Crowning Lithium Ions in Hole-Transport Layer toward Stable Perovskite Solar Cells

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State-of-the-art perovskite solar cells (PSCs) exhibit comparable power conversion efficiency (PCE) to that of silicon photovoltaic devices. However, the device stability remains a major obstacle that restricts widespread application. Doping-induced hygroscopicity, ion diffusion, and use of polar solvents in the hole-transport layer are detrimental factors for performance degradation of PSCs. Here, phase-transfer-catalyzed LiTFSI doping in Spiro-OMeTAD is developed to address these negative impacts. 12-Crown-4 as an efficient phase-transfer catalyst promotes the dissolution of LiTFSI without requiring acetonitrile. A combined experimental and theoretical study demonstrates the host–guest interaction between Li+ ions and 12-crown-4. Crowning Li+ ions by forming more stable and less diffusive crown-ether–Li+ complexes retards the generation of hygroscopic lithium oxides and mitigates Li+-ion migration. Optimized PSCs deliver enhanced PCE and significantly improved stability under humid and thermal conditions compared with a control device. This method can also be applied to dope π-conjugated polymer. The findings provide a facile avenue to improve the long-term stability of PSCs.

1. Introduction

Despite an encouraging power conversion efficiency (PCE) exceeding 25% for state-of-the-art perovskite solar cells (PSCs) being sufficient for practical applications,[1–6] a huge concern over the device stability remains to be addressed. Except for the vulnerability of perovskite layers toward ambient conditions,[7] the most frequently used small-molecule hole-transporting layer (HTL) for highly efficient PSCs, Spiro-OMeTAD (2,2′,7,7′-tetrakis(N,N-di(4-methoxyphenyl)amino)-9,9-spirobifluorene), shows a poor stability toward humid and thermal conditions. Limited by an intrinsically low mobility of pristine Spiro-OMeTAD, LiTFSI (bis(trifluoromethanesulfonyl)imide) as a p-type dopant to increase the conductivity,[8] LiTFSI, however, has low solubility in chlorobenzene (CB), the solvent for dissolving Spiro-OMeTAD. It is usually predissolved in a polar solvent, typically acetonitrile.[9] The instability of Spiro-OMeTAD mainly arises from the indispensable dopants. On the one hand, the metal halide perovskite film is vulnerable to polar solvent and it is desired to avoid or reduce the use of acetonitrile.[10] On the other hand, the hygroscopic lithium salt facilitates moisture penetration and Li+-ion migration that is accelerated under high temperature conditions induces lithium intercalation into the perovskite layer with the formation of deleterious defects.[11]

Thus far, considerable efforts have been devoted to optimizing the HTL of PSCs for enhanced PCE and stability.[12–14] The research community is actively searching for equivalent substitutes[15–18] to Spiro-OMeTAD for simple synthesis and cost reduction. Notwithstanding the recent success, LiTFSI is essential to these newly synthesized HTLs and Spiro-OMeTAD still represents the best choice for PSCs at the current stage owing to its high compatibility with dopants and energy band matching with perovskite.[19–21] Toward Spiro-OMeTAD-based HTL, alternative dopants instead of LiTFSI such as Spiro(TFSI)2,[22] lithium-ion endohedral fullerene,[23] and lithium-ion-free salts,[24,25] have been studied to eliminate the notorious effect of Li+ ions. These advances bring the benefit of enhanced device stability but there is still room for improvement in the PCE. The progress in boosting the long-term stability of PSCs lags far behind the rapid increase in PCE. Therefore, it is an urgent need to minimize the negative effects of dopants while maintaining device performance not only for Spiro-OMeTAD but also for other candidate HTLs. Developing a simple yet efficient method to solve these problems is expected but now it remains challenging.

