# Improving Thermal Stability of Perovskite Solar Cells by Suppressing Ion Migration

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Ion migration presents a formidable obstacle to the stability and performance of perovskite solar cells (PSCs), hindering their progress toward commercial feasibility. Herein, the degradation mechanism of PSCs caused by iodide ion migration, which leads to abnormal changes in photoluminescence transients at the buried interface of perovskite films, is investigated. In light of this problem, a novel strategy is proposed to mitigate ion migration by introducing poly(2vinylnaphthalene) into poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] as the hole transport layer with improved ion-blocking capability. Consequently, this layer effectively reduces defect concentration, suppresses ion migration, and modulates energy level alignment, leading to an impressive efficiency exceeding 23% for doctor-bladed FAPbI<sub>3</sub> PSCs. Moreover, the corresponding unencapsulated devices demonstrate remarkable durability, maintaining over 80% of their initial value after undergoing rigorous stress tests in accordance with the International Electrotechnical Commission 61215 standard for temperature, humidity, and illumination. These tests include 1000 h of thermal cycling and a long-term operational test lasting 600 h under maximum power point tracking.

### 1. Introduction

Perovskite solar cells (PSCs) have witnessed rapid advancements in high-impact optoelectronics, particularly in the field of perovskite photovoltaics.<sup>[1–3]</sup> Single-junction PSCs have demonstrated impressive power conversion efficiencies (PCEs) up to 26.1%<sup>[4]</sup>, surpassing those of mature polycrystalline silicon solar cells. However, a notable challenge is in long-term stability, exacerbated under external stressors, including moisture, heat, and solar illumination.<sup>[5–7]</sup> As a result, the operational lifetime of

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PSCs consistently falls short of that required for commercialization.

In recent years, extensive efforts have been devoted to enhancing stability. Previous studies have effectively protected perovskite devices from extrinsic factors via improved encapsulation techniques.<sup>[8-10]</sup> Yet, addressing intrinsic degradation induced by light and heat during extended device operation remains a formidable challenge.<sup>[11]</sup> Formamidinium lead iodide  $(FAPbI_3)$  stands out as one of the most stable organic-inorganic hybrid perovskite compositions,<sup>[12]</sup> with long carrier lifetime and improved (compare to methylammonium-containing compositions) thermal and photostability in photovoltaic applications, making it an important focus of ongoing research in the community.<sup>[13]</sup> However, the migration of halide ions remains problematic. The electrochemical reactions that release ions, as well as their migration, are thermally activated pro-

cesses, which are crucial to address to prevent the formation of non-photosensitive and insulating PbI<sub>2</sub>.<sup>[14–16]</sup> This issue is particularly critical in p–*i*–n PSCs employing organic polymers as the lower transport layer.<sup>[17,18]</sup> Therefore, it is imperative to explore effective strategies for mitigating ion migration for device stability improvement.

To suppress the iodide migration, several common approaches are employed, including adjusting the energy level alignment by modifying the transport layer materials to reduce the driving force for ion migration, stabilizing the crystal lattice

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structure of the perovskite layer through perovskite doping to make the surface more resistant to ion movement, and introducing additional ion-blocking layers to create physical barriers that impede the migration of iodide ions through the device. For example, Hong et al. introduced MoO<sub>3</sub> into 4,4',4"-tris[(3-methylphenyl)phenylamino]triphenylamine to enhance its p-doping effect and iodine blocking capability in the composite hole-transport layer (HTL), resulting in improved stability under thermal and voltage bias stress.<sup>[19]</sup> In another approach, Wang et al. introduced a long-alkyl-chain anionic surfactant into the perovskite precursor, enhancing perovskite crystallization kinetics and suppressing ion migration, achieving 85.7% performance retention after 3000 h of maximum power point (MPP) tracking.<sup>[20]</sup> Furthermore, Bi et al. designed a nanostructured carbon layer as a blocking layer to hinder ions/molecules diffusion within PSCs, demonstrating a thermal aging test for over 500 h and a light-soaking test for 1000 h.<sup>[21]</sup> Overall, these strategies have proven effective in enhancing the thermal stability of PSCs, offering optimism for the practical operation and application of PSCs. However, it is essential to remain aware that the mechanisms governing perovskite degradation in real-world conditions, especially under serious thermal aging, are still not well understood. This lack of comprehensive understanding highlights the need for further research to elucidate the underlying processes and develop targeted solutions for improving the longterm stability and reliability of PSCs in practical applications.

