Interaction Mechanisms between Lithium Polysulfides/Sulfide and Small Organic Molecules

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ABSTRACT: Lithium polysulfides (LiPSs)/sulfide are essential in secondary lithium batteries. In this work, we used density functional theory computational methods to obtain the law of constraining lithium polysulfides/sulfide by the affinitive interactions at the electronic level. The proton transfer, the orientation of polysulfides, the electron affinity, and the acid dissociation constant of small organic molecules were examined to elucidate the lithium polysulfides/sulfide binding mechanism with functional groups. The carboxyl groups exhibited a strong ability to dissolve the low-order polysulfides via proton transfer, although this type of group is highly unstable. In comparison, 1,2-diaminopropane with adjacent amino groups can strongly anchor the high-order polysulfides. The electrostatic attractions between lithium-ion and the electron-rich groups and their number and location dominated the binding energetics. Also, the entropy contribution to the binding should be considered. The information gained from these results can serve as a criterion for the selection of co-solvent for the electrolyte or postmodified functional groups for decorating the cathode in the lithium−sulfur system.
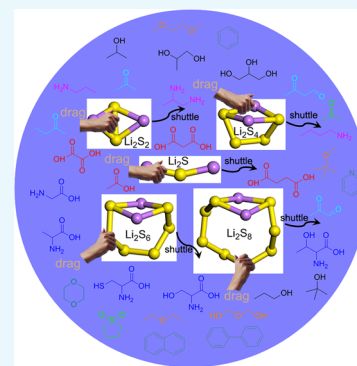
1. INTRODUCTION

Lithium−sulfur chemistry has drawn significant attention among various types of secondary batteries mainly due to its conspicuous merits by delivering a theoretical gravimetric energy density of 2600 Wh kg⁻¹ applied in Li−S batteries.[1,2] Currently, lithium−sulfur chemistry faces critical challenges in controlling the conversion reaction between elemental sulfur and lithium sulfide and the shuttling of lithium polysulfides (LiPSs), impeding the practical applicability of Li−S batteries.[3−5]

Enormous efforts were devoted to investigating lithium polysulfides, which can diffuse into the organic electrolyte and cause an undesired "shuttle effect", weakening the performance of Li−S-based batteries.[6−13] Although the Li−S phase diagram cannot provide proof for the existence of lithium polysulfides (Li_2S_x, $4 \leq x \leq 8$),[14] direct observation of lithium polysulfides in liquid electrolytes has already been achieved.[15] This inconsistency may indicate that the intermediates of lithium polysulfides can be stabilized by the solvent molecules. Considering the soluble nature of lithium polysulfides, their interactions with solvent molecules can directly influence the structural stability and the mass shuttle between the cathode and the anode. On the other hand, the shortest lithium polysulfides (Li_2S_2/Li_2S) as the reduction products are insoluble and prefer to wrap the active S materials by forming a passivation layer. Removing the Li_2S and Li_2S_2 on the cathode of the Li−S battery is helpful to recover the electrochemical reactions and the capacity.[16−18] To solve both issues of the Li_2S_2/Li_2S passivation layer and the shuttle effect of lithium polysulfides, the standard electrolyte (1M LiTFSI in dioxolane/dimethoxyethane with 0.2 M LiNO₃) is required to be modified by adding other solvents to form a co-solvent system.[19−22] Furthermore, the specified functional groups were grafted on the cathode of Li−S batteries to anchor lithium polysulfides.[7] Various functional groups of polymer and deoxynucleotides were employed to anchor lithium poly-sulfides, where multiforces (electrostatic attraction, hydrogen bonding, and others) can contribute to their binding properties.[8,23] Moreover, the molecules consisting of many functional groups, such as chitosan grafted with the catecholic moiety, can efficiently drag the lithium polysulfides.[24] However, it is unclear which type of groups or forces contributes to the affinitive interaction between polysulfides/sulfide and the substrate.

Considering the aspects mentioned above, in the present paper, we investigated the binding of lithium polysulfide/sulfide with small organic molecules, based on the electronic level calculations. The proton transfer, electron affinity, acidic dissociation of the organic molecules, and the orientation of polysulfides were examined in depth to uncover the binding strength between lithium polysulfide/sulfide and the functional groups. Both molecular orbitals and electron density distributions were used to understand the nature of anchoring lithium polysulfide/sulfide structures.

