A novel dopant for spiro-OMeTAD towards efficient and stable perovskite solar cells

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ABSTRACT 2,2',7,7'-tetrakis-(*N,N*-di-4-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD), as the most commonly used hole transport material (HTM), plays a significant role in the normal structured (n-i-p) high-efficiency perovskite solar cells (PSCs). In general, it is prepared by a halogen solvent (chlorobenzene, CBZ) and needs an ion dopant (lithium bis(trifluoromethanesulfonyl)imide, Li-TFSI) to improve its conductivity and hole mobility. However, such a halogen solvent is not environmentally friendly and the widely used Li-TFSI dopant would affect the stability of PSCs. Herein, we develop a non-halogen solvent—tetrahydrofuran (THF)-prepared spiro-OMeTAD solution with a new p-type dopant, potassium bis(fluorosulfonyl)imide (K-FSI), to apply into PSCs. By this strategy, high-hole-mobility spiro-OMeTAD film is achieved. Meanwhile, the potassium ions introduced by diffusion into perovskite surface passivate the interfacial defects. Therefore, a hysteresis-free champion PSC with an efficiency of 21.02% is obtained, along with significantly improved stability against illumination and ambient conditions. This work provides a new strategy for HTMs toward hysteresis-free high-efficiency and stable PSCs by substituting dopants.

Keywords: perovskite solar cells, spiro-OMeTAD, K-FSI, hysteresis-free

INTRODUCTION

Organic-inorganic metal halide perovskite solar cells (PSCs) have been regarded as one of the most promising photovoltaics due to their high power conversion efficiency (PCE) and low-cost production, attracting more and more attention in recent years [1]. They exhibit in-

comparable rapid progress with the PCE increasing from initially 3.8% to 25.5% this decade [2,3], owing to the outstanding properties of perovskite absorber such as high optical absorption coefficients [4], long charge diffusion length [5,6], tunable band gaps, and further careful modifications [7,8]. For commercialization, PSCs are required to improve their stability. Besides perovskites, hole transport materials (HTMs) conducting the extraction and collection of photo-generated holes, also greatly affect the stability of devices. Different molecular structures of HTMs as well as additives have a great influence on the device performance and stability [9–11].

In a normal structure (n-i-p) of PSC, 2,2',7,7'-tetrakis-(*N,N*-di-4-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD) is the most widely used HTM. In general, dopants are needed to improve the hole mobility because the pristine spiro-OMeTAD shows poor electrical properties [12]. For example, lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) is added to accelerate the oxidation of spiro-OMeTAD [13], and 4-*tert*-butylpyridine (*t*-BP) is used to not only enable an effective p-doping through interface interaction between *t*-BP and the perovskite layer but also increase the solubility of Li-TFSI in the spiro-OMeTAD solution [14,15]. However, these standard bi-dopants of Li-TFSI and *t*-BP have been identified to conjointly destroy the morphology of hole transport layers (HTLs) and long-term stability due to the hygroscopicity of Li-TFSI and the low boiling point of *t*-BP [16–18]. In the case of exposure to the ambient, the evaporation of *t*-BP leads to aggregation and hydration of Li-TFSI, which eventually results in the destruction of the PSC devices [15,19]. Hence, several groups utilized hy-

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drophobic salts as dopants of spiro-OMeTAD to improve the device performance and stability. Seo *et al.* [20] replaced Li-TFSI with Zn-TFSI₂, leading to a higher PCE over 22% and improved illumination stability with non-migration of zinc ions in HTL. Li *et al.* [21] developed high-performance PSCs based on copper salts-doped spiro-OMeTAD, suppressing its aggregation and crystallization. In addition, Ca-TFSI₂, Mg-TFSI₂, and several ion liquids are alternative dopants as well [22–24]. These studies promote the PCE and stability mostly by acquiring superior hole transport and ambient resistance capacity. Actually, as the spiro-OMeTAD is deposited on the top of perovskite, it will alter the interface properties, and thus not only improve the hole extraction but also improve the stability related to the interface, such as hysteresis. Furthermore, the hypertoxicity of chlorobenzene (CBZ), the solvent for spiro-OMeTAD, is another challenge in the PSC fabrication technology. It is desirable to develop environment-friendly solvents in place of CBZ before commercialization.