In this work, we observed abnormal changes, including a prolonged photoluminescence (PL) lifetime at the HTL/perovskite interface during PSCs degradation. Through time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements, we demonstrated that the migration of iodide ions toward the HTL occurs during the thermal aging process, affecting the recombination of electrons and holes, resulting in abnormal changes in the transient behavior. To address this issue, we introduced poly(2-vinylnaphthalene) (PVN), into poly[bis(4phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) to inhibit the diffusion of iodide ions. The PVN-modified devices exhibited superior photovoltaic performance, with increased efficiency of FAPbI3-based doctor blading devices from 20.82% to 23.19%. More notably, the PVN-modified devices demonstrated excellent stability, particularly in terms of thermal stability and long-term operational stability. The corresponding unencapsulated devices retained over 80% of their initial value after 1000 h of thermal cycling aging test between -40 °C and 85 °C in open circuit in accordance with International Electrotechnical Commission (IEC) 61215 acceleration stability test standard, or after a long-term operational test lasting 600 h under the MPP tracking. These outstanding stability data indicate the successful application of PVN in suppressing iodide ion migration, marking a significant step toward the commercialization of PSCs.

#### 2. Results and Discussion

#### 2.1. Effect of HTL on the Degradation of Perovskite Films

To study the effect of HTL on the degradation of perovskite films, we coated FAPbI<sub>3</sub> films onto the 100 nm thick PTAA + indium

tin oxide (ITO) glass and bare ITO glass for comparison. Subsequently, these films were then subjected to decay tests under moisture, heat and solar illumination conditions. We observed that perovskite films on PTAA decomposed much faster than bare perovskite films. Notably, the contrast between films with and without a PTAA underlayer under thermal treatment (80 °C) exhibited significant changes within a week. Films with a PTAA underlayer started to exhibit whitening along the substrate outline, progressing to a yellowish hue by day 7, whereas the bare films remained stable after 1 week of thermal treatment (Figure 1a). The complete degradation process is illustrated in Figure S1, Supporting Information, depicting the successive changes overtime. For the in situ PL characterization, we employed thermal treatment at 80 °C, measuring the fluorescence intensity at the same position after each half-hour thermal cycle (TC). During the TC treatment, perovskite films with a PTAA underlayer showed a more pronounced PL peak decay within the initial few cycles compared to bare films (Figure 1b and S2, Supporting Information). Through time-resolved PL (TRPL) measurements, we first observed the upper interface degradation of the perovskite film from the air side. After one cycle of TC, the bare perovskite film experienced a negligible decrease in PL lifetime from 1.5 µs to 1.3 µs, while the film with a PTAA underlayer exhibited a more significant decrease in PL lifetime from 1 µs to 0.2 µs (Figure 1c,d). Furthermore, we conducted TRPL tests on the bottom interface of the films from the ITO side. For the bare FAPbI<sub>3</sub> film, the lifetime of the bottom interface did not exhibit significant degradation and followed a trend consistent with that of the top interface (Figure 1e). On the contrary, the film with a PTAA underlayer, unlike the top interface where the lifetime shortened after TC degradation, exhibited an elongation of the PL lifetime after TC for the bottom interface of the film (Figure 1f).

# 2.2. Mechanism of Prolonged Fluorescence Lifetime at the Perovskite-HTL Interface

To elucidate the reason for the prolonged PL lifetime observed from the bottom interface of perovskite, we conducted ToF-SIMS analysis on the perovskite films with different underlayers before and after thermal treatment at 80 °C. As shown in Figure 2a.b. before thermal treatment, the intensity of iodine ions (I<sup>-</sup>) in films with PTAA exhibited a direct attenuation at the perovskite/PTAA interface, aligning with the trend of the formamidinium cation (FA<sup>+</sup>) signal. However, following 1 h of heating in ambient air, a distinct peak in I<sup>-</sup> emerged at the location where the FA<sup>+</sup> signal decreased and the O<sup>-</sup> signal rose, thereby confirming the accumulation of I<sup>-</sup> at the perovskite/ PTAA interface. On the contrary, no iodine accumulation was observed in the bare FAPbI<sub>3</sub> film after heating, indicating that the accumulation of  $I^-$  is induced by PTAA (Figure 2c,d). Therefore, we infer that iodine ions migrate into PTAA during the thermal treatment process, which leads to the loss of iodine from the perovskite layer, accelerating the degradation process. Figure 2e provides a schematic representation of the recombination process of stimulated charge carriers at perovskite layer and PTAA. Process 1 depicts the radiative recombination (RR) of carriers, which is a primary recombination pathway.



