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Supramolecular Regulation of Anions Enhances Conductivity and Transference Number of Lithium in Liquid Electrolytes

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Supporting Information

ABSTRACT: Achieving high ionic conductivity in lithium-ion battery (LIB) electrolytes requires dissociation of Li-salts; however, though the generation of free Li^+ from salt dissociation is advantageous, the presence of freely diffusing anions may reduce the Li^+ transference number. The use of supramolecular anion recognition to regulate and modify ion-pairing and diffusion of anions in battery electrolytes is yet to be deeply understood. Herein, we demonstrate that addition of a selective and strong PF_6^--binding macrocycle to a solution of $LiPF_6$ in low dielectric media leads to enhanced ion pair dissociation and an increased Li^+ transference number. This work provides a well-defined model system to study the effects of anion binding in battery electrolytes.

The transport of ions is ubiquitous and critical for a range of biological processes,[1] chemical systems,[2,3] and electronic devices.[4] In particular, the efficient conduction of Li^+ in electrolytes is crucial for the development of high-performance lithium-ion batteries (LIBs).[5] For solvent,[6] gel,[7] and polymer electrolytes,[8] where the lithium salt and the electrolyte form a homogeneous and/or isotropic mixture, the counteranion of the lithium salt has a significant impact on the concentration[6,9] and mobility[10,11] of free Li^+. Thus, the regulation of anions to tune these parameters has become one of the major goals of novel electrolyte materials. Specific strategies to regulate anions include high dielectric solvents,[12] novel synthetic anions,[13,14] single-ion conducting polymers,[15] ionic liquids,[16] and Lewis acidic electrolytes.[17−19] Despite these efforts, the use of selective anion binding to achieve supramolecular modification and regulation of anions is yet to be fully explored.[20] Herein, we report unambiguous spectroscopic evidence that correlates selective anion recognition with increases in both free Li^+ concentration and transference number (t_+).

It is well established that anions can negatively impact the conduction of lithium by forming nonconductive ion pairs.[6,9,21] The diffusion of anions also reduces the t_+ of Li^+.[10,11] Previous studies have demonstrated that the use of anion receptors (e.g., calix-pyrrole derivatives,[22−24] aza-crown ethers,[25,26] and urea functionalized calix-arene derivatives[27−29]) as additives in polymer electrolytes has the potential to increase the conductivity and t_+ of Li^+; however, the detailed mechanisms that underpin the performance of these anion binding additives is still unclear.[22,23,29] For example, the binding affinity, selectivity, and the degree of lithium dissociation in these systems is unknown. In addition, the receptors may act as kinetic traps for freely diffusing anions or they may diffuse together with the anions as a complex. Moreover, the receptors used in these studies (e.g., calix[4]pyrrole) are known to bind small and charge-dense halides,[30,31] but fail to selectively recognize the large anions typically used in lithium electrolytes.[32] Here, to gain a deeper understanding of this relatively new concept, we use cyanostar (**CS**, Figure 1a),[33] a well characterized macrocyclic receptor that uniquely and strongly binds large anions,[33−39] to investigate the supramolecular regulation of anions in lithium electrolytes.

CS is a shape-persistent macrocycle that has strong binding affinity toward large and charge-diffuse anions (e.g., the 2:1 stabilization constant, β_{anion}, of PF_6^- and ClO_4^- were reported to be 2.7 and 1.3×10^{12} M^{-2} in 40:60 $CH_3OH{:}CH_2Cl_2$, respectively).[33] The characteristic anion recognition of **CS** gives rise to high-fidelity 2:1 sandwich complexes (Figure 1b).[33,37] In this study, we select three representative Li-salts as guests for **CS**: LiBr, $LiPF_6$, and Li-bis(trifluoromethane)-sulfonimide (LiTFSI), which vary by the size of the anions (Figure 1a).[40] We expect the ion pairing association of these salts, K_{ip}, to follow the trend: LiBr > $LiPF_6$ > LiTFSI.[41] The binding association of the anions with **CS**, β_{anion}, is dictated by size matching[33,36] with the binding cavity of the macrocycle: $LiPF_6 \approx$ LiBr > LiTFSI (Section S2 in SI). We use tetrahydrofuran (THF, dielectric constant, ε, is 7.6) as the solvent as **CS** and the lithium salts studied here have good solubilities in THF and solution-phase studies allow for clear spectroscopic evidence of anion binding, lithium concentration, ion diffusion, and lithium t_+.