Herein, we employ a new dopant of potassium bis (fluorosulfonyl)imide (K-FSI) and a non-halogenated solvent of tetrahydrofuran (THF) to prepare spiro-OMeTAD HTLs. In general, hysteresis in a normal planar structured device is eliminated by passivating the bottom interface of electron transport layer (ETL) and perovskite film. However, by this approach, suppressed hysteresis is realized through the modification of the top interface. As a result, PSCs based on the K-FSI dopant achieved a champion PCE of 20.94% for reverse scan (RS) and 21.02% for forward scan (FS), *versus* the PCE of Li-TFSI-doped device, 19.75% for RS and 16.37% for FS. Characterizations demonstrate that part of K⁺ ions incorporated in the HTL are prone to migrating to the HTL/perovskite interface to passivate surface defects according to the strong interaction between K and Br/I. Further, the passivated device shows improved stability under continuous illumination and humid conditions.

EXPERIMENTAL SECTION

Materials

Unless specified, all chemicals were purchased from Alfa Aesar or Sigma-Aldrich and used as received. SnCl₂·2H₂O was purchased from Aladdin. Lead iodide (PbI₂) was purchased from TCI. Methylammonium bromine (MABr), lead bromine (PbBr₂), formamidinium iodide (FAI) and spiro-OMeTAD were purchased from Xi'an Polymer Light Technology Corp. K-FSI was purchased from Ark Pharm, Inc.

Preparation of perovskite precursor

The Cs_{0.05}(FA_{0.85}MA_{0.15})_{0.95}Pb(I_{0.85}Br_{0.15})₃ (labelled as CsFAMA)-mixed perovskite precursor was prepared by dissolving 1.3 mol L⁻¹ organic cation (FAI:MABr = 0.85:0.15, by mole) and 1.4 mol L⁻¹ mixture of metal lead salts (PbI₂:PbBr₂ = 0.85:0.15, by mole) in 0.8 mL mixture solvent of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) (DMF:DMSO = 4:1, by volume), and then 34 μL CsI solution (pre-dissolved as a 2 mol L⁻¹ stock solution in DMSO) was added to achieve the desired CsFAMA perovskite precursor solution.

Preparation of the spiro-OMeTAD solution

The Li-spiro solution was prepared by dissolving 73 mg spiro-OMeTAD in 1 mL CBZ. The molar ratios of additives for spiro-OMeTAD were 0.55, 3.47 and 0.09 for Li-TFSI, *t*-BP and tris(2-(1H-pyrazol-1-yl)-4-*tert*-butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl)imide) (FK209), respectively.

The K-spiro solution was prepared by dissolving 20 mg spiro-OMeTAD in 1 mL THF. The molar ratios of additives for spiro-OMeTAD were *x* (*x* = 0.2, 0.3, 0.4, 0.5), 6.3*x* and 0.16*x* for K-FSI, *t*-BP and FK209, respectively.

Device fabrication

Fluorine-doped tin oxide (FTO) glass substrate was etched by a laser machine (Universal Laser Systems, VLS2.30), and followed by ultrasonic cleaning through detergent, pure water and ethyl alcohol for 20 min, respectively. They were then dried with dry-air gas flow and then treated by plasma for 5 min. The compact SnO₂ film was achieved by a chemical bath deposition (CBD) method according to a previous report [25]. The perovskite absorber was deposited on the UV-processed SnO₂ substrates (UV illuminated for 15 min) by spun 25 μL mixed perovskite solution at 6000 rpm for 30 s, and 100 μL of ethyl acetate as the anti-solvent was dropped at the last 5th second, followed by annealing at 120°C for 45 min. After cooling down, Li-spiro (in CBZ) was deposited on the top of the perovskite layer directly by spin-coating at 3000 rpm for 30 s. Alternatively, K-spiro (in THF) was deposited on top of the perovskite layer by dynamic spin-coating at 3000 rpm for 30 s. Finally, 80 nm of gold was evaporated on the top of spiro-OMeTAD as the back electrode to complete the whole devices.