Here, we demonstrate a phase-transfer catalyzed method for LiTFSI doping in Spiro-OMeTAD to improve the stability of PSCs. Crown ether is a class of ligands that can bind various cations depending on the cavity diameter and the target ion size. 12-crown-4, a typical representative of crown ether family, is added into the Spiro-OMeTAD precursor to replace the acetonitrile. The modified composition in Spiro-OMeTAD precursor solution is superior to the conventional recipe in following aspects. First, 12-crown-4 as a lithium ionophore can selectively bond with Li+ ions through host–guest interaction and promote the dissolution of LiTFSI in CB without requiring acetonitrile. The introduction of the Li(12-crown-4)+ complexes can also passivate the defects and reduce the charge recombination in the perovskite film both

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at the interface and in the bulk. Second, the crowned Li\(^+\) ions with a larger size and mass become less active and more difficult to migrate, in turn posing a lowered threat to the device stability. Third, crowning Li\(^+\) ions with 12-crown-4 can reduce the hygroscopicity of LiTFSI and thus increase the moisture stability of the HTL so that the perovskite film can be well maintained even in a humid condition. As a result, the optimized Spiro-OMeTAD precursor enables PSCs to deliver an impressive PCE of 23.24%, which is higher than that of the control device (22.32%). The stability of PSCs is significantly improved due to crowning Li\(^+\) ions in the HTL with an increased resistance toward moisture and decreased Li\(^+\)-ion migration. The phase-transfer-catalyzed LiTFSI doping can also be applied on π-conjugated polymer HTL, showing a universal application.

2. Results and Discussion

The sandwich structure of PSCs with LiTFSI-doped Spiro-OMeTAD as the HTL is shown in Figure 1a. The components in conventional precursor solution include Spiro-OMeTAD, LiTFSI, acetonitrile, 4-tert-butylpyridine (TBP), and CB, in which TBP assists a uniform dispersion of LiTFSI. The related molecule structures are provided in Figure 1b. LiTFSI as an ionic compound has low solubility in CB (Figure 1c). Crown
ether possesses a specific charge distribution and cavity size that can bind alkali-metal cation with a fitted size through host–guest assembly. Particularly, 12-crown-4 has an interior cavity diameter that matches well with Li⁺ ion size. In this study, it was chosen to promote the dissociation of LiTFSI and increase the solubility through the following coordination reaction: LiTFSI + 12-crown-4 → Li(12-crown-4)⁺ + TFSI⁻. After adding 12-crown-4, LiTFSI can be dissolved quickly in CB and we successfully prepared transparent precursor solution without requiring acetonitrile. For simplicity, the precursor solution (HTL or PSCs) prepared with conventional or modified recipe are denoted as control and target precursor (HTL or PSCs), respectively, in the following discussion unless otherwise stated.

According to the electrospray ionization mass spectrometry (ESI-MS) in Figure 1d, a mass/charge ratio \((m/z)\) of 136.1 that is indicative of \(\text{H(TBP)}^+\) can be detected in the control precursor but the signal of \(\text{Li(TBP)}^+\) is not present, which implies easy desolvation between Li⁺ ions and TBP. An extra intense peak with a \(m/z\) of 183.1 can be assigned to \(\text{Li(12-crown-4)}^+\) in the target precursor, confirming the specific coordinating reaction. The interaction between 12-crown-4 and Li⁺ ion was further characterized by nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR) spectroscopy, and Raman spectroscopy. Compared with the mixed solution without LiTFSI (acetonitrile+12-crown-4), a positive \(^1\text{H} NMR\) chemical shift of 12-crown-4 after being combined with Li⁺ ion is discerned for the mixture with LiTFSI (Figure 1e), which suggests a strong Li–O solvation. Both \(^1\text{H} NMR\) spectra have an intense peak at 1.99 ppm that is characteristic of the H atoms in acetonitrile. A distinct shift can also be observed in the FTIR spectra (Figure S1, Supporting Information) and Raman spectra (Figure S2, Supporting Information), validating the formation of crown-ether–Li⁺ complex.