2. RESULTS AND DISCUSSION

The geometrical optimization of lithium polysulfides showed that the structures of Li_2S and Li_2S_2 were symmetrical, while Li_2S_4, Li_2S_6, and Li_2S_8 were deviations from the symmetric structures (Figure 1a). The highest occupied molecular orbital
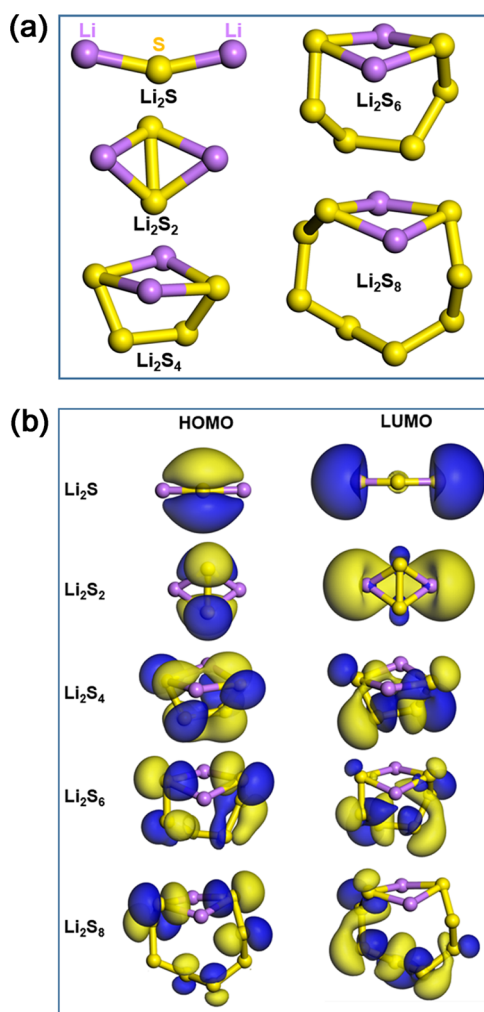

Figure 1. (a) Optimized structures and (b) molecular orbitals of lithium polysulfides (Li_2S_x, where x = 1, 2, 4, 6, 8). The blue and yellow indicate positive and negative regions, respectively.

(HOMO) and the lowest unoccupied molecular orbital (LUMO) were localized on S atoms and Li atoms of the symmetrical lithium polysulfides (Li_2S and Li_2S_2), respectively (Figure 1b), indicating that Li was more likely to withdraw electrons and S preferred to donate an electron, following the reported results.[8] However, the HOMO and LUMO of high-order polysulfides (Li_2S_4, Li_2S_6, and Li_2S_8) were almost localized on the S atoms, which weakened the charge transfer ability of Li atoms. It should be noted that Li_2S_3 is not presented in the current study, due to its stability dependence on high-dielectric solvents. The commonly used dimethoxy-ethane (DME) and dioxolane (DOL) solvents in Li−S batteries have low dielectric constants, which limited the presence of Li_2S_3.[25,26]

The polysulfides' calculated binding energies could also reflect the different abilities of charge transfer in Li_2S_x to small molecules (Figures S1−S3), including dimethoxyethane (DME) and dioxolane (DOL) as the most commonly used

solvents for Li−S batteries. We found that the interactions between single DME or DOL molecule and polysulfides were not outstanding (Figures S2 and S5). The synergic performance among many DME or DOL molecules should be considered in a practical system. Here, we focused on the nature of the polysulfides−solvent intermolecular interactions via employing the single-molecule model. Figure 2a shows the representative results derived from lithium polysulfides' interaction with different organic molecules. The strength of binding energy between Li_2S (or Li_2S_2) and small molecules mainly depended on the functional groups of the organic molecules. The binding become weaker following the sequence of oxalic acid (two carboxyl groups), alanine (one amino and one carboxyl group), 1,2-diaminopropane (two amino groups), glycerin (three hydroxyl groups), methyl *tert*-butyl ether (MTBE), and sulfone (Figure 2a). As the S content increased, the carboxyl groups' interactions with polysulfides rapidly decreased, and 1,2-diaminopropane with two amino groups became the structure with the strongest binding with the high-order polysulfides. The contribution of entropy in the binding between polysulfides and small organic molecules was included in the computation of free energies (Figure 2b). The free energies follow the variation trend of the total energies, except that the glycerin molecule exhibits stronger binding with polysulfides. This can be attributed to the configuration distortion of lithium polysulfides after binding with the glycerin molecule (Figure S4).