Characterizations

The perovskite films were investigated using field-emission scanning electron microscope (SEM) (S-4800, Hitachi, Japan), atomic force microscope (AFM) (NX10,

Park, Korea) and X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi). The steady-state photoluminescence (PL) spectra were obtained using a PL microscopic spectrometer (Flex One, Zolix, China), and the time-resolved PL (TRPL) was measured at 770 nm using excitation with a 478-nm light pulse from Delta Flex Fluorescence Lifetime System (Horiba Scientific Com., Japan). The current density-voltage (*J-V*) curves of these PSCs were measured using a Keithley 2400 source meter in the room environment. The light source was a solar simulator (Oriel 94023 A, 300 W) matching AM 1.5 G. The intensity of the light was 100 mW cm⁻² calibrated by a standard silicon reference solar cell (Oriel, VLSI standards). All the devices were tested using a black metal aperture with a defined active area of 0.16 cm² for the small devices. Time-of-flight secondary-ion mass spectrometry (TOF-SIMS) was performed by time-of-flight secondary-ion mass spectrometer (ION-TOF GmbH 5, Germany).

The samples for X-ray photoelectron spectroscopy (XPS) measurement were prepared as follows: the SnO₂/perovskite/HTLs films were fabricated on the FTO substrate without the deposition of Au. After five days in dark, a subsequent CBZ wash was conducted to remove the spiro-OMeTAD layer. First, CBZ was dropped onto the surface of HTL to dissolve spiro-OMeTAD, then CBZ was dropped onto the exposed perovskite layer spinning at a preset rate of 3000 rpm to remove the residual spiro-OMeTAD. THF was used to wash the perovskite surface again to ensure that K-FSI was completely removed.

RESULTS AND DISCUSSION

Properties of the HTLs

Fig. 1a shows a typical normal structure of a PSC and the molecular structure of spiro-OMeTAD that is employed as the HTM. Due to the low hole mobility of spiro-OMeTAD, it is necessary to introduce an efficient p-type dopant for improving its property. Li-TFSI is a conventional p-type dopant for spiro-OMeTAD and its molecular structure is shown in Fig. 1b. However, it brings about the stability issue. In order to balance the efficiency and stability simultaneously, a new dopant of K-FSI as shown in Fig. 1c was used instead. In addition, to replace the toxic solvent of CBZ, a non-halogen solvent of THF was used to dissolve spiro-OMeTAD and K-FSI. For comparison, the spiro-OMeTAD HTL prepared from the conventional dopant (Li-TFSI) with halogen solvent (CBZ) was chosen as the reference, denoted as Li-spiro. Due to the high volatilization of THF solvent, the K-FSI-

doped spiro-OMeTAD (denoted as K-spiro) was deposited by a dynamic spin-coating method. Firstly, the optimal concentration of spiro-OMeTAD in THF was determined to be 20 mg mL⁻¹, as shown in Fig. S1. The spiro-OMeTAD was deposited on the CsFAMA perovskite film that has large grains as shown in Fig. S2a. The SEM images of the Li-spiro and K-spiro HTLs deposited on the perovskite show a similar morphology (Fig. S2b and c). The morphology and uniformity of perovskite and HTL films were further examined by AFM, as shown in Fig. 1d, f. The perovskite film exhibits a relatively rough surface with an average surface roughness (*R_a*) of 15.82 nm. After deposition of spiro-OMeTAD, the films exhibit more uniform and smooth surfaces, and the corresponding roughness values of Li-spiro and K-spiro films reduce to 3.15 and 6.84 nm, respectively. The roughness of K-spiro film is slightly higher than that of Li-spiro film, possibly due to the thinner thickness. Different evaporation rates of different solvents would result in different packing orders of the spiro-OMeTAD. The thickness of the optimized K-spiro HTL is around 140 nm, which is slightly thinner than that of Li-spiro HTL, confirmed by the cross-sectional SEM images (Fig. S2d and e).