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**Figure 1.** Degradation of perovskite film. a) The 1 week degradation of unencapsulated perovskite films with and without a PTAA underlayer under 80 °C thermal treatment. b) In situ PL peak decay analysis of perovskite films with a PTAA underlayer during TC treatment. TRPL measurements excited from c,d) the air side and e,f) ITO side for perovskite films with and without a PTAA underlayer.



**Figure 2.** Mechanism of prolonged PL lifetime at the perovskite–HTL interface caused by perovskite degradation. ToF–SIMS analysis for samples a,b) with and c,d) without HTLs before and after thermal treatment. e) Schematic of the recombination process of stimulated charge carriers at perovskite layer and HTL.



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Another pathway involves two processes for carriers after being captured by defects. Process 2 describes the nonradiative recombination (NRR) process, while Process 3 represents the return of holes to the excited state and their recombination with electrons. Due to iodine-ions migration, anions accumulate at the perovskite–HTL interface, leading to the formation of more NRR centers. Consequently, more carriers undergo Processes 2 and 3. Moreover, the negative charges carried by I<sup>-</sup> attract holes and repel electrons, prolonging the duration of Process 3, thereby explaining the extended fluorescence lifetime. Hence, enhancing device stability requires improving the PTAA films to suppress iodine-ion migration.

# 2.3. Effort of Dielectric Polymers on Suppressing Iodine-Ions Migration

According to previous reports, the diffusion rates of iodine ions in organic HTLs are dictated by their highest occupied molecular orbital (HOMO) energy level.<sup>[22,23]</sup> To mitigate iodine diffusion, we introduced two widely employed insulating polymers, PVN and poly(N-vinylcarbazole) (PVK), both of which were reported to have deeper HOMO levels than PTAA.<sup>[24–26]</sup> Specifically, PVN materials have been previously employed as an additive to enhance the stability of N-type organic semiconductors.<sup>[27]</sup> The molecular structures of those polymers are shown in Figure S3, Supporting Information. We performed ultraviolet photoemission spectroscopy (UPS) measurements to evaluate the HOMO levels of those polymer films (Figure S4, Supporting Information). For comparison, we used poly(3-hexylthiophene (P3HT),<sup>[28]</sup> a polymer with a shallow HOMO, and PMMA,<sup>[29]</sup> a polymer with a deep HOMO, as benchmarks. The measured HOMO levels of those polymers are shown in Figure 3a and summarized in Table S1, Supporting Information. Among them, PVK and PVN films exhibited slightly deeper HOMO levels compared to PTAA films, which are closer to the valence band maximum (VBM) position of FAPbI<sub>3</sub> (marked as the dashed line), indicating better ion-blocking ability and energy-level alignment for FAPbI<sub>3</sub>-based devices. Unfortunately, despite PVK and PVN being more suitable in terms of performance as HTLs for FAPbI<sub>3</sub> devices, the contact angle for a droplet of perovskite precursor on those HTLs increased from 42.8° (PTAA) to 54.6° (PVK) and 63.4° (PVN), and the root mean square roughness of HTLs measured by atomic force microscopy (AFM) increased from 0.18 nm (PTAA) to 0.49 nm (PVK) and 0.69 nm (PVN), indicating poorer wettability and greater roughness for PVK and PVN (Figure S5 and S6, Supporting Information). The reduced wettability and increased roughness lead to incomplete coverage of the perovskite film during the coating process, especially in large-area module fabrication. Therefore, we incorporated these polymers into PTAA at a volume ratio of 1:4, which represents the maximum dosage allowing for the coating of a complete perovskite film, while maintaining the same concentration, to mitigate those adverse effects. Based on the results obtained from AFM and Kelvin probe force microscopy, it is evident that the roughness of the mixed-coating films is consistent with that of the PTAA film. Moreover, the similar surface potentials suggest that the charge extraction ability of PVN-modified PVK-modified films remains largely unaffected and