The binding of low-order polysulfides with the organic molecules was also sensitive to the pK_a value, which is the negative base-10 logarithm of the acid dissociation constant (K_a). Although the available experimental dissociation constants were obtained in water, instead of in an organic electrolyte of Li−S batter, their association with the computed binding energies is still instructive. The lower the pK_a value of the organic molecules, the stronger the binding energies interacting with Li_2S (Figure 3). A small pK_a value means high acidity of the organic molecules, making it easy to drive the proton transfer from the −COOH group to the S atoms of Li_2S or Li_2S_2 (upper part of Figure 4). The carboxyl group becomes more electronegative after the proton transfer, causing a strong attraction to the Li atoms in low-order polysulfides. The proton transfer was also observed in the Li-ion batteries, where the Li salt received the proton and then caused oxidation instability of solvent molecules.[28] The carboxyl molecule with an active proton was highly unstable with a lithium anode but with a potential to dissolve the Li_2S precipitation as a passive layer on the S cathode of Li−S batteries.

In addition to the proton transfer, the functional groups' electron affinity is an essential factor influencing the binding energies between polysulfide and organic molecules. Amino, hydroxyl, and ether groups (electron donors) mainly donate electrons to Li atoms with a low electron density and then form strong binding with polysulfides by their electron-donation ability. This law is consistent with the reported data, employing the polymer's substrate, deoxynucleotides, or chitosan grafted with the catecholic moiety.[8,23,24] While the same affinity (electron-withdrawing) can be found, the interactions between the sulfone and the Li atoms of polysulfides should be electrostatic repulsion. Still, the sulfone group preferred to interact with the Li atoms instead of S atoms of polysulfides (lower part of Figure 4). Although the overall sulfone group was electropositive, the O atoms' local
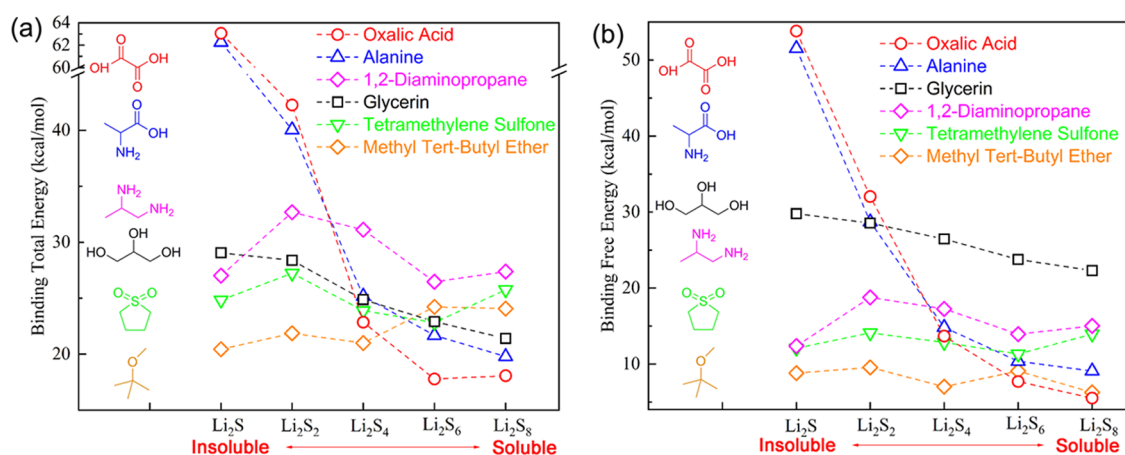
Figure 2. (a) Binding total energies (0 K) and (b) free energies (298.15 K) of different lithium polysulfides (Li_2S_x, x = 1, 2, 4, 6, 8) to small organic molecules.
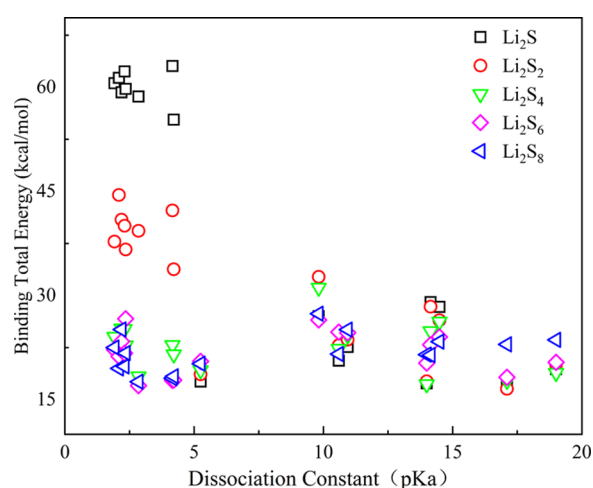