In order to evaluate the hole transporting property of these two spiro-OMeTAD films, the hole mobility was measured with a hole-only device of indium tin oxide-coated glass substrate (ITO)/poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) (40 nm)/spiro-OMeTAD/MoO₃ (10 nm)/Ag using the space charge limited current (SCLC) method as shown in Fig. 2a. The hole mobility can be calculated from Equation (1):

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3}, \quad (1)$$

where μ is the hole mobility, ε_0 is permittivity of free space ($\varepsilon_0 = 8.8542 \times 10^{-14}$ F cm⁻¹), ε_r is the dielectric constant of spiro-OMeTAD ($\varepsilon_r = 3$), and d is the film thickness. To maintain consistency with the HTL for photovoltaic devices, the composition of the HTLs contain spiro-OMeTAD, *t*-BP, FK209 and either Li-TFSI or K-FSI for the hole mobility measurements. By fitting the *J-V* curves, the hole mobility of pristine spiro-OMeTAD without any additives is calculated to be 4.71×10^{-4} cm² V⁻¹ s⁻¹, which is consistent with the previous report [21]. With the doping of Li-TFSI, the hole mobility significantly increases to 2.61×10^{-3} cm² V⁻¹ s⁻¹, exhibiting one order of magnitude improvement compared with the undoped spiro-OMeTAD. When Li-TFSI

Figure 1 (a) A typical normal structure of planar PSCs, and the molecular structure of spiro-OMeTAD. (b, c) The schematic of the different dopants and solvents for HTL. (d-f) AFM images of the perovskite film, perovskite/Li-spiro, and perovskite/K-spiro, respectively.

Figure 2 (a) *J-V* characteristics of hole-only devices of pristine spiro-OMeTAD, Li-spiro and K-spiro films. (b) Steady-state PL and (c) TRPL measurements of perovskite (PSK), perovskite/Li-spiro and perovskite/K-spiro films.

is substituted by K-FSI, the hole mobility further increases to $3.62 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, about 40% higher than

that of Li-TFSI. Li-TFSI promotes the generation of holes through forming a radical cation (spiro-OMeTAD^{•+}).

TFSI⁻), which is weakly bound by the extensively delocalized charge on the TFSI anion [13]. This anionic charge is highly delocalized on the disulfonylimide moiety, which is the main component for both TFSI and FSI anions [26]. Thus, we speculate that K-FSI can also result in the effective generation of mobile holes on the organic matrix by the formation of spiro-OMeTAD⁺⁺FSI⁻.

Mott-Schottky analysis was used to further explore the carrier concentration of different HTLs (Fig. S3). The carrier density of K-spiro was calculated to be $1.42 \times 10^{20} \text{ cm}^{-3}$, which is slightly higher than that of Li-spiro ($1.27 \times 10^{20} \text{ cm}^{-3}$), reflecting an increase in the hole concentration. Meanwhile, the HOMO level of K-spiro is calculated to be -5.226 eV from Mott-Schottky analysis, lower than that of Li-spiro (-5.212 eV), obtaining a better energy level match between the HTL and perovskite layer.

The conductance properties of different HTLs were characterized by *J-V* curves. The device structure is FTO/spiro-OMeTAD/Au. It can be found that the slope of the *J-V* curve follows a trend of K-spiro > Li-spiro > pristine spiro (Fig. S4), indicating that the K-spiro exhibits the best conductance property.