**Figure 3.** Effect of dielectric polymers on suppressing iodine-ion migration. a) Measured HOMO levels of dielectric polymers used in this study, with P3HT and PMMA as benchmarks. The VBM position of FAPbI<sub>3</sub> is marked as the dashed line. b) Normalized current transients of  $Ag/I_2$  corrosion tests for PTAA mixed with different dielectric polymers. c) Schematic diagram illustrating the use of dielectric materials as an ion-blocking layer.



(Figure S7, Supporting Information). Detailed data regarding roughness and charge potential are provided in Table S2, Supporting Information, Additionally, as depicted in Figure S8, Supporting Information, the contact angles of modified PVK and PVN films closely resemble that of PTAA (43.9° and 44.2°, respectively). Subsequently, we characterized the diffusion rates of iodine through HTLs using an Ag/I<sub>2</sub> corrosion experiment.<sup>[21,30]</sup> The schematic and the device structure are shown in Figure S9, Supporting Information. Since iodine can convert conductive silver into insulating silver iodide, thereby interrupting the current, we can reflect the diffusion rate of iodine in these polymers through the change in current duration. The thicknesses of the studied films have been confirmed to be similar, ensuring a reasonable comparison (Figure S10, Supporting Information). Notably, the thickness of the ionblocking layer is significantly greater than that of the HTL, facilitating hole transport through the insulating layer via tunneling effect, while impeding ion passage. Consequently, the inclusion of PVN does not impede hole transport.<sup>[31]</sup> As shown in Figure 3b, the current of the PTAA device disappeared after 1090 s, while the PTAA films modified by PVK and PVN show longer lifetime of 1230 s and 1470 s, respectively, indicating a slower iodine diffusion rate, which is consistent with our expectation interface. Therefore, Figure 3c shows the effect of dielectric polymers on suppressing iodine-ions migration, the mixed HTLs served as an ion-blocking layer, inhibiting ion migration to HTLs, particularly under thermal heating conditions, to enhance device stability.

# 2.4. Improved Inhibition of Ion Migration via PVN and PVK Modification

To further investigate the effect of introduced PVK and PVN, we conducted additional experiments with an ITO/HTL/FAPbI3 structure. First, the perovskite films remain intact on modified HTLs after 2 weeks of exposure in the same thermal conditions (80 °C), demonstrating the improved thermal stability of perovskite films with modified HTLs as shown in Figure S11, Supporting Information. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) measurements were conducted to investigate the impact of HTL modification on the crystallization process of the perovskite. The top-view SEM images reveal that the film on PVN-modified HTL exhibited a larger grain size  $(\approx 2 \,\mu m)$  and greater uniformity than the control films. After 1 week of exposure to ambient air, the precipitation of PbI<sub>2</sub> on the surface was also significantly suppressed (Figure S12, Supporting Information). The cross-sectional SEM images indicate that, while the perovskite films on both pristine PTAA (control) and PVN-modified PTAA (target) exhibited vertically aligned grains, the grains of the target sample appeared more orderly than the control. The XRD spectra of perovskite films coated on each polymer are shown in Figure S13, Supporting Information, revealing no additional diffraction peaks except for an increase in the characteristic peak at  $\approx 14.2^{\circ}$ . We then repeated elemental distribution measurements on the films modified with PVK and PVN. The ToF-SIMS results in Figure 4a-c demonstrate better suppression of iodine-ion migration in the PVN-modified HTL, with no new peaks indicating

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iodine-ion aggregation. To confirm the diffusion length of iodine, we conducted the cross-sectional scanning transmission electron microscopy energy-dispersive X-ray spectroscopy (STEM-EDX) measurements. By comparing the distribution of iodine and lead elements at the perovskite/HTL interface, the extent of iodine diffusion can be determined. We defined the distance between the positions where the intensities of iodine and lead elements drop to the baseline as the diffusion length of the iodine into HTL. After 1 h of thermal treatment at 80 °C, the STEM-EDX results of perovskite films on three different HTLs are shown in Figure 4d-f. We found that the diffusion length of iodine into HTL decreased from 68 nm to 26 nm with PVN mixing (53 nm with PVK mixing). Additionally, the TRPL results show stable PL transients in the PVN-modified sample, with a negligible change of PL lifetime after 1h of TC treatment (Figure 4g-i). Overall, the mixing of PVN is more effective than PVK in inhibiting the migration of iodine ions, making it a more suitable material for enhancing the thermal stability of PSCs.

