Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary information

Insight on lithium polysulfide intermediates in Li/S battery by density functional theory

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Table S1 Distances of all S-S bonds in lithium polysulfides after optimization in DOL solvent, and the distance unit is Å.

DOL	S^1-S^2	S^2-S^3	S^3-S^4	S^4-S^5	S^5-S^6	S^6-S^7	S^7-S^8
Li_2S_2	2.20189	-	-	-	-	-	-
Li_2S_3	2.14693	2.12456	-	-	-	-	-
Li_2S_4	2.12243	2.10735	2.12132	-	-	-	-
Li_2S_5	2.10766	2.12658	2.11271	2.10400	-	-	-
Li_2S_6	2.10135	2.12399	2.14055	2.10063	2.08735	-	-
Li_2S_7	2.09159	2.09946	2.13469	2.12781	2.11365	2.08695	-
Li_2S_8	2.08069	2.09840	2.15181	2.09993	2.14279	2.11088	2.08087

Table S2 Distances of all S-S bonds in lithium polysulfides after optimization in DME solvent, and the distance unit is Å.

DME	S^1-S^2	S^2-S^3	S^3-S^4	S^4-S^5	S^5-S^6	S^6-S^7	S^7-S^8
Li_2S_2	2.21815	-	-	-	-	-	-
Li_2S_3	2.17060	2.12733	-	-	-	-	-
Li_2S_4	2.10845	2.16787	2.10845	-	-	-	-
Li_2S_5	2.13036	2.10508	2.10587	2.12093	-	-	-
Li_2S_6	2.10600	2.09059	2.13978	2.09059	2.10601	-	-
Li_2S_7	2.10778	2.09207	2.11718	2.12543	2.09536	2.09715	-
Li_2S_8	2.09488	2.08775	2.14047	2.09418	2.14003	2.08737	2.09505

Table S3 The energy of polysulfide ions, lithium ions, lithium polysulfides and binding energy between polysulfide ions and lithium ions in DOL solvation.

	S_n^{2-} （Ha）	$2Li^+$ (Ha)	Li_2S_n (Ha)	Binding energy(Ha)	Binding energy(Kcal/mol)
Li_2S	-398.065	-14.452	-413.340	0.823	516.455
Li_2S_2	-796.354	-14.450	-811.599	0.795	498.686
Li_2S_3	-1194.636	-14.477	-1209.814	0.701	439.887
Li_2S_4	-1592.904	-14.490	-1608.041	0.648	406.340
Li_2S_5	-1991.155	-14.486	-2006.275	0.633	397.381
Li_2S_6	-2389.406	-14.496	-2404.507	0.605	379.752
Li_2S_7	-2787.643	-14.488	-2802.736	0.605	379.540
Li_2S_8	-3185.881	-14.489	-3200.965	0.595	373.480

Table S4 The energy of polysulfide ions, lithium ions, lithium polysulfides and binding energy between polysulfide ions and lithium ions in DME solvation.

	S_n^{2-} （Ha）	$2Li^+$ (Ha)	Li_2S_n (Ha)	Binding energy(Ha)	Binding energy(Kcal/mol)
Li_2S	-398.065	-14.448	-413.346	0.833	522.806
Li_2S_2	-796.354	-14.441	-811.612	0.817	512.617
Li_2S_3	-1194.635	-14.437	-1209.854	0.782	490.810
Li_2S_4	-1592.900	-14.448	-1608.085	0.738	462.799
Li_2S_5	-1991.138	-14.399	-2006.339	0.802	503.175
Li_2S_6	-2389.391	-14.404	-2404.574	0.779	488.801
Li_2S_7	-2787.632	-14.405	-2802.801	0.765	479.996
Li_2S_8	-3185.873	-14.413	-3201.030	0.745	467.472

Table S5 The binding energies between polysulfide ions and lithium ions in DOL solvation, the energy is corrected by Basis Set Superposition Error (BSSE). The unit is kcal/mol.

DOL	Li_2S	Li_2S_2	Li_2S_3	Li_2S_4	Li_2S_5	Li_2S_6	Li_2S_7	Li_2S_8
BSSE	0.99084	1.34426	1.14259	1.03896	1.0484	1.0857	1.11414	1.15713
Binding energy	515.464	497.342	438.744	405.301	396.333	378.666	378.426	372.323

Table S6 The binding energies between polysulfide ions and lithium ions in DME solvation, the energy is corrected by BSSE. The unit is kcal/mol.