PL spectra were further employed to evaluate the hole extraction properties for these two spiro-OMeTAD films. Fig. 2b shows the steady-state PL spectra for the neat perovskite film and perovskite films covered with the Li-spiro and K-spiro films, respectively. The pristine perovskite film presents a strong PL peak at 765 nm, which is diminished by attaching Li-spiro film obviously. The intensity can be further diminished by the K-spiro film, reflecting faster charge separation and extraction and less charge recombination at the interface compared with the Li-spiro. This consequence is subsequently evident from the TRPL measurements, as depicted in Fig. 2c. The TRPL spectra are fitted on the basis of a biexponential PL decay process [27], and the fitted parameters are listed in Table S1. The fast decay component (τ_1) mainly represents the non-radiative recombination induced by trap states at grain boundaries and surfaces. The τ_1 of the perovskite/K-spiro sample (1.6 ns) and the average PL decay time (10.1 ns) are shorter than those of the perovskite/Li-spiro sample (3.0 and 21.1 ns, respectively), demonstrating more rapid and efficient hole transfer into spiro-OMeTAD with less non-radiative recombination due to the decreased interfacial trap state and defect passivation. The better charge extraction ability of the K-spiro should have benefited from the effective interface passivation by K ions and the enhanced conductivity and hole mobility of the K-spiro. Therefore, an increased open-circuit voltage (V_{OC}) could be expected in the PSCs.

Photovoltaic performance

Fig. 3a shows the *J-V* curves of the champion Li-spiro and K-spiro devices, and the corresponding photovoltaic characteristics are listed in Table 1. Under the optimal doping concentration of 40% K-FSI, the K-spiro device exhibits the highest PCE of 20.94% under RS and 21.02% under FS, with a V_{OC} of 1.159 V, a short-circuit current density (J_{SC}) of 22.98 mA cm^{-2} and a fill factor (FF) of 0.79. As a contrast, the champion PSC device utilizing Li-TFSI shows a relatively low PCE of 19.75%, with a V_{OC} of 1.128 V, a J_{SC} of 22.62 mA cm^{-2} and an FF of 0.77. Obviously, the improvement of these photovoltaic characteristics is due to the substitution of the Li-spiro with the K-spiro. We can observe an increase of V_{OC} from 1.128 to 1.159 V, which is consistent with the speculation according to the PL measurement. External quantum efficiency (EQE) characterization was conducted to evaluate the increase in J_{SC} . A slightly higher EQE of the K-spiro device than that of the control device occurs in the spectra range from 630 to 750 nm (Fig. 3b). Thus, the integrated J_{SC} is calculated to be 22.26 mA cm^{-2} for the K-spiro device, higher than 21.84 mA cm^{-2} of the Li-spiro device, matching well with the J_{SC} obtained from the *J-V* curves. Moreover, Fig. 3c records the stabilized power output (SPO) measurement of above devices, the K-spiro device achieves a stabilized PCE of $20.00\% \pm 0.10\%$ in 120 s at the maximum power point (MPP) at a bias of 0.98 V, whereas the PCE of Li-spiro device decreases slowly from 17.56% to 16.97% during the same test duration at a bias of 0.93 V, obtaining an average PCE of 17.21%. This result indicates superior photostability of the K-spiro device compared with the Li-spiro one. Simultaneously, to further examine the reproducibility of these enhancements, 12 PSCs based on the Li-spiro and K-spiro HTLs were fabricated and tested under AM 1.5 G illumination with RS and FS (Fig. 3d). Statistical results for the photovoltaic parameters with respect to the HTLs are displayed in Fig. S5, showing an overall higher average PCE for the K-spiro device ($20.31\% \pm 0.31\%$) than that of the Li-spiro device ($19.30\% \pm 0.27\%$). The above results clearly show the benefit of K-FSI as the HTL dopant.