# 2.5. Photovoltaic Performance and Stability of Devices with PVN Modification

To assess the impact of PVN on device performance, we fabricated p-i-n-structured devices with a structure of ITO/PTAA/ FAPbI<sub>3</sub>/C<sub>60</sub>/BCP/Cu. The PCE of the device significantly improved from 20.82% (control) to 23.19% (target) after PVN modification, with a short-circuit current density  $(I_{SC})$  of 24.52 mA cm<sup>-2</sup>, an open-circuit voltage ( $V_{OC}$ ) of 1.16 V, and a fill factor of 81.55% (Figure 5a). The hysteresis is almost completely eliminated in the target devices under forward and reverse scans due to better energy level alignment and a decrease in charge accumulation (Figure S14, Supporting Information). The statistical distribution of efficiencies and corresponding photovoltaic characteristics are presented in Figure 5b and Table S3, Supporting Information. We find that the average PCE of 80 target cells exhibit an approximately 14% improvement compared to that of the control cells. The enhancement of  $V_{\rm OC}$  is attributed to the increase of grain size and the removal of many small seed crystals, resulting in a more orderly grain arrangement. To quantify the influence of charge transfer following PVN modification, the space-charge-limited current (SCLC) characterization was performed on the hole-only devices (Figure S15, Supporting Information). The calculated hole-trap density (N<sub>t</sub>) is  $4.06 \times 10^{15} \text{ cm}^{-3}$  for the control device and  $3.11 \times 10^{15}$  cm<sup>-3</sup> for the target device, reflecting a reduced defect concentration in the target device. The hole mobility of the target device improved from  $3.74 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  to  $5.61 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which suggests that the incorporation of PVN effectively blocked iodine migration without affecting hole transport, thereby explaining the unchanged Isc. The improved hole mobility should attribute to the larger grains and less trapping. PL quantum yield (PLQY) measurement was performed to quantify the  $V_{\rm OC}$  losses of the PSCs (Figure S16, Supporting Information). The PLOY of the bare perovskite film is 9.49%. Upon introducing PTAA, the PLQY of the perovskite film decreased to 0.892% for the control sample and 1.874% for the target sample, respectively. This indicates a significant mitigation of voltage loss in the target sample compared to the



(a) (d) 1500 (g) ΡΤΑΑ Perovskite ITO Pristine Pb Au 10<sup>0</sup> After TC Intensity (a.u.) 10 Intensity (a.u.) 0 01 01 Distance (nm) FA 10 10<sup>-3</sup>  $\cap$ 10 10<sup>0</sup> 0 50 100 150 200 250 300 350 Ó 100 200 ò Intensity (a.u.) Etching time (s) Decay time (ns) (b) (e) 1500 (h) Perovskite ITO PTAA@PVK Pristine Pb Au a 10<sup>0</sup> Intensity (a.u.) 10 After TC Intensity (a.u.) -10-1 10-3 -10-3 -10-3 Distance (nm) 000 000 000 FA 10<sup>2</sup> 10<sup>0</sup> 10 Au n 100 150 200 250 300 350 50 Ó 100  $2\dot{0}0$ Intensity (a.u.) Etching time (s) Decay time (ns) (c) (f) (i) 1500 PTAA@PVN Pristine a Pb Au 10<sup>0</sup> After TC Intensity (a.u.) Distance (nm) Intensity (a.u.) 10 FA 10<sup>-2</sup> 10<sup>2</sup> 10<sup>-3</sup> 0 10-4 10 0 50 100 150 200 250 300 350 100 200 Ò 0 Intensity (a.u.) Etching time (s) Decay time (ns)