DME	Li_2S	Li_2S_2	Li_2S_3	Li_2S_4	Li_2S_5	Li_2S_6	Li_2S_7	Li_2S_8
BSSE	1.04462	1.42934	1.43523	1.53625	1.53208	1.40446	1.54225	1.53783
Binding energy	521.761	511.188	489.375	461.263	501.643	487.397	478.454	465.934

Table S7 Distances of Li-S bonds after optimization in DOL and DME, respectively; and the distance unit is Å.

	DOL		DME	
Li_2S	2.25753	2.25832	2.17529	2.17529
Li_2S_2	2.39106	2.39301	2.32978	2.33183
Li_2S_3	2.35952	2.38079	2.34182	2.41264
Li_2S_4	2.36824	2.37939	2.40977	2.40985
Li_2S_5	2.39378	2.38893	2.48436	2.52353
Li_2S_6	2.38463	2.37727	2.48595	2.48556
Li_2S_7	2.40748	2.39998	2.49301	2.48415
Li_2S_8	2.40267	2.40697	2.50133	2.50186

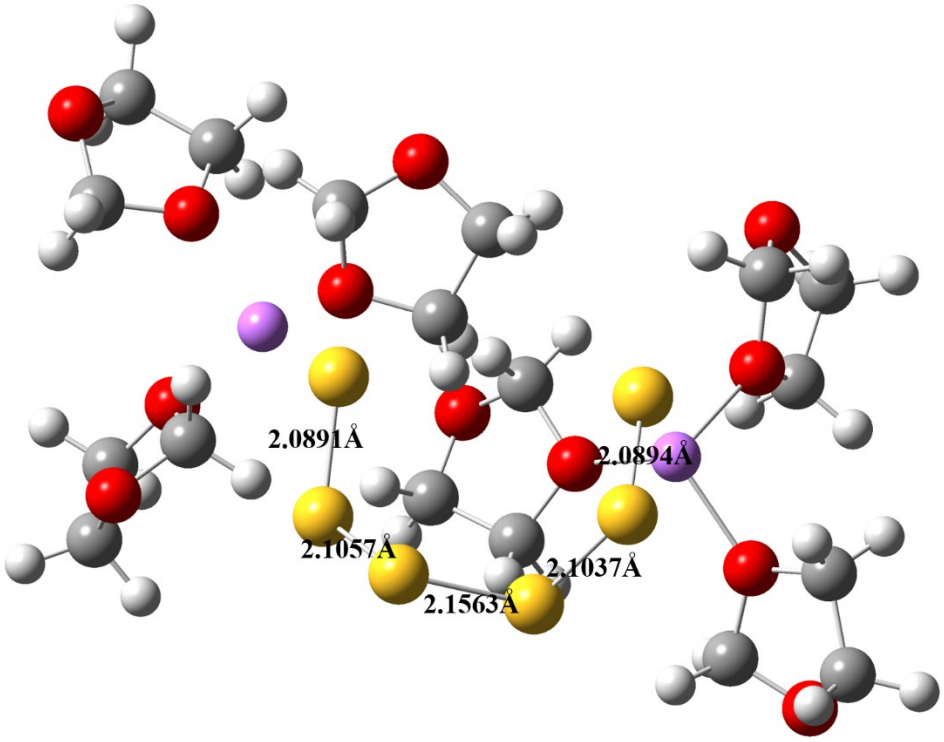

Fig. S1 The solvation structure of Li_2S_6 which is surrounded by six DOL molecules. The outer solvation shells are also considered by using the polarized continuum model in DOL solvent (dielectric constant of 7.1). Dark gray, white, red, yellow and violet spheres denote C, H, O, S and Li atoms/ions, respectively.