Hysteresis study

Hysteresis is a common issue in normal planar PSCs [28], which has been proved to have an impact on the device performance and stability without a unified solution. The main causes of this phenomenon are regarded as ion migration and charge trapping related to defects [28–30]. Usually, hysteresis index (HI) is employed to quantify this

Figure 3 (a) The J - V curves of the champion Li-spiro and K-spiro devices tested under 1 Sun AM 1.5G. (b) The corresponding EQE spectra of these devices. (c) Steady-state output of photocurrent density measured at the MPP and illuminated under 1 Sun AM 1.5G. (d) Statistical distribution of the PCEs for the Li-spiro and K-spiro devices under RS and FS.

Table 1 Photovoltaic characteristics of PSCs prepared with different HTLs

HTL	Sweep	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF	PCE (%)	HI
Li-spiro	RS	1.128	22.62	0.77	19.75	0.171
	FS	1.073	22.64	0.67	16.37	
K-spiro	RS	1.159	22.98	0.79	20.94	0.004
	FS	1.149	22.93	0.80	21.02	

discrepancy of photovoltaic performance by the following equation: $HI = (PCE_{RS} - PCE_{FS})/PCE_{RS}$. In the literature, Li, Na, Mg, Ca, Ag, and Zn-TFSI have been used as dopants, but all have a high HI (Table S2). However, it is found that the PSCs based on the K-spiro exhibit a negligible hysteresis with the HI of only 0.004, whereas the PSCs based on the Li-TFSI show obvious hysteresis with the HI of 0.171 (Fig. 3d). We proceeded to investigate which component of K-FSI was dominant for hysteresis elimination by fabricating devices with different compositions of dopants for HTLs. The PSCs with Li-TFSI/*t*-BP and Li-FSI/*t*-BP were first characterized to probe the impact of TFSI and FSI anions. As presented in Table S3, the Li-FSI/*t*-BP device achieves PCEs of 19.06%

and 14.58% under RS and FS, respectively, with no suppression of hysteresis compared with Li-TFSI/*t*-BP device. Thus the replacement of TFSI by FSI anion has only a slight effect on hysteresis. Meanwhile, we also find that cobalt salt is not the decisive factor for hysteresis elimination. Device containing only cobalt salts and *t*-BP presents PCEs of 17.98% and 15.47% under RS and FS with an HI of 0.140; the decrease of HI could be attributed to the absence of lithium in the device. It has been proven that suppressing the migration of lithium from HTL to ETL could result in the reduced hysteresis of the PSCs [17,31]. In the absence of cobalt salt, devices involving K-FSI/*t*-BP obtain PCEs of 19.88% and 19.45% under RS and FS, higher than that of 19.16% and 14.57% for the devices using Li-TFSI/*t*-BP (Table S3). The tendency of HI between K-FSI and Li-TFSI was similar with or without cobalt salt. Hence, we can conclude that the negligible hysteresis results from the inclusion of K cation in HTL, while cobalt salt plays a role in improving the overall PCEs by helping oxidization of spiro-OMeTAD [32]. It is noteworthy that although with excessive K doping, the PCE decreases, all the devices with different K doping concentrations display a negligible hysteresis under different concentrations of K-FSI (Table S4). To in-

investigate the intrinsic reason of the suppression of hysteresis, TOF-SIMS measurement was conducted to detect the distribution of several key elements in the whole device. It is important to note that the thickness of each layer is not in direct proportion to the sputter time because different layers behave different sputtering rates, which is related to the bond strength of materials. Fig. 4a shows the TOF-SIMS analysis of the Li-spiro device, which reveals that Li is located in the spiro-OMeTAD layer. Besides, there is also a comparable amount of Li at the perovskite/SnO₂ interface, while only a small amount of Li remains in the perovskite layer, which does not follow the Fick's law of diffusion. This suggests that the Li⁺ ions in HTL tend to migrate through the perovskite layer and accumulate at the perovskite/SnO₂ interface on account of the smaller radius of Li than other constituent elements of PSCs and a higher affinity of Li⁺ ions to SnO₂ than to perovskite [29]. However, the distribution of K shows a different tendency from Li, as depicted in Fig. 4b. More K⁺ ions remain in the spiro-OMeTAD layer than at the perovskite/SnO₂ interface as K⁺ is much larger than Li⁺.