Our central hypotheses are (1) Upon anion binding, the high-fidelity complex formed between **CS** and the salt anion will interact weakly with Li^+, which will elevate the free lithium concentration even in low dielectric media that otherwise favors ion pairing (Figure 1b); (2) The 2:1 **CS**:anion complex

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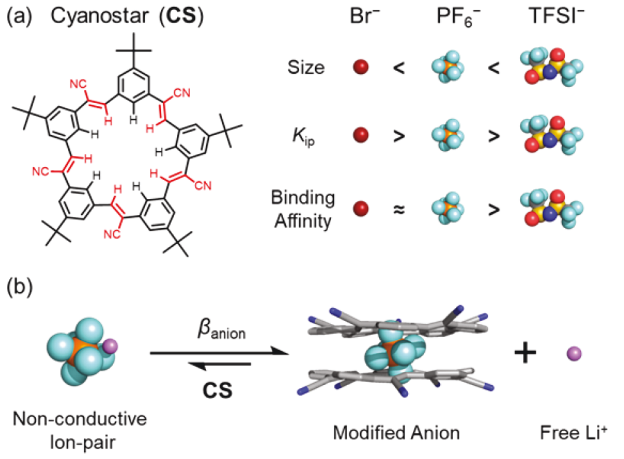

Figure 1. (a) Chemical structure of cyanostar (**CS**) and molecular models of Br^-, PF_6^-, and $TFSI^-$ anions. (b) Scheme of supramolecular anion modification. K_{ip} is the ion-pairing association constant of the salts; β_{anion} is the overall association constant of the **CS**:anion complex.

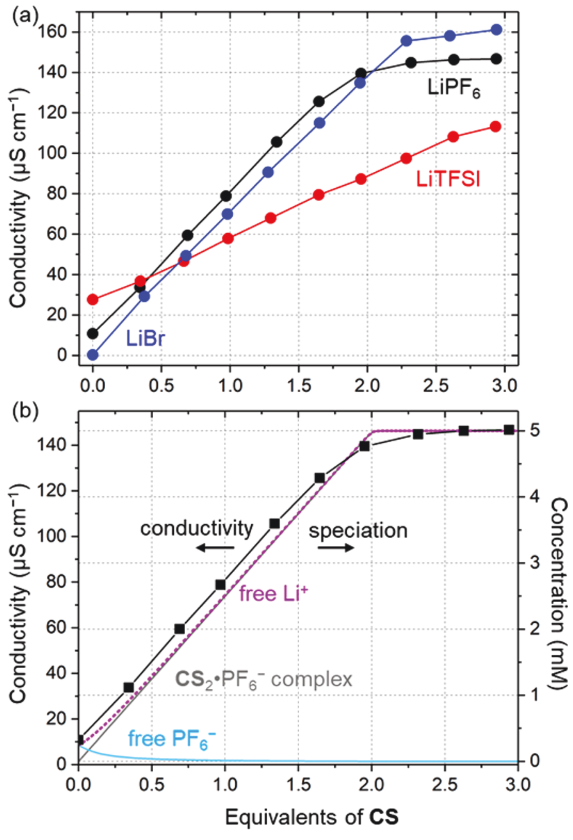

Figure 2. (a) Conductivity of LiBr, $LiPF_6$, and LiTFSI in THF (5 mM, 298 K, the error in conductivity is ∼1 μS cm^{-1}; see S8 in the SI for error analysis) with increasing equivalents of **CS**. (b) Conductivity (black dots) and the calculated concentrations (gray, purple and cyan lines) of species formed when **CS** was added to $LiPF_6$ (5 mM, THF). The calculation was based on a 3-equilibria model: ion paring of $LiPF_6$ (log K_{ip} = 4.9), $\mathbf{CS}\cdot PF_6^-$ 1:1 binding (log K_1 = 5.3), and $\mathbf{CS}_2\cdot PF_6^-$ 2:1 binding (log β_{anion} = 13.5). See SI for detailed thermodynamic analysis.

is larger than the parent anion, which will result in reduced anion diffusion and enhanced lithium t_+ (Figure 1b).