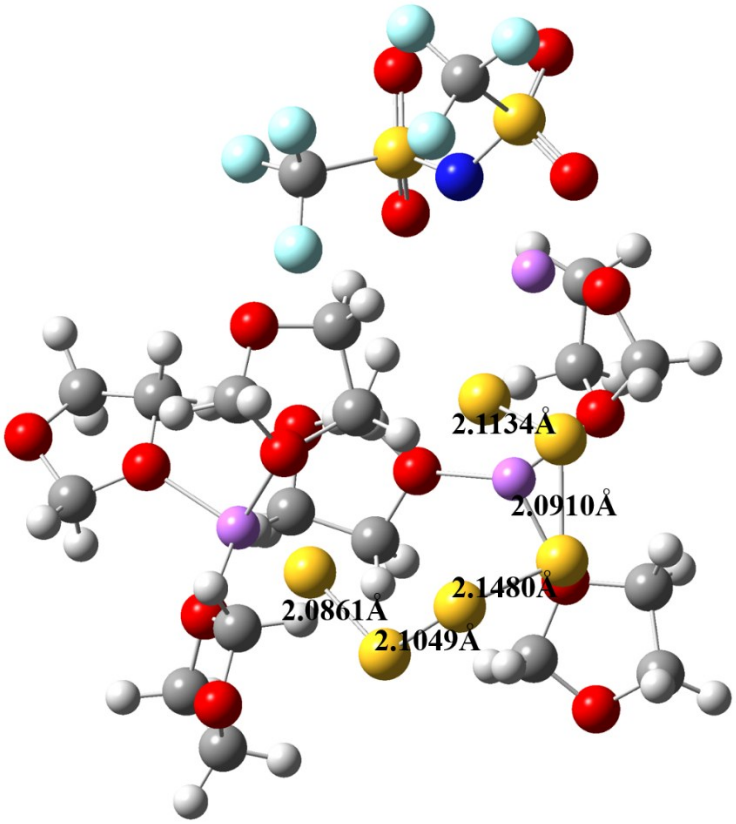

Fig. S2 The solvation structure of Li_2S_6 which is surrounded by six DOL molecules and one LiTFSI molecule. Dark gray, white, red, yellow, violet, light blue and dark blue spheres denote C, H, O, S, Li, F and N atoms/ions, respectively.

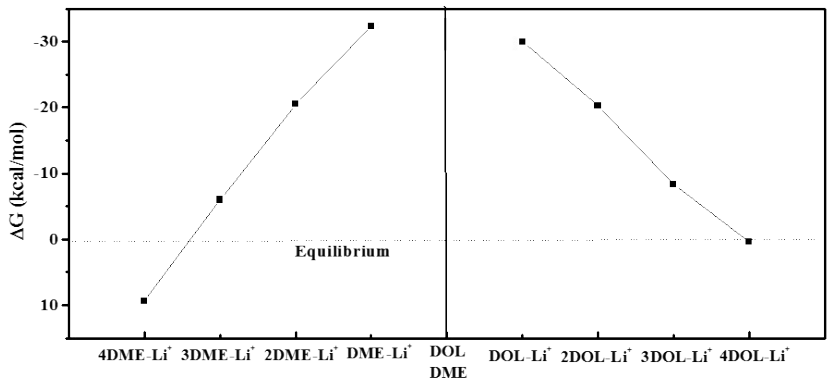

Fig.S3 The curve of Gibbs free energy (△G) of Li^+ solvation with DOL/DME molecule as solvent number changes by DFT calculation.

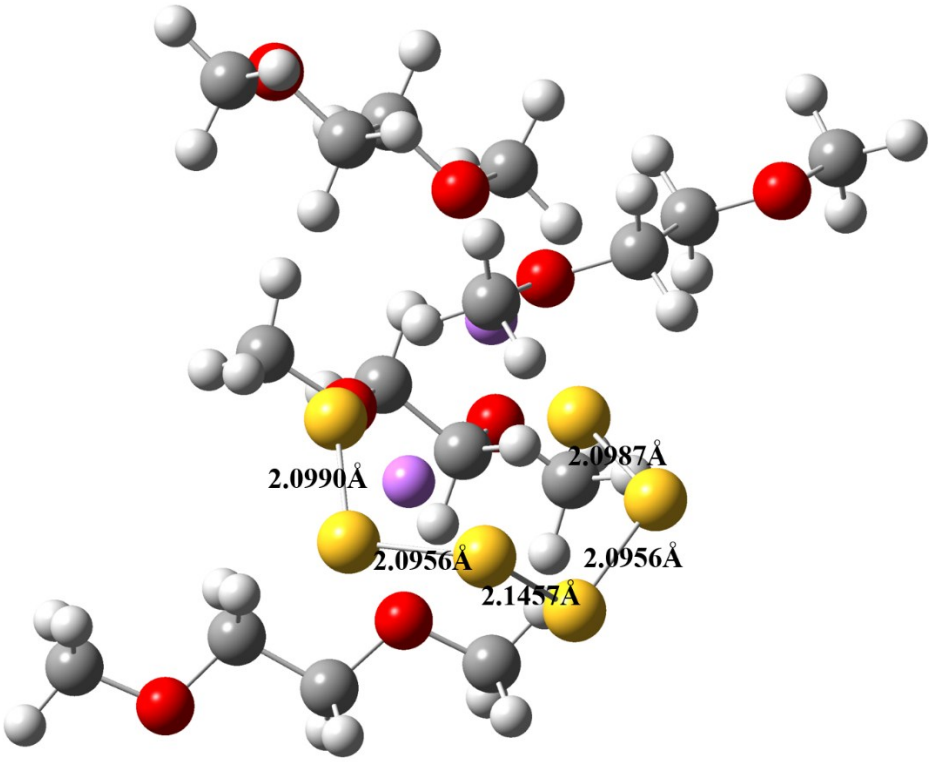

Fig. S4 The solvation structure of Li_2S_6 which is surrounded by for DME molecules. The outer solvation shells are also considered by using the polarized continuum model in DME solvent (dielectric constant of 7.2). Dark gray, white, red, yellow and violet spheres denote C, H, O, S and Li atoms/ions, respectively.