To confirm that potassium exists in some form at the HTL/perovskite interface, we carried out XPS to probe

the surface electronic properties of the perovskite films after removal of the top HTLs. The devices were firstly fabricated as usual without the subsequent deposition of Au and kept in dark for five days. Then the HTLs were removed with CBZ and the HTL doped by K-FSI was additionally removed with THF. It is long enough for Li⁺ and K⁺ to diffuse from HTL to perovskite or even SnO₂ layer in five days. After the removal of Li-spiro, no obvious lithium signal is detected on the surface of the perovskite film as seen in the XPS spectrum (Fig. 4c), which indicates that Li⁺ does not tend to interact with the elements in perovskite at the HTL/perovskite interface. However, an apparent peak of K 2p orbital appears in the sample with K-FSI after treatment with CBZ and THF, as shown in Fig. 4d. This result suggests that K⁺ ions could bond with perovskite rather than simply being coated on the perovskite surface. Therefore, it is reasonable to believe that the K⁺ at the HTL/perovskite interface leads to the enhancement of voltaic performance and hysteresis elimination, which could be explained from two respects. On the one hand, the electron clouds around Br can be substantially diminished when the HTL/perovskite interface is modified with K⁺, weakening dangling bonds on the perovskite surface [33]. We believe that the K-Br and

Figure 4 The TOF-SIMS depth profiles of (a) Li-spiro device and (b) K-spiro device. The XPS spectra of perovskite films after removal of (c) Li-spiro and (d) K-spiro deposited five days ago.

K-I bonds will preferentially form due to the strong ionic interaction between K^+ and halide ions. The interaction between K and Br/I passivates the halide defects at the interface to reduce the non-radiative recombination and ion migration in perovskite films [34–36]. On the other hand, Frenkel defect is also supposed to cause the hysteresis effect, which occurs with the accumulation of excess electrons at the cathode under illumination. K^+ ions (radius of 1.38 Å) can be well stabilized in the octahedral site to protect the Frenkel defect due to the appropriate radius ratio while Li^+ and Cs^+ ions fail to occupy the interstitial sites stably in octahedron [28]. This is also the reason why hysteresis can be largely suppressed by K^+ passivation whereas devices with Li or Cs still exhibit severe hysteresis.

To further investigate the charge recombination in PSCs, we measured the V_{OC} of the Li-spiro and K-spiro devices under various light intensities, as shown in Fig. S6. It is known that the deviation of the slope from kT/q (where k is the Boltzmann constant, T represents the absolute temperature, and q denotes the elementary charge) reflects a trap-assisted recombination in PSCs [37]. The K-spiro device has a slope of $1.52kT/q$, which is lower than that of the Li-spiro device ($2.22kT/q$). It indicates a suppressed trap-assisted recombination at the interface after K^+ passivation, revealing that the K-spiro provides a better interface contact for the PSCs. This is also confirmed by the characterization of electrochemical impedance spectroscopy (EIS), which is utilized to eval-

uate the charge transport resistance (R_{ct}) and recombination resistance (R_{rec}) [38,39]. As presented in Fig. S7, EIS was measured at a bias of 1.0 V under simulated AM 1.5 illumination, two semicircle regions can be observed in the Nyquist plot where the high frequency component correlates with the charge transfer process and the low frequency region stands for charge recombination at the interface. The fitted R_{ct} of the K-spiro device is lower than that of the Li-spiro device according to the first arc located on high frequency, while the second arc indicates a larger R_{rec} of the K-spiro device than that of the Li-spiro device, demonstrating a reduced charge recombination and hence a higher V_{OC} . Therefore, the above results reveal that the K-spiro reduces defects and traps at the perovskite/HTL interface and provides a better interface contact for the PSCs.