**Figure 4.** Improved inhibition of ion migration via PVN and PVK modification. a–c) ToF–SIMS analysis of ITO/HTL/perovskite structure with different HTLs after heating. d–f) Cross-sectional STEM–EDX measurements on glass/HTL/perovskite/Au structure with different HTLs. g–i) TRPL measurements excited from the ITO side for ITO/HTL/perovskite structure with different HTLs before and after TC treatment.

control. Furthermore, the perovskite film with double-side transport layers exhibited the smallest PLQY values of 0.320% for the control sample and 1.02% for the target sample, respectively. From the internal electron-hole quasi-Fermi level splitting (QFLS) calculation,<sup>[32,33]</sup> the voltage loss at the p interface was reduced from 62 meV to 42 meV, which represents a significant reduction in defects, resulting in a high  $V_{OC}$  of 1.16 V obtained in the target device (Figure 5c). The slightly improved integrated  $J_{SC}$  values obtained from the external quantum efficiency (EQE) closely agree with  $J_{SC}$  extracted from current density–voltage (J–V) curves (Figure S17, Supporting Information). The improved crystallinity and better energy level alignment contributes to an outstanding PCE enhancement of over 14%.

In addition to the enhanced photovoltaic performance, the PVN-modified device exhibits remarkable stability, with the thermal stability showing the most significant improvement. When exposed to a thermal cycling environment based on the IEC 61215 standard, the target devices exhibited superior stability

compared to the control device, maintaining over 80% of their initial efficiency after 1000 h of aging (Figure 5d). Subsequently, we investigated the stability of unencapsulated PSCs against humidity. After being stored in a 50% humidity environment for 1100 h, the PCE of the target devices remained over 90% of its initial value, whereas that of the control device decayed to 61% (Figure S18, Supporting Information). The enhanced stability can be attributed to the inhibition of iodide ion migration, which preserves the integrity of the perovskite crystal structure, rendering it less susceptible to decomposition under humid and heat conditions. Additionally, long-term operational stability was further examined using MPP tracking under 1 sun illumination. After 600 h of operation, the PCE of the target devices retained 80% of their initial value, while the PCE of control devices significantly decreased to 39.45% of their initial value (Figure 5f). The *I*-V curves of target device before and after MPP tracking are depicted in Figure S19, Supporting Information. These outstanding stability data indicate the successful

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**Figure 5.** Photovoltaic performance of PSCs with PVN modification. a) J-V curves of doctor-blading FAPbI<sub>3</sub> PSCs before and after PVN modification (active area: 8 mm<sup>2</sup>). b) The statistical PCE distribution for the control and target devices. c) Voltage loss mechanism for the control and target devices. d) Thermal stability through IEC 61215 standard for control and target devices in open circuit. e) MPP tracking for the control and target devices under 1 sun illumination in a nitrogen atmosphere.

application of PVN in suppressing iodine-ion diffusion and represent a crucial step forward for the commercialization of PSCs.

### 3. Conclusion

In summary, we propose a synergistic strategy by introducing PVN into PTAA, functioning as an ion-blocking HTL. This layer effectively inhibits the migration of iodine ions to the HTL and passivates defects at the HTL/perovskite interface, resulting in high-quality perovskite films with improved stability. The reduction of defects, suppression of ion migration, and modulation of energy level alignment result in a remarkable efficiency exceeding 22% for doctor-bladed FAPbI<sub>3</sub>–PSCs. Moreover, the corresponding unencapsulated PSCs demonstrate impressive

stability, retaining over 80% of their initial value after 1000 h of IEC 61215 standard thermal aging, or after a long-term operational test spanning 600 h under MPP tracking. This exceptional strategy constitutes a pivotal advancement toward the commercialization of PSCs.