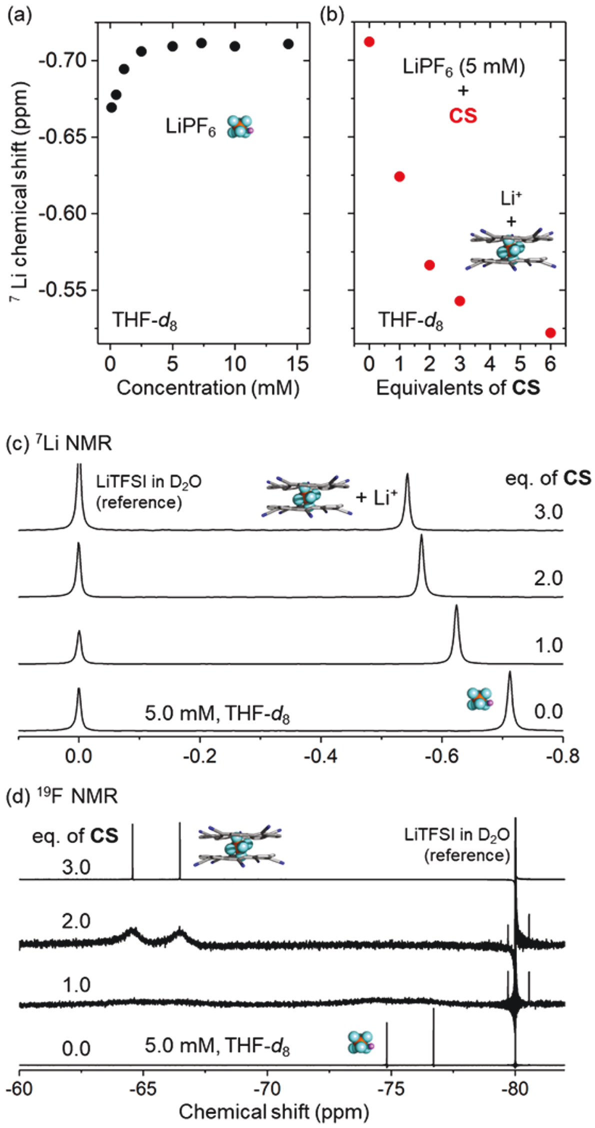

Figure 3. ^7Li chemical shift of $LiPF_6$ (THF-d_8, 298 K) as a function of (a) concentration and (b) **CS** equivalents. (c) ^7Li and (d) ^{19}F NMR spectra of $LiPF_6$ with increasing equivalents of **CS** (5 mM, THF-d_8, 400 MHz for ^1H, 298 K, δ referenced to LiTFSI in D_2O).

We observed that the addition of **CS** into solutions of LiBr, $LiPF_6$, and LiTFSI in THF (5 mM) significantly increased their conductivities (Figure 2a), which lends support to our hypothesis that the formation of the **CS**:anion complex dissociates the nonconductive LiX ion pairs. At 0 equiv of **CS**, the conductivity values of the parent salts (0.27, 10.7, and 27.6 μS cm^{-1} for LiBr, $LiPF_6$, and LiTFSI, respectively) are consistent with the expected ion pair association strength of the salts (LiBr > $LiPF_6$ > LiTFSI).[41] The conductivities of the three salts as a function of **CS** equivalents resemble the known binding behaviors of **CS** with PF_6^-, Br^-, and $TFSI^-$ (Section S2 in SI). For example, the conductivity of $LiPF_6$ saturates sharply at 2 equiv, which is consistent with the strong 2:1 binding of PF_6^-.[33,36] We observed similar changes in the conductivity of LiBr with the addition of **CS** (Figure 2a). The final conductivities of $LiPF_6$ and LiBr are similar, which suggests that the anions are completely converted to similarly sized 2:1 complexes. In contrast, the conductivity of LiTFSI increases much less and fails to show saturation even at 3.0