Notably, the control and target precursor exhibit a slightly different color (Figure S3, Supporting Information) and absorption pattern (Figure 1f). We also studied the effect of 12-crown-4 content in the target precursor on the absorption (Figure S4, Supporting Information). To find the reason for the changed color of the precursor, we studied the solvation energy of \(\text{Li}^+\) ions with density functional theory (DFT) calculations (Figure S5, Supporting Information). The interaction between \(\text{Li}^+\) ion and TBP molecule induces the formation of \(\text{Li}^+\)/TBP complexes. As the number of surrounding TBP molecules increases, the solvation energy gradually decreases and the configuration becomes more stable. In the control precursor, four TBP molecules surrounding a \(\text{Li}^+\) ion is most favorable from the perspective of energy reduction and a stable solvation shell consequently forms. However, stable solvated structure cannot be obtained when more TBP molecules interact with \(\text{Li}^+\) ion. This could be attributed to the fact that four is the maximum number of unoccupied orbitals for \(\text{Li}^+\) (one 2s and three 2p orbitals) to accept donated lone electron pairs. The \(\text{Li}^+\)-ion solvation in the target precursor, however, is different. \(\text{Li}^+\) ion can tightly bond with 12-crown-4 with a strong bonding and the crowned \(\text{Li}^+\) ion can further interact with a TBP molecule with a reduction in system energy according to the DFT calculations. The steric hindrance effect blocks the interaction with one more TBP molecule. Thus \(\text{Li}^+\) ions in the target precursor exist most likely in the form of \(\text{Li}^+\)/12-crown-4/TBP. Compared with the binding energy of \(\text{Li(TBP)}^+\) and \(\text{Li(12-crown-4)}^+\) complex, it can be found that much more energy is needed to desolvate 12-crown-4 than TBP, which can explain the fact that we only observe the signal of \(\text{Li(12-crown-4)}^+\) complex in the ESI-MS spectra of the target precursor. As a consequence of less anchoring sites available, there will be more free TBP molecules that can induce Spiro-OMeTAD dedoping because of the chemical reaction with oxidized Spiro-OMeTAD, which is responsible for the reduced light absorption intensity for the target precursor as aforementioned. In short, the different color of the two precursors is caused by the change in the \(\text{Li}^+\)-ion solvation after modifying the precursor recipe. A schematic drawing that depicts the \(\text{Li}^+\)-ion solvation shell is shown in the inset of Figure 1f.

The absorption spectra of the control and target HTLs were measured after an oxidation process under oxygen exposure. Both the HTLs show high absorption intensity in the UV range and an extra band appears around 500 nm (Figure 1g). The former absorption band is assigned to the pristine Spiro-OMeTAD and the latter arises from oxidized species. The absorption intensity for the oxidized control HTL is a little higher than that of the oxidized target HTL. We also measured the conductivity of the two oxidized HTLs. By fitting the \(I–V\) curves (inset in Figure 1g), the conductivity can be calculated and the difference in conductivity for the two HTLs is very small. Both the absorption spectra and the conductivity measurement certify that the modification toward the HTL recipe will not greatly affect the generation of oxidized species and the charge transport. We further monitored the time-dependent change in the photoluminescence (PL) spectra of unoxidized HTLs in ambient air (Figure 1h). Pristine Spiro-OMeTAD under UV excitation emits intense blue light with an emission peak around 420 nm while p-type doping results in PL quenching. The PL intensity of both the HTLs gradually decrease as the exposure time, a phenomenon of doping in progress. The decrease in PL intensity is nearly in step with each other, proving a negligible impact of 12-crown-4 on the oxidation rate of Spiro-OMeTAD. Ultraviolet photoelectron spectroscopy of the oxidized HTLs was measured to study the energy band structure (Figure S6, Supporting Information). The two HTLs after oxidation show only a small difference in the energy band position and work function, which suggests a similar p-type doping level regardless of the HTL composition.