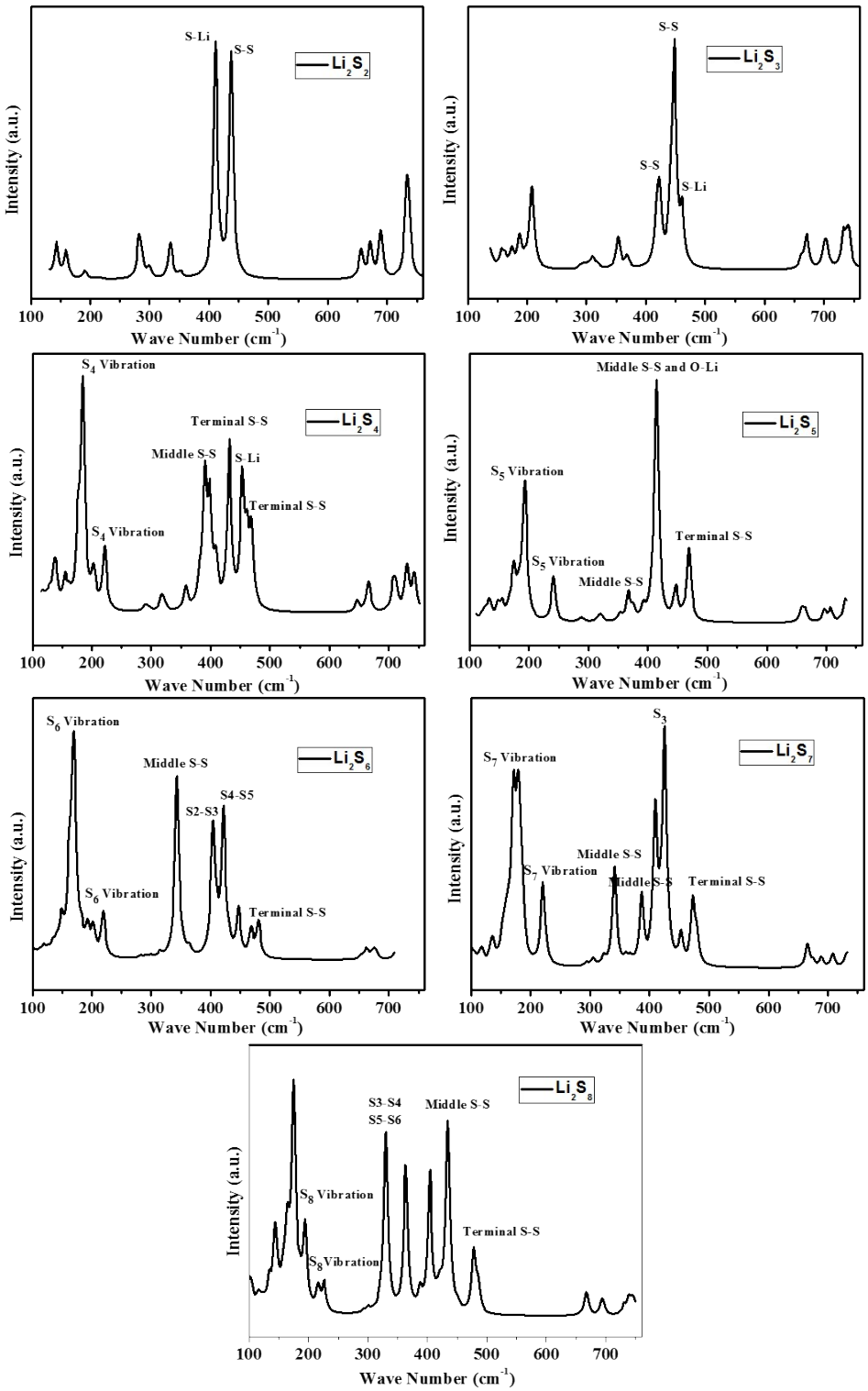

Fig. S5 The calculated Raman spectroscopy of lithium polysulfides in DOL solvation structure.