Stability

The stability of devices based on different dopants was also characterized against light illumination and humid environment. It is observed that the K-spiro device shows a good photo-stability. As shown in Fig. 5a, the encapsulated K-spiro device maintains about 82% of the initial PCE under continuous 0.6 sun illumination during 250 h, while the PCE of the Li-spiro device reduces to 69% compared with the initial value. The improvement of photo-stability is mainly attributed to the K^+ passivation of interfacial trapping defects and the suppression of ion migration, which is prone to being triggered under the

Figure 5 (a) The long-term photo-stability of devices under continuous 0.6 sun light illumination in air with encapsulation. (b) Stability test of the devices without encapsulation aged in air (relative humidity 25%, at 25°C). Contact angle measurements of (c) Li-spiro and (d) K-spiro films.

light illumination. On the contrary, the migration and accumulation of Li^+ at the perovskite/ETL interface have been regarded to be detrimental to the photo-stability of the devices. Moreover, Fig. 5b displays the normalized PCE of unencapsulated devices with respect to the dopant under a condition of 25% relative humidity (RH) after 140 days. The K-spiro device exhibits a superior humidity stability with only 3% decrease of the PCE, while the Li-spiro device shows 22% drop in the same condition. In addition, we measured the water contact angles of the different spiro-OMeTAD films (Fig. 5c and d). It can be seen that the K-spiro displays a larger contact angle (104°) than the Li-spiro (94°), resulting in the enhanced hydrophobicity of the K-spiro. Thus, K-FSI is a more reliable dopant for spiro-OMeTAD to promote the operational long-term stability of PSCs.

CONCLUSIONS

In summary, we develop an innovative p-dopant for spiro-OMeTAD HTL to improve the performance and stability of PSCs by substituting the traditional additive of Li-TFSI with K-FSI. The K-doped HTL attains a higher conductivity and hole mobility, and provides significantly enhanced hole extraction as well as reduced charge recombination for the PSCs. As a consequence, the device with K-FSI achieves an impressive PCE of 20.94% for RS and 21.02% for FS based on an increased V_{OC} . The most remarkable thing is that the notorious hysteresis effect is completely eliminated. Characterizations suggest that K^+ ions migrate from the HTL to perovskite to form K-Br/I , thus passivating the surface defects and mitigating halide migration at the HTL/perovskite interface, which results in the high-performance and hysteresis-free PSCs. Meanwhile, the stability of devices against light illumination and ambient environment are both enhanced by the incorporation of K. In addition, THF successfully replaces the toxic CBZ as the solvent for spiro-OMeTAD, which is more conducive to the industrial production of PSC devices. This work provides a new way to fabricate efficient, stable and hysteresis-free PSCs.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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用于制备高效稳定钙钛矿太阳能电池的新型 spiro-OMeTAD 添加剂

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摘要 作为最常用的空穴传输材料, spiro-OMeTAD在正式结构的高效钙钛矿太阳能电池(PSCs)中起着重要作用. 一般来说, spiro-OMeTAD是基于卤素溶剂氯苯制备的, 并且需要离子型添加剂(Li-TFSI)来提高其导电性和空穴迁移率. 然而, 这种卤素溶剂并不环保, 而且普遍使用的Li-TFSI会影响PSCs的稳定性. 在此, 我们针对spiro-OMeTAD开发出一种新型的p型添加剂(双氟磺酰亚胺钾, K-FSI)并且以无卤素溶剂四氢呋喃作溶剂将其应用于PSCs器件. 通过该方法制备的spiro-OMeTAD薄膜具有更高的空穴迁移率、载流子浓度以及导电性. 同时, 由空穴传输层引入的钾离子可以扩散到钙钛矿表面使界面缺陷得到钝化. 因此, 基于K-spiro薄膜的钙钛矿太阳能电池获得了21.02%的最高光电转化效率并且无迟滞现象存在, 而且电池器件的光照稳定性和环境稳定性显著提高. 这项工作为通过替换空穴传输材料的添加剂实现无迟滞、高效稳定的PSCs提供了新的策略.