To deepen our perception about the role of 12-crown-4 in the doping process, cyclic voltammetry (CV) was conducted to study the oxygen redox couple in LiTFSI-containing electrolyte without or with 12-crown-4. As a demonstration, dimethyl sulfoxide was chosen as the solvent since it would not consume lithium oxides. It is widely accepted that the reactions occurred on CV sweeps abide to following principles. On the cathodic sweep, the reduction reactions of \(\text{O}_2\) to oxygen-reduction species adhere to an order of priority: \(\text{O}_2^-\), \(\text{O}_2^{2-}\), and \(\text{O}^{2-}\). On the return anodic sweep, the oxidation reaction releasing \(\text{O}_2\) from these oxygen-related anions will proceed with a reverse order. The CV curve without 12-crown-4 has an obvious oxidation peak of \(\text{O}_2^{2-}\) at 0.01 V while no oxidation peak of \(\text{O}_2^-\) can be found (Figure 2a). This proves that \(\text{O}_2^-\) has converted into \(\text{O}_2^{2-}\) during the cathodic sweeping. According to the hard–soft
acid–base theory, the hard Li\(^{+}\) ions have a higher affinity for hard Lewis bases such as O\(_{2}^{-}\) and O\(_{2}\)\(^{-}\) than moderately soft base (O\(_{2}\)\(^{-}\)). LiO\(_{2}\) is quite unstable and it appears as an intermediate phase. However, after adding 12-crown-4, an oxidation peak at \(-0.40\) V increases remarkably and the oxidation peak of O\(_{2}^{-}\) declines. The extra oxidation peak is assigned to the oxidation reaction from O\(_{2}\)\(^{-}\) to O\(_{2}\), which confirms the existence of O\(_{2}^{-}\) and a strong interaction between O\(_{2}^{-}\) and the crown-ether–Li\(^{+}\) complexes. The Lewis acidity of Li\(^{+}\) ion is decreased with an increased radius through coordinating with 12-crown-4. For this reason, the moderately soft base O\(_{2}^{-}\) will have an increased affinity for the Li(12-crown-4)\(^{+}\) complex. We conclude that the addition of 12-crown-4 can substantially improve the stability of the O\(_{2}^{-}\) ions and inhibit the formation of Li\(_{2}O_{2}\).

\(^{7}\)Li NMR spectra of the precursor solutions before and after \(O_2\)-bubbling (Figure 2b) were measured to further clarify the difference between the two HTLs in the oxidation process. The \(O_2\)-bubbling process is an effective method to pre-oxidize HTL precursor solution. The control and target HTL precursor without pre-oxidization has a peak around \(-0.85\) and \(-0.78\) ppm, respectively. A positive chemical shift in the \(^{7}\)Li NMR spectra suggests a different coordination condition for Li\(^{+}\) ion due to the formation of crown-ether–Li\(^{+}\) complexes in the target HTL precursor solution. The 12-crown-4 induced chemical shift can be explained by a different coordination environment. This phenomenon is in agreement with the result of \(^{1}\)H NMR as discussed above. After \(O_2\)-bubbling, the dominating peak position remains almost the same for the control precursor and the signal at the positive side slightly increases as the formation of Li\(_{2}O_{2}\) that contains Li vacancies. The \(^{7}\)Li NMR signal of the target precursor shifts to \(-0.97\) ppm after \(O_2\)-bubbling. We speculate that this change is connected to the replacement of TBP with O\(_{2}^{-}\) as the ligand for the crowned Li\(^{+}\) ion. In lithium oxides, the \(^{7}\)Li NMR peak position follows the order: LiO\(_{2}\) < Li\(_{2}O_{2}\) < Li\(_{2}O\) because of a different coordination number for the Li\(^{+}\) ion and the peaks at lower frequencies can be assigned to Li species with a higher coordination number. The oxidation induced chemical shift is consistent with the enhanced coordination number for Li\(^{+}\) ions after the bonding between O\(_{2}^{-}\) and the crowned Li\(^{+}\) ion.

To obtain an in-depth understanding of the molecular interaction at the nanoscale, we calculated the binding energy of involved configurations (Figure 2c–e) by DFT calculations. The binding energy for Li\(^{+}\) ion and 12-crown-4 complexation is \(-4.23\) eV. Such a high binding energy ensures the stable existence of the Li(12-crown-4)\(^{+}\) complex. The system energy decreases by \(-1.28\) eV when the crowned Li\(^{+}\) ion further interact with a TBP molecule, which suggests that Li\(^{+}\) ions in the target precursor exist most likely in the form of Li(12-crown-4)\(^{+}\)TBP complex. When the ligand of the crowned Li\(^{+}\) ion is substituted...
with $O_2^-$, the decrease in energy can reach up to $-5.15$ eV. Thus, $O_2^-$ can bond with crowned Li$^+$ ion more tightly than TBP molecule and supports our speculation that the crowned Li$^+$ ion will be finally stabilized with $O_2^-$ after O$_2$-bubbling.

