f**).

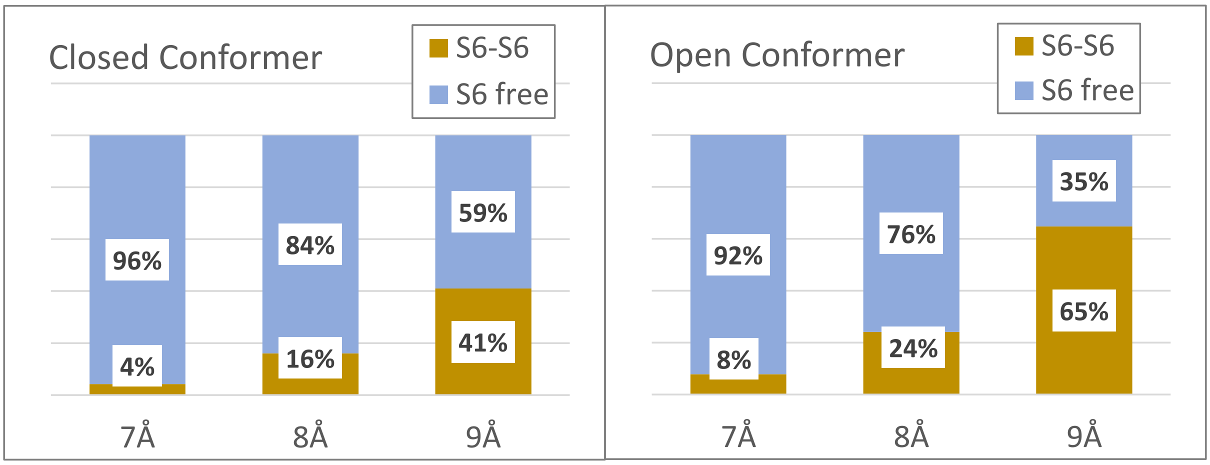

Figure S10. Fraction of S_6^{2-} anions with no other S_6^{2-} anions around it (“S6 free”, in light blue) within various cutoff compared to “S6-S6” pairs (in brown), for the closed conformer (left) and the open conformer (right).

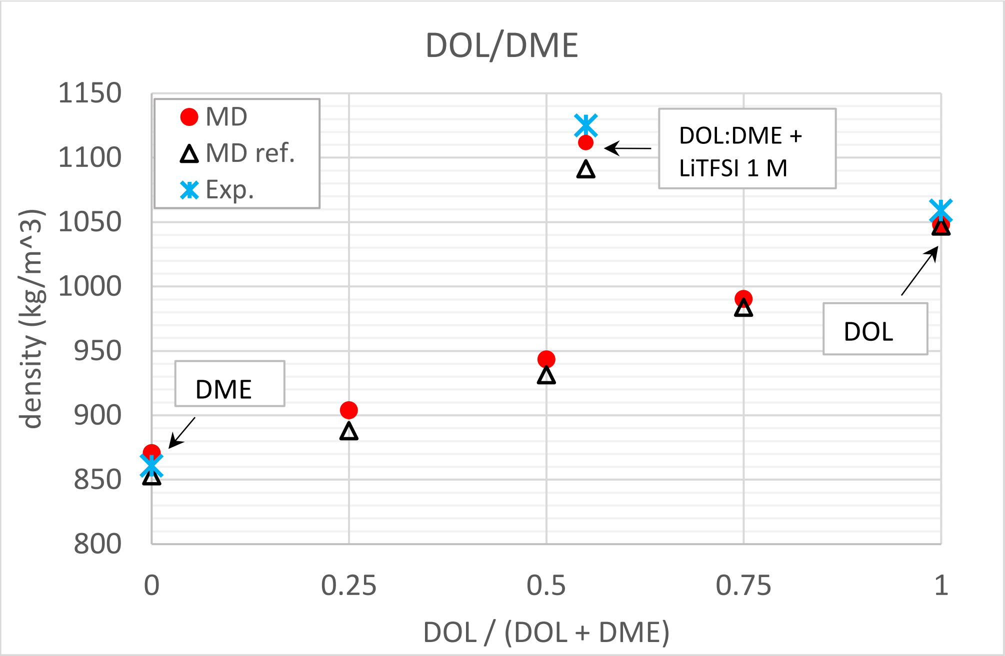

Figure S11. Density of the equilibrated simulation boxes of pure 1,2-dioxolane (DOL), pure dimethoxyethane (DME), DOL:DME mixtures of different molar fractions (MD, red points), and the "system IVb" of MD reference (MD ref., black triangles) and experimental data (Exp., blue stars) of Park et al.[1] containing LiTFSI 1M.

Table S3. Number of ions and molecules inside the simulation boxes according to the electrolyte composition. The initial cubic box length was set 1.5 times larger than those yielding the reference MD density of only solvent systems, according to the DOL:DME molar fraction (red points in figure S9).

System	Li^+	S_6^{2-}	DOL	DME	$TFSI^-$	Initial box length (nm)	Equilibrated box length (nm)	Equil. Box density (kg/m^3)
Li_2S_6 0.5 M pure DME	130	65	-	1500	-	9.6	6.42	933.678
Li_2S_6 0.5 M pure DOL	130	65	1500	-	-	8.4	5.69	1123.27
Li_2S_6 0.25 M	64	32	750	750	-	9.0	6.04	977.807
Li_2S_6 0. 5 M	130	65	750	750	-	9.0	6.07	1013.95
Li_2S_6 1 M	260	130	750	750	-	9.0	6.14	1074
Li_2S_6 0.5 M + LiTFSI 1 M	260	65	750	750	130	9.0	6.29	1154.71

References

(1) Park, C.; Kanduč, M.; Chudoba, R.; Ronneburg, A.; Risse, S.; Ballauff, M.; Dzubiella, J. Molecular Simulations of Electrolyte Structure and Dynamics in Lithium–Sulfur Battery Solvents. *J. Power Sources* **2018**, *373* (October 2017), 70–78. https://doi.org/10.1016/j.jpowsour.2017.10.081.

(2) Rajput, N. N.; Murugesan, V.; Shin, Y.; Han, K. S.; Lau, K. C.; Chen, J.; Liu, J.; Curtiss, L. A.; Mueller, K. T.; Persson, K. A. Elucidating the Solvation Structure and Dynamics of Lithium Polysulfides Resulting from Competitive Salt and Solvent Interactions. *Chem. Mater.* **2017**, *29* (8), 3375–3379. https://doi.org/10.1021/acs.chemmater.7b00068.