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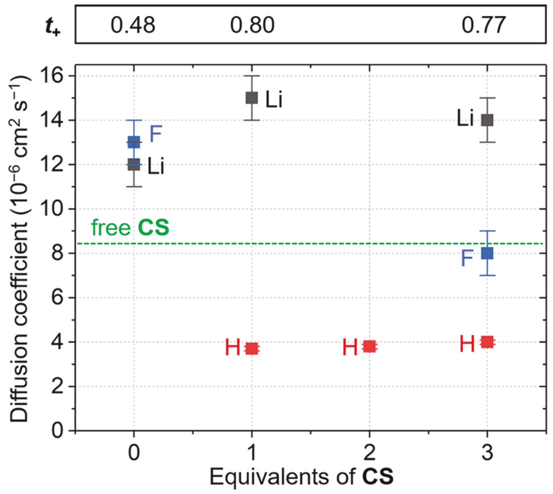

Figure 4. Transference numbers (t_+) and diffusion coefficients obtained from ^{7}Li, ^{19}F, and ^{1}H diffusion NMR with various equivalents of **CS** (5 mM LiPF$_6$, THF-d_8, 298 K, 400 MHz for ^{1}H). The dashed line indicates the diffusion coefficient of free **CS** (10 mM, THF, 298 K).

equiv of **CS**, which is consistent with the low binding affinity of TFSI$^-$ with **CS** (Figure S1 and S2).[33,36] It is worth noting that THF solutions of free **CS** have minimal conductivity (Table S5), and that **CS** does not reduce the viscosity of THF (Table S6).

NMR studies of LiPF$_6$ in THF were used to understand the physical origin of the observed conductivity enhancement (Figure 2a). The ^{7}Li NMR resonance of LiPF$_6$ in solution (referenced to LiTFSI in D$_2$O) was found to shift to upfield positions with increasing concentration (0.12−2.5 mM, THF-d_8, Figure S16 and 3a) and reach an almost constant chemical shift (−0.711 ppm) when the salt concentration is higher than 2.5 mM (Figure 3a). The change in peak position is consistent with greater ion-pair association at higher concentrations; ion-paired Li$^+$ is more shielded by the negatively charged counteranion.

The addition of **CS** to a solution of LiPF$_6$ (5 mM, THF-d_8, Figure 3b,c) verifies that the binding of PF$_6^-$ leads to ion pair dissociation. The resonance for ^{7}Li significantly shifts downfield with increasing amounts of **CS** (Figure 3b), from −0.712 ppm (0 equiv) to −0.522 ppm (6.0 equiv). The direction of this shift is opposite to what is observed for increasing ion pairing with increasing salt concentration (*cf.* Figures 3a and 3b), which suggests that complexation with **CS** leads to a more dissociative anion and generates more free Li$^+$. Formation of the 2:1 complex is confirmed by ^{1}H (Figure S20) and ^{19}F NMR (Figure 3d), in which the addition of **CS** into LiPF$_6$ results in ^{1}H and ^{19}F peaks moving to positions that are completely different from free **CS** and free PF$_6^-$. The ^{19}F NMR features medium to slow exchange between the free PF$_6^-$ and the **CS**$_2$PF$_6^-$ complex on the ^{19}F NMR time scale (∼10 μs at 9.4 T field).[42] Above 2 equiv of **CS**, the ^{19}F resonance appears at a greatly downfield-shifted position, which is indicative of the completely bound anion.

An estimation of the free energies of LiPF$_6$ ion pairing association (K_{ip}) and **CS**-PF$_6^-$ binding affinity (β_{anion}) in THF can be acquired from thermodynamic analysis of the NMR and UV−vis titration data (see Section S2 in the SI for detailed analysis). On the basis of these equilibrium constants ($\log K_{\mathrm{ip}} = 4.9$ and $\log \beta_{\mathrm{anion}} = 13.5$), we calculated the speciation curves of LiPF$_6$ at 5 mM with increasing **CS** equivalents (Figure 2b and S19). The calculation shows that the increase of free lithium ion concentration correlates well with the enhanced conductivity (Figure 2b).