## 4. Experimental Section

*Materials*: PTAA (average  $M_n$  7000 to 10 000), bathocuproine (BCP), lead (II) iodide (PbI<sub>2</sub>, 99.99% trace metals), formamidinium iodide (FAI), and methylammonium chloride (MACl) were purchased from Xi'an Polymer Light Technology Corp. N,N-dimethylformamide (99.9%), dimethyl sulfoxide (DMSO, 99.9%), 2-methoxyethanol (2-ME, 99.8%), chlorobenzene (CB, 99.8%), isopropanol (IPA, 99.5%), anilinium hypophosphite, and L- $\alpha$ -phosphatidylcholine (L- $\alpha$ -PC) were purchased from **4DVANCED** 

Sigma-Aldrich. PVK and PVN were purchased from Sigma Aldrich. C<sub>60</sub> was purchased from Advanced Election Technology Co., Ltd. The ITO glass substrates ( $15 \Omega sq^{-1}$ ) were purchased from South China Science & Technology Co., Ltd. All materials were used directly without any further purification. Copper for thermal evaporation was obtained from ZhongNuo Advanced Material (Beijing) Technology Co., Ltd.

*Precursor Preparation*: PTAA solution was prepared by dissolving PTAA powder into CB with a concentration of 20 mg mL<sup>-1</sup>. PVN solution (20 mg mL<sup>-1</sup>) was prepared by dissolving PVN in CB and added in PTAA solution with varying weight ratios. The 2.0 M FAPbI<sub>3</sub> precursor solutions were prepared by dissolving FAI and PbI<sub>2</sub> in 2-ME and stirring overnight. Before blade-coating, the precursor solutions were diluted to 1.1 M., L-α-PC (0.4 mg mL<sup>-1</sup>), MACI (0.2 mg mL<sup>-1</sup>), and DMSO (2.8% v/v) were added as additives into the precursor solution.

Device Fabrication: We utilized ITO glass substrates, which were sequentially cleaned with detergent, deionized water, acetone, and IPA, followed by ultraviolet-ozone treatment for 20 min prior to use. The substrates were then blade-coated with a modified PTAA solution at a speed of 20 mm s<sup>-1</sup> and a coating gap of 250 µm, followed by annealing for 10 min. Subsequently, the precursor solution was blade-coated onto the PTAA-covered ITO glass substrate with a gap of 300 µm, using a N<sub>2</sub> knife with a wind speed of 3 m s<sup>-1</sup>. After that, the perovskite films were annealed at 100 °C for 15 min in air. The devices were completed by thermally evaporating 30 nm C<sub>60</sub>, 6 nm BCP, and 100 nm copper.

*Characterization:* Films characterization. The PL and TRPL measurements of perovskite samples were achieved with a 405-nm picosecondpulsed diode laser on a laser-scanned fluorescence lifetime/intensity imaging system (FLRM300, Time-Tech Spectra, LLC). The in situ PL measurement involved continuous picosecond laser irradiation at the same position. The samples underwent half-hour temperature cycles from room temperature to 80 °C, with measurements taken at room temperature after each cycle. The TRPL lifetime measurement was carried out on the timecorrelated single-photon counter setup with a 0.2 MHz laser repetition.

The chemical composition of perovskite films was probed using ToF–SIMS with a state-of-the-art spectrometer (PHI nano TOF3, Ulvac-Phi, INC.). The instrument was equipped with a  $Bi^{3++}$  primary ion beam cluster and  $Ar^+$  ion beam sputtering, allowing for high-resolution imaging and chemical mapping of the entire analysis area (15  $\mu$ m  $\times$  15  $\mu$ m) in a single experiment. A sputtering time of 350 s was employed, with each sputtering time being 10 s, ensuring comprehensive coverage of the perovskite films.

UPS measurements were performed in an ultrahigh vacuum at room temperature. He I photons (21.22 eV) generated by a discharged lamp were used to determine the work function and valence band edges of each sample, and thus the HOMO energy levels. The experimental energy resolution for UPS was typically 0.10 eV.

For Ag/I<sub>2</sub> tests, the samples were thermally evaporated a 100 nm thick Ag on a patterned ITO substrates to form a bridge between ITO electrodes, the channel length is 5 mm. Three kinds of polymer solutions  $(50 \text{ mg mL}^{-1})$  were spin-coated on top of the Ag to form the whole devices. The devices were exposed to a saturated I<sub>2</sub> vapor atmosphere in a conical flask at room temperature, and the current was monitored at a constant bias of 100 mV during the I<sub>2</sub> exposure using a Keithley 2400 source meter.