Under the circumstance with $O_2$ and light, electrons that absorbs the energy from photons are excited from the highest occupied molecular orbital to the lowest unoccupied molecular orbital (LUMO) of Spiro-OMeTAD molecule and then the photoexcited electrons in the LUMO can be captured by $O_2$ molecules due to a lower standard reduction potential for the reaction of $O_2$ to $O_2^-$ compared with the LUMO of Spiro-OMeTAD.\[33\] Other anions such as $O_2^{2-}$ and $O_2^-$ can be generated subsequently. Along with the reactions, the oxidized Spiro-OMeTAD radical cations form stable complexes with TFSI$^-$, contributing to the p-type conductivity. At the presence of Li$^+$ ions, it is generally accepted that the chemical reactions occur following these orders: $Li^+ + O_2 + e^- \rightarrow LiO_2$, $LiO_2 + Li^+ + e^- \rightarrow Li_2O_2$, $Li_2O_2 + 2Li^+ + 2e^- \rightarrow 2Li_2O$. In the control HTL, lithium oxides including $Li_2O_2$ and $Li_2O$ eventually form after the oxidative reaction (Figure 2f).\[39\] Lithium oxides are extremely hygroscopic and can easily react with moisture to form lithium hydroxide.\[38,39\] This is one of the main reasons for the instability of Spiro-OMeTAD-based HTL and will be discussed later. In the target HTL, Li$^+$ ions are crowned by 12-crown-4 and the direct reaction with oxygen-reduction species is postponed, leaving less opportunity for the generation of lithium oxides. Before exposed to O$_2$ atmosphere, the crowned Li$^+$ ion in the unoxidized target HTL is bonded with a TBP molecule from the perspective of system energy reduction according to the results of the DFT calculations. The introduction of O$_2$ and light induces the formation of $O_2^-$ and oxidized Spiro-OMeTAD radical cation. The crowned Li$^+$ ion with a decreased Lewis acidity has a stronger interaction with the moderately soft base $O_2^-$ compared with TBP molecule due to a higher binding energy for the former supported by the DFT calculations. The crowned Li$^+$ ion can be finally stabilized by $O_2^-$ in the oxidized target HTL as confirmed by the CV analysis. At this point, the oxidation mechanism of the p-type doping in the target HTL is straightforward and the involved oxidation process is presented in Figure 2g. It should be mentioned that the oxidized Spiro-OMeTAD radical cations that are stabilized by TFSI$^-$ ions are responsible for the p-type doping in the target HTL. Raman spectra has been used to analyze the oxidation mechanism of Spiro-OMeTAD-based HTL in an earlier report.\[40\] We compared the Raman spectra of the oxidized target HTL and the LiTFSI/12-crown-4 complex and identified the peak shift for the functional groups of the TFSI$^-$ ion (Figure S7, Supporting Information), which is caused by the interaction with oxidized Spiro-OMeTAD radical cation.

Both the control and target HTLs deposited on perovskite films are compact according to the scanning electron microscopy (SEM) and atomic force microscopy images (Figure S8, Supporting Information). The perovskite/HTL films have quenched PL intensity compared with the pristine perovskite film and the one with a target HTL display a little stronger PL intensity than that with a control HTL (Figure 3a). We further performed time-resolved photoluminescence (TRPL) spectra to study the charge dynamics in the perovskite film. The
TRPL spectra (Figure 3b) can be divided and fitted into two parts (Table S1, Supporting Information). With the existence of HTL, the fast process ($\tau_f$) relates to the charge extraction and the slow one ($\tau_s$) represents the radiative recombination.[43] The perovskite film with a target HTL has a lower $\tau_f$ and higher $\tau_s$. These results suggest that the target HTL possesses a better capability in extracting charge carriers from perovskite[42] and the charge recombination is decreased for perovskite film with a target HTL. It is noted that the control and target HTL is different in composition as discussed above.