Figure 3. Available experimental dissociation constants of different organic molecules (standard condition: in water, 20−25 °C)[27] associated with the computed binding energies.

electron density was higher than that on the S atom of the sulfone group (Figure S5). Thus, the Li−S−Li angle of Li_2S shrinks from 156 to 98°, interacting with the two O atom branches of the sulfone group (Figure 4). The reported experimental results show that the addition of sulfone as a co-solvent in Li−S battery has outstanding cyclic performance and rate capability,[20] where the contribution of the affinitive interactions between the sulfone group and lithium poly-sulfides/sulfide should not be ignored.

Targeting the strong-electronegativity amino groups of 1,2-diaminopropane, only one Li atom in high-order polysulfides (Li_2S_x, x > 2) interacted with the amino group (Figure 5). Especially in Li_2S_4, the Li atom resided in the two amino groups' middle site and then exhibited the strongest binding. Although only one Li−amino interaction existed in Li_2S_6 and Li_2S_8, the high binding energy was attributed to the hydrogen-bond interactions between S atoms and the 1,2-diaminopropane molecule.[8] Two types of hydrogen bonds should contribute to anchoring Li_2S_6 or Li_2S_8 by the 1,2-diaminopropane molecule. The $S_6^{2−}$ or $S_8^{2−}$ anion can access
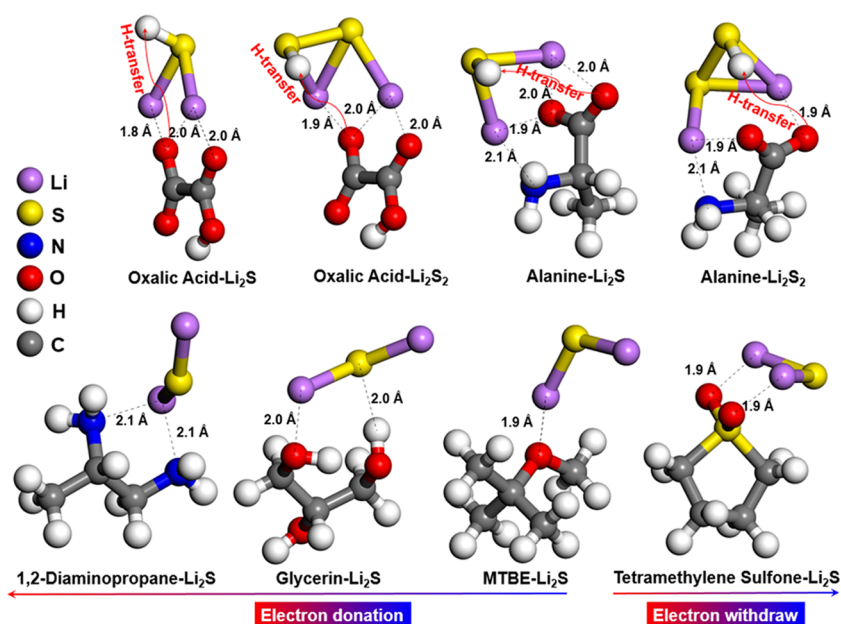

Figure 4. Optimized geometries of low-order polysulfides' interaction with different organic molecules (MTBE refers to methyl *tert*-butyl ether).
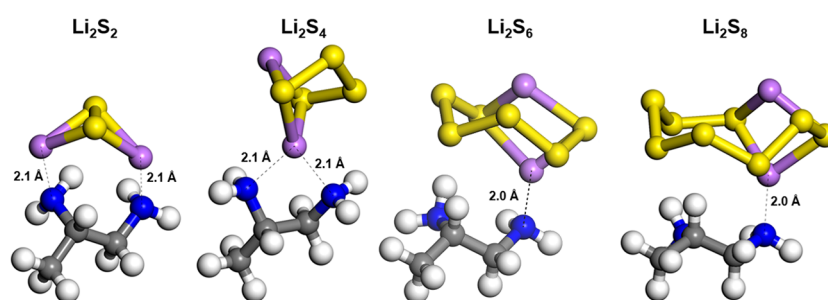
Figure 5. Optimized geometries of the 1,2-diaminopropane molecular interaction with different lithium polysulfides (Li_2S_x, x = 2, 4, 6, 8).

the amino groups to form hydrogen bonds (S······H−N) with a bond length and angle of 2.8 Å and 140°, respectively, except that the S_6^{2-} or S_8^{2-} anion also forms a longer hydrogen bond with the −CH groups on the 1,2-diaminopropane molecule, which gives rise to excessive stabilization of the binding structures.