The surface and cross-section morphologies of the perovskite films were obtained on a focused ion beam SEM (Carl Zeiss AURIGA Cross Beam) working at a 30 kV and a distance of  $\approx$ 7.7 mm. The STEM images and EDX measurements were carried out in Thermo Scientific Talos F200X transmission electron microscope, and all imaging was carried out in high-angle annular dark-field mode.

The crystal structure and phase of the perovskite films were characterized by XRD measurement on a PANalytical Empyrean diffractometer using Cu-K $\alpha$  radiation ( $\lambda$  = 1.5406 Å, 40 kV, 40 mA).

Device Characterization: For FAPbI<sub>3</sub> solar cells, *J*–V characteristics of the devices were measured using a source measure unit (Keithley 2400) in a N<sub>2</sub> glove box under AM 1.5G solar illumination (100 mW cm<sup>-2</sup>) from an Enlitech SS-F5S solar simulator. The scans were taken from forward bias to reverse bias with a scan rate of 0.02 V s<sup>-1</sup>. To prevent external rays from affecting the measurements, an opaque mask with an aperture

 $(0.0615\ \text{cm}^2)$  smaller than the active area  $(0.08\ \text{cm}^2)$  was applied to the light-incident surface of the device.

The SCLC characterization was conducted using hole-only devices (ITO/modified PTAA/perovskite/PTAA/Au), and the voltage was scanned from -0.1 to 3 V with step size of 0.02 V under dark conditions. The hole mobility was calculated by fitting the curve using Mott–Gurney law in Child's region with the following equation:<sup>[34]</sup>

$$J = \frac{9\epsilon_0\epsilon_r \mu (V_{app} - V_{bi})^2}{8L^3}$$
(1)

where  $\varepsilon_0$  is the vacuum permittivity;  $\varepsilon_r$  (i.e., 25) is the relative dielectric constant;  $\mu$  is the charge mobility;  $V_{app}$  and  $V_{bi}$  are the applied voltage and built-in voltage, respectively; *L* is the thickness of perovskite (800 nm); and *J* is the current density.

The trap density was calculated on the basis of the following equation:

$$n_{\rm trap} = \frac{2\varepsilon_0 \varepsilon_r V_{\rm TFL}}{qL^2} \tag{2}$$

where  $V_{\text{TFL}}$  chooses the crossing point between the tangent space-charge-limited regime at high voltages and the trap-filled-limited regime.

The PLQY was measured using a home-built setup and excited by a 365-nm laser. PLQY data was used to quantify the  $V_{\rm OC}$  losses of the PSCs. The internal electron-hole QFLS was then calculated from the PLQY according to the following formula:<sup>[35]</sup>

$$QFLS = k_{B}T \times ln\left(PLQY \times \frac{J_{G}}{J_{0,rad}}\right)$$
(3)

where  $J_{\rm G}$  is the current density generated by the device under 1-sun illumination, and  $J_{0,rad}$  is the RR current in the dark.

The EQE spectra were measured in DC mode to determine the current density of PSCs at each wavelength using a spectrum corresponding system (Enlitech QE-R) at room temperature, calibrated by Si reference solar cell.

Stability Measurements: The long-term operational stability of control and target PSCs was carried out under AM 1.5G solar illumination by MPP tracking method using Keithley 2420 source meter. To evaluate the thermal stability and water–oxygen stability, we followed the testing requirements outlined in the IEC 61215 standard by the technischer überwachungs-verein organization, which specify condition for temperature, humidity, and illumination. The unencapsulated devices were subjected to cycling from -40 °C to 85 °C while loaded in an open-circuit state. This procedure simulates the durability of photovoltaic modules under various environmental conditions. Each temperature cycle lasted 2 h, with efficiency testing conducted every 10 h.

## **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.

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### **Author Contributions**

Y.S. and Y.Z. conceived the idea and designed the experiment. Y.S. fabricated the devices. Y.S., D.F., Y.L., and G.Z. conducted the characterization measurement. Y.Z. and Y.S. directed and supervised the project. Y.S. wrote the first draft of the paper. Y.Z., B.P.R., and Z.X. revised the article. All the authors analyzed their data and commented on the article.

### **Data Availability Statement**

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

#### **Keywords**

commercializations,  $\mathsf{FAPbI}_3,$  ion migrations, ion-blocking layers, perovskite solar cells, stabilities

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