The lifetime decay behavior is in connection with the crown-ether–Li$^+$ complexes, which can passivate the perovskite and reduce charge recombination.[29] We make such a conclusion based on the following facts. After a thin layer of the crown-ether–Li$^+$ complexes was deposited onto the perovskite film, the PL intensity of perovskite can be markedly enhanced if the excited light is incident from the surface (Figure S9, Supporting Information). In addition, when we excited the treated perovskite from the glass side, enhanced PL intensity can also be observed. Because we pumped the perovskite films with high-energy photons (400 nm), we expect that the incident light was absorbed strongly in the top or bottom region.[44] This indicates that there is a certain degree of migration for crown-ether–Li$^+$ complexes into the inner part of perovskite. A similar phenomenon had been reported elsewhere.[29] The defect passivation will exert a positive influence on the device performance.[43] In addition, we measured the space charge limited current of the HTLs (Figure S10, Supporting Information). The $I–V$ curves can be divided into three parts: the Ohmic region at low bias voltage, the trap-filling limited region with greatly increased current, and the trap-free child’s region. The defect state density ($n_d$) can be calculated according to the equation: $n_d = 2e_0eV_{TFL}/qL^2$, where $q$, $L$, $V_{TFL}$, $\varepsilon$, and $e_0$ are the elementary charge, the thickness of HTL, the trap-filling limit voltage, the relative dielectric, and the vacuum permittivity, respectively. The defect state density in the target HTL is lower than that in the control HTL.

We fabricated PSCs with a regular-type structure of ITO/ SnO$_2$/perovskite/HTL/Ag to investigate the photovoltaic performance (Figure 3c). The perovskite layer has a bandgap of 1.56 eV. The control PSCs exhibit a PCE of 22.32% with an open-circuit voltage ($V_{OC}$) of 1.11 V, a short-circuit current density ($J_{SC}$) of 24.88 mA cm$^{-2}$, and a fill factor (FF) of 81.08%. In contrast, the target solar cell reached a $V_{OC}$ of 1.14 V, a $J_{SC}$ of 24.97 mA cm$^{-2}$, and an FF of 81.53%, yielding a PEC of 23.24%. We sent one target device to a qualified lab and the certified PCE reached 22.31% (Figure S11, Supporting Information). The corresponding external quantum efficiency curves and maximum power point tracking are shown in Figures S12 and S13, Supporting Information, respectively. We further evaluated the hysteresis behavior of the PSCs using the two types of HTLs. The control device suffers a small degree of hysteresis and the hysteresis behavior is negligible for the target device (Figure S14, Supporting Information).

The corresponding external quantum efficiency curves and maximum power point tracking are shown in Figures S12 and S13, Supporting Information, respectively. We further evaluated the hysteresis behavior of the PSCs using the two types of HTLs. The control device suffers a small degree of hysteresis and the hysteresis behavior is negligible for the target device (Figure S14, Supporting Information). The statisitic distributions of photovoltaic parameters based on 20 individual devices for each category (Figure 3d and Figure S15, Supporting Information) claim that $J_{SC}$ is slightly influenced by the changed HTL, and the improvement in PCE is mainly attributed to the enhancement in FF and $V_{OC}$. We also systematically investigated the effect of the concentration of 12-crown-4 and LiTFSI on the photovoltaic performance. The results are summarized in the Tables S2 and S3, Supporting Information. It is worth noting that the target precursor enables the fabrication of highly efficient PSCs without using acetonitrile. TBP is another polar solvent additive in the control precursor and its major role is considered to assist the dispersion of the lithium salt. Recent studies unveil the additional function of stabilizing the doped Spiro-OMeTAD film as the HTL by forming Li$^{+}$–TBP complex. However, the relative low boiling point of TBP makes it easy to escape from the HTL and it thus deteriorates the performance of PSCs during aging. In fact, we find that the PCE of the PSCs drops appreciably if the target precursor does not contain TBP, which demonstrates that TBP is still essential to the Spiro-OMeTAD-based HTL at the current stage. A comprehensive investigation is needed to further explore the exact role of TBP and seek a suitable alternative.

To evaluate the stability of the perovskite films at the presence of HTL, as-prepared perovskite films with different HTLs were stored in an ambient condition with a relative humidity (RH) of 40–60%. The fresh samples are dark in color (Figure 4a). After aging for 550 h, the perovskite film with a control HTL turns yellow while the one with a target HTL still keeps a dark color. To obtain more insights into the degradation, we measured the XRD patterns of the sample before and after aging (Figure 4b). Regarding the perovskite film with a control HTL, the signal from PbI$_2$ increases markedly and an extra peak appears at 11.6° resulting from $\delta$-phase perovskite,[46] which indicates a severe degradation of perovskite caused by the moisture. Conversely, the PbI$_2$ content of the perovskite film with a target HTL holds constant and the $\delta$ phase has not formed during aging, suggesting a better resistance toward the moisture. The change in nanoscale morphology by comparing the cross-sectional SEM images between the fresh and aged samples[45] and the water contact angle of the HTLs (Figures S16 and S17, Supporting Information) further illustrate the better moisture stability of the target HTL. We also tracked the weight change of LiTFSI and LiTFSI/12-crown-4 complex when exposed to a humid condition[30] and find that the existence of 12-crown-4 can reduce the hygroscopicity of LiTFSI (Figure S18, Supporting Information).