Figure 6 shows the horizontal and vertical orientations of Li_2S_8 interacting with different organic molecules. Strong
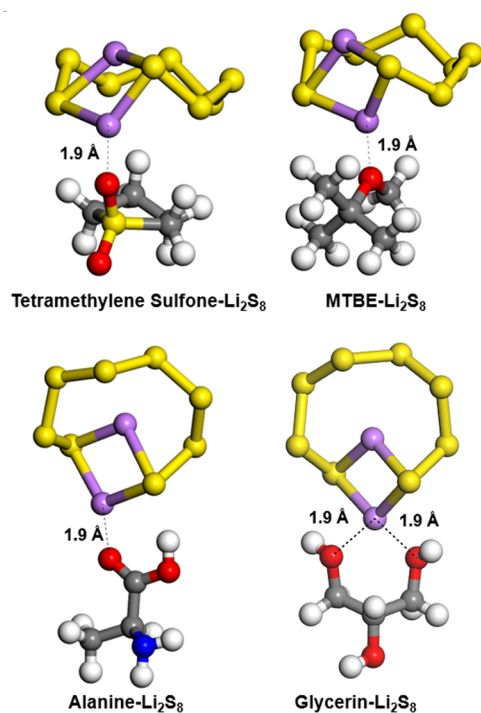

Figure 6. Optimized geometries of the high-order polysulfide (Li_2S_8) interaction with different solvent molecules.

bindings (1,2-diaminopropane and MTBE) corresponded to the horizontal Li_2S_8, while weak bindings reduced the constrain of polysulfides, and then the vertical Li_2S_8 was observed (alanine, oxalic acid, and glycerin). One exception was tetramethylene sulfone, where the horizontal Li_2S_8 was due to the two molecules' ring−ring interaction.

The differences in electron density patterns further uncovered the electrostatic interactions between polysulfide and small molecules (Figure 7). The = O in the carboxyl group was the electron-rich domain (red), the −OH in the carboxyl group showed a relatively narrow electron-rich area, and the H atom in −OH was electron-lean (blue). Once the proton in −OH was transferred from the carboxyl group to Li_2S, two
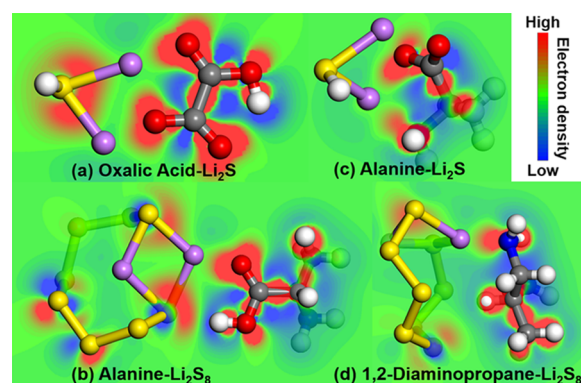

Figure 7. Differences in electron densities of Li_2S-based (Li_2S_8) solvent molecules. The densities were obtained by subtracting the density of the isolated atoms from the total density.

strong electronegative O atoms were left, and then the Li^+ preferred to form strong bonding with them, following the Lewis acid−base theory (Figure 7a). Comparatively, no proton transfer was observed in the case of the alanine−Li_2S_8 interaction (Figure 7b), and it showed weak bonding between one Li^+ and = O of the carboxyl group. Besides the proton transfer, the strongly electronegative amino group exhibited a pure character of electron-rich properties and then relatively excellent binding with both low- and high-order polysulfides (Figure 7c,d).

In addition, the number and the location of functional groups influence their binding with lithium polysulfides (Li_2S_x, x = 1, 2, 4, 6, 8) (Figure 8). Two amino or hydroxyl groups exhibit stronger binding with lithium polysulfides/sulfide than one isolated group and, especially, the strongest binding with two adjacent groups. However, compared to the number of groups, the ether's location dominates more in their binding. Thus, while decorating the electrolyte or the cathode of Li−S batteries, the distribution and the number of functional groups should be considered.

Strong binding with lithium polysulfides is one promising property of the functional groups. The attractive co-solvent as electrolyte also requires high permittivity, high viscosity, etc. Decorating the electrolyte in real systems is actually a complicated process, which requires the combination of multiphysical and -chemical properties. This study shed light on how to choose the proper organic molecules to anchor lithium polysulfides/sulfide. More research work on choosing high-performance electrolytes will be performed later.

3. CONCLUSIONS

In this work, the interactions between polysulfides and several types of organic molecules with different functional groups
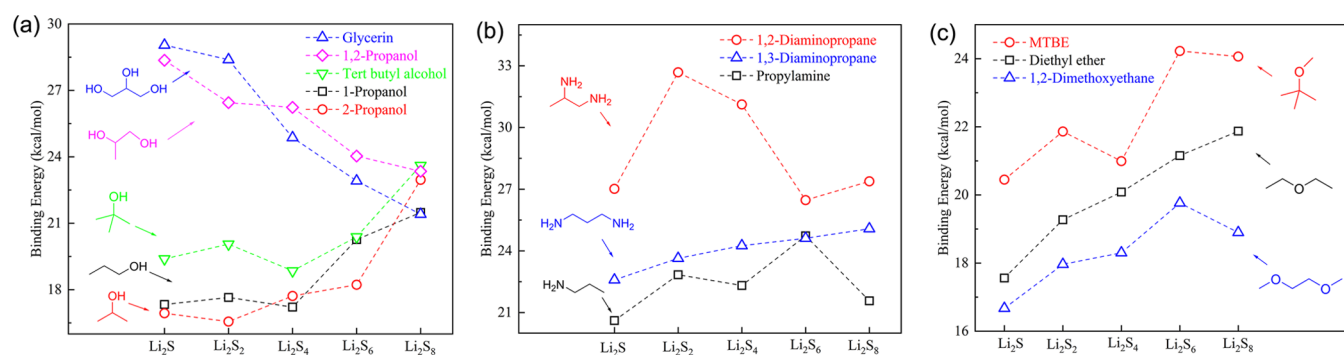
Figure 8. Binding energies of (a) hydroxyl groups, (b) amino groups, and (c) ether groups to different lithium polysulfides (Li_2S_x, $x = 1, 2, 4, 6, 8$).

were investigated by density functional theory (DFT) calculations. The low-order polysulfides (Li_2S_x, $x \leq 2$) exhibited strong bindings with the carboxyl molecules. It was also found that the proton could be transferred from the carboxyl group to the sulfur atom of the polysulfides, and then the strong Lewis acid−base pair could be formed. Although the carboxyl molecules were highly unstable, they exhibited a strong ability to dissolve the low-order polysulfides. Besides the proton transfer, anchoring polysulfides mainly depends on the electron affinity and the number and the location of functional groups in solvent molecules. The 1,2-diaminopropane molecule has two amino groups with an adjacent arrangement and strong electron-donation ability and exhibits strong binding with polysulfides. More contribution of the entropy was found in the binding between polysulfides and the glycerin molecule, while the location of the ether group, compared to its number, contributes more to the binding with polysulfides. The horizontal and vertical orientations of polysulfides were assigned to the strong and the weak bindings with functional groups. For the horizontal orientation of high-order polysulfides, hydrogen bonds' contribution should be considered. The laws of constraining lithium polysulfides by the affinitive interactions can provide one fundamental criterion for the theoretical and experimental selection of a co-solvent for the electrolyte or decorating the cathode in Li−S batteries.

4. COMPUTATIONAL METHODS

The calculations were performed at the density functional theory (DFT) level using the Dmol3 code.[29,30] The exchange−correlation energy was described by the PW91 functional within the generalized gradient approximation (GGA-PW91)[31] with parameters of OBS dispersion corrections.[32] The conductor-like screening model (COSMO) was chosen to include the solvation effect. Ether was employed as the solvent with a permittivity of 7.6, which is the average permittivity value of DME and DOL commonly used in Li−S batteries. DFT semicore pseudopotentials were used for all atoms. Also, the double-numeric basis with polarization (DNP) functions was used for all atoms. We took the global real-space orbital cutoff of the atomic basis sets to be 5.1 Å. The convergence criteria for structural optimization and energy calculations were 1.0×10^{-6} for SCF, 1.0×10^{-5} au for energy, 2.0×10^{-3} au for maximum force, and 5.0×10^{-4} nm for maximum displacement. The standard Gibbs free energy at room temperature (298.15 K) was obtained through the analysis of the vibration frequencies.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c06067.

The calculated binding energy values and all possible binding geometries (PDF)

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Notes

The authors declare no competing financial interest.

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