We further show that anion binding slows the diffusion of anions and increases the t_+ of Li$^+$ using diffusion NMR data of the mobility of Li$^+$ and its corresponding counter-anions in solution (Figure 4, Table S4). At 0 equiv of **CS**, the diffusion coefficients of ^{7}Li and ^{19}F are identical, which is consistent with strong ion pairing at this concentration ($t_+ = 0.48$). With 2 equiv of **CS**, PF$_6^-$ is completely captured by the macrocycle (Figure 3d). The diffusion coefficient of the complexed anion acquired from ^{1}H NMR is much lower than that of both the parent salt and free **CS** (Figure 4). In contrast, the diffusion of ^{7}Li with **CS** present is not significantly different from the parent salt. As a result, Li$^+$ t_+ increases due to the modified diffusion of the 2:1 **CS**:PF$_6^-$ complex. For example, the t_+ at 3 equiv of **CS** (0.77, Figure 4) is much higher than that of the parent LiPF$_6$ salt alone (Figure 4).

It should be noted that we did not obtain strong enough signals for ^{7}Li at 2 equiv and ^{19}F at 1 and 2 equiv for diffusion NMR analysis, presumably due to dynamic exchange between species, which reduces peak intensity.[43] At 3 equiv of **CS** the ^{19}F diffusion has dropped below that of the LiPF$_6$ ion pair, but is different from ^{1}H diffusion, presumably due to the exchange behavior of the PF$_6^-$ anion.

To bring our findings into a practical context, we compare the supramolecular anion recognition regulated conductivity of Li$^+$ in THF ($\varepsilon = 7.6$) to conductivities achieved using the current commercial solvent standards: ethylene carbonate (EC, $\varepsilon = 90.8$ at 309 K)[44] and dimethyl carbonate (DMC, $\varepsilon = 3.1$). At the solubility limited concentration of **CS** (40 mM), the THF electrolyte possessing **CS** (Table 1, Entry 3) showed higher t_+ (0.67 > ∼0.35) and Li$^+$ conductivity ($\sigma \cdot t_+$: 320 > 240 μS cm^{-1}) than the standard DMC:EC mixture (Entry 1).

Interestingly, in the mixture of THF and EC (Entries 4 and 5), where LiPF$_6$ is likely fully dissociated based on the conductivity value (868 μS cm^{-1}), adding **CS** lowers the conductivity to 627 μS cm^{-1} but increases the t_+. In this

Table 1. Conductivity of LiPF$_6$ under Various Conditions[a,b]

Entry	1	2	3	4	5
Solvent	DMC:EC	THF	THF	THF:EC	THF:EC
Composition	50:50 w/w	100	100	80:20 w/w	80:20 w/w
c(**CS**) (mM)	0	0	40	0	40
σ (μS cm^{-1})	690	35.3	470	868	627
t_+	0.3−0.4[45]	∼0.5	0.66	0.55	0.74
$\sigma \cdot t_+$ (μS cm^{-1})	240	18	320	480	460

[a] c(LiPF$_6$) = 20 mM. [b] Errors in conductivity is ∼1%. Errors in t_+ is ∼10% (Table S4).

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solvent mixture, the high-fidelity 2:1 complex was confirmed by ^{1}H, ^{19}F, and ^{7}Li NMR spectra (Figure S21 and S22). This observation shows that under highly dissociative conditions, binding the anion no longer generates more charge carriers, but can still slow down the anions and increase t_+ (from 0.56 to 0.74). Consistent with this observation, the Li$^+$ conductivity ($\sigma \cdot t_+$) of entries 4 and 5 are the same within the error of t_+ (~10%).

In conclusion, we show that selective supramolecular recognition of anions provides conductivity performance (Table 1, Entries 3 and 5) that is competitive with current commercial standard electrolytes (Entries 1 and 4) at solubility-allowed concentrations. We demonstrate a quantitative correlation between selective anion binding and enhanced conductivity and transference number. This work demonstrates that commonly accepted nonideal solvents (e.g., THF) and nonideal salts (e.g., LiBr, Figure 2a) can be potent electrolyte candidates when paired with anion recognition. These findings open new opportunities for the development of novel battery electrolytes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b05915.

> General methods, titrations monitored by NMR and UV−vis spectroscopy, thermodynamic analysis of the titrations, and diffusion NMR (PDF)

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Notes

The authors declare no competing financial interest.

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