We then explored the Li$^+$-ion distribution in the PSCs by measuring time-of-flight secondary-ion mass spectrometry (ToF-SIMS). ToF-SIMS depth profiles and corresponding 3D mapping are provided in Figure 4c–f. In both the PSCs, Li$^+$-ion concentration does not obey a simple Fickian diffusion distribution and there is a higher concentration in the SnO$_2$ layer than that in the perovskite layer. This suggests a lower affinity of Li$^+$ ions to perovskite than SnO$_2$. The same trend of Li$^+$-ion distribution had been reported in previous reports in the literature.[46,47] For the control device, a much higher Li$^+$-ion signal at the SnO$_2$ layer than that at the HTL can be found, suggesting a rather serious Li$^+$-ion migration. In sharp contrast, Li$^+$ ions primarily located within the target HTL and a relatively small portion of Li$^+$ ions are diffused out and detected at the SnO$_2$ layer, indicating the ion migration has been greatly suppressed.[47] The Li$^+$-ion signal intensity over the perovskite range in the target device is a little higher than that for the control, which...
is due to the migration of Li(12-crown-4)$^+$ complexes into the inner part of perovskite film where the 12-crown-4 has a high affinity to Li$^+$ ions.

To assess the moisture stability of the resultant PSCs, we traced the photovoltaic performance during storing the unencapsulated devices in the dark at 25 °C and 30–50% RH. The target device retains 95.9% of the initial PCE after aging over 2400 h, whereas a significant degradation in PCE with only 67.6% of the initial value being preserved after 1400 h occurs for the control device (Figure 4g). The thermal stability of control and target PSCs were tested with unencapsulated devices aged at 85 °C in a N$_2$ glove box. The target device can keep 81.6% of the initial PCE after thermal aging over 450 h, while only 62.2% of the initial value can be maintained for the control device with the same aging condition (Figure S19, Supporting Information). The lowered Li$^+$-ion diffusivity in the target HTL due to a strong complexation of the Li$^+$ ion with 12-crown-4 contributes to a higher degree of thermal stability. These results fully demonstrate that the stability of the target solar cell is better than that of the control device, which is ascribed to the use of high-quality HTL.

π-Conjugated polymers can be also used as HTL for PSCs in spite of less satisfactory performance compared with that of Spiro-OMeTAD-based device. Finally, we performed phase-transfer-catalyzed LiTFSI doping in poly(3-hexylthiophene-2,5-diyl) (P3HT), a well-known π-conjugated conductive polymer. The addition of 12-crown-4 into the P3HT-based HTL precursor also avoid the use of acetonitrile and convert the mobile Li$^+$ ions into the crown-ether-Li$^+$ complexes. PSCs fabricated using P3HT as the HTL with a phase-transfer-catalyzed
LiTFSI doping exhibit comparable PCE compared with the device using conventional P3HT as the HTL (Figure S20, Supporting Information). The P3HT layer with phase-transfer-catalyzed LiTFSI doping protects the perovskite film from moisture attacks in humid conditions (Figure S21, Supporting Information). The improvement in stability arises primarily from the crown-ether–Li⁺ complexes in the HTL with an enhanced resistance against the moisture.

3. Conclusions
We have demonstrated the feasibility of phase-transfer-catalyzed doping in small molecule and conjugated polymer as HTL for stable and high-efficiency PSCs. We show that 12-crown-4, as an efficient phase-transfer catalyst, can ensure a successful p-type doping and capturing Li⁺ ions by forming crown-ether–Li⁺ complexes in the HTL greatly reduces dopant-induced side effects such as ion migration, moisture sensitivity, and perovskite-layer degradation. This simple but effective doping process can simultaneously improve the photovoltaic performance and long-term stability, which may help pave the way for the commercialization of PSCs